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Effect of MgO on phase equilibria of copper matte and SiO_2-saturated iron silicate slag in smelting complicated copper resources

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Abstract: The effect of MgO on the phase equilibria between matte and tridymite-saturated FeO_x−SiO_2−MgO slag was investigated using high-temperature equilibration and microanalysis technique. The results showed that at 1300 °C and $p(SO_2)$ of 10 kPa, the presence of MgO reduced the FeO activity of the slag, leading to the decrease in the oxygen partial pressure ($p(O_2)$) over the slag and the Cu solubility in the slag. Due to the lower FeO activity, FeS was oxidized from matte into slag, increasing the Cu concentration of the matte. In high-SiO_2 concentration slags, excessive MgO in the liquid slag recrystallized as solid olivine (Mg_2SiO_4−Fe_2SiO_4), increasing the slag viscosity and copper losses in the slag. The maximum MgO solubility in the FeO_x−SiO_2−MgO slag increased from 3 wt.% to 8 wt.% when the temperature raised from 1200 to 1300 °C under $p(O_2)$ of 10^{-6} kPa. At higher MgO content, the slag composition could be optimized by increasing temperature and adding SiO_2 flux to maintain a fully molten slag or avoid high proportions of solids.

Key words: MgO; iron silicate slag; copper matte smelting; phase equilibria; element distribution

1 Introduction

In the copper smelting industry, with the increasing utilization of complex minerals and secondary copper resources like waste electrical and electronic equipment (WEEE) [1], a significant amount of MgO is introduced to the copper smelting system, producing FeO_x−SiO_2−MgO slags. The MgO in the slag originates from the gangues in ores, glass fiber in WEEE, fluxing additives, and dissolved magnesia−chromite refractories [2,3]. The presence of MgO brings significant effects on the slag chemistry, such as emerging solid phases and entrained metal particles in slag [4−6]. To clarify the effect of MgO on equilibrium phase compositions and elemental distribution, phase equilibria between matte and FeO_x−SiO_2−MgO slag are of great industrial interest for efficient recovery of valuable metals.

In previous studies, the phase equilibria of MgO-containing iron silicate slag systems and copper matte or copper alloy were investigated extensively by high-temperature experiments and thermodynamic evaluation. In the copper smelting conditions, ABDEYAZDAN et al [7] and SINEVA et al [8] studied the effects of MgO on the matte−slag−tridymite equilibria at 1200−1300 °C and $p(SO_2)$ of 25 kPa. They found that the solubility of Cu and S in the slag decreased with increasing the MgO concentration, while the matte composition had no apparent changes. The liquidus contours of spinel-saturated FeO_x−SiO_2−MgO slags that equilibrated with matte were studied by SUN et al [6]

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at 1180−1250 °C and $p(SO_2)$ of 30 and 60 kPa with a fixed matte grade of 72 wt.% Cu. ROGHANI et al [9,10] investigated the effects of MgO and CaO on phase equilibria between matte and SiO_2-saturated FeO_x−SiO_2 slags at 1300 °C and $p(SO_2)$ of 10, 50, and 101 kPa by high-temperature experiments and wet chemical analysis technique, resulting in the non-detect inhomogeneity and uncertainty of the phase compositions.

In general, only limited data exist for the matte and SiO_2-saturated FeO_x−SiO_2−MgO slag system at 1300 °C and $p(SO_2)$ of 10 kPa. This study aims to characterize the impact of MgO concentration in slag on the phase equilibria and element distribution between the matte and tridymite-saturated FeO_x−SiO_2−MgO slag at 1300 °C and $p(SO_2)$ of 10 kPa. The experimental thermodynamic data for equilibrium phase relations of matte and FeO_x−SiO_2−MgO slags could be enriched. The results obtained in this work could provide fundamental clues for regulating flux strategies and optimizing operations in smelting of the MgO-containing complicated copper resources.

2 Experimental

High-temperature equilibration, quenching, and electron probe X-ray micro-analyzer (EPMA) were applied in the present experiments. High-purity chemical reagents were employed for preparing the initial materials of the matte and FeO_x−SiO_2−MgO slags to obtain stable reactants. The initial samples were equilibrated at 1300 °C and $p(SO_2)$ of 10 kPa in a controlled atmosphere by mixing CO, CO_2, SO_2 and Ar gases. After equilibration, the samples were quenched rapidly in an ice-water mixture within seconds to retain the high-temperature phase assembles. The compositions of the quenched samples were directly analyzed by EPMA to minimize the statistical uncertainty of the phase compositions during equilibration [11].

2.1 Materials

Cu_2S (99.99 wt.%, Aladdin) and FeS (99.99 wt.%, Alfa Aesar) were weighed to prepare the initial copper matte mixtures in Cu_2S/FeS mass ratios of 70:30 for the target matte grades of 55−70 wt.% Cu, and 80:20 for a target matte grade of 75 wt.% Cu to shorten the required equilibration time [12]. Fe_2O_3 (99.99 wt.%, Macklin), SiO_2 (99.90 wt.%, Macklin), and MgO (99.99 wt.%, Aladdin) were employed to synthesize the slag mixtures with the Fe_2O_3/SiO_2/MgO mass ratio of 61:36:3.

Approximately 0.1 g of the sulfide mixtures were equilibrated with an equal amount of the oxide mixtures and copper powder (99.999 wt.%, Alfa Aesar) in each experiment. The copper powder was added to the mixtures to investigate the reaction mechanism of the metallic copper in the smelting conditions. The metallic copper was transformed to copper matte in the matte−tridymite−liquid equilibria system. The initial materials were roughly mixed in an agate mortar and pressed into a 5 mm tablet in a mold. Subsequently, the initial sample was placed into a SiO_2 crucible (height of 88 mm and out diameter of 10 mm, Haoming, China) for the equilibration experiment.

2.2 Experimental procedure

The high-temperature experiments were conducted at 1300 °C in a vertical tube furnace (length of 1000 mm and out diameter of 60 mm, SGL−1700C, Jujing, China) equipped with $MoSi_2$ heating elements. The SiO_2 crucible with the initial sample was put into a platinum basket and hung in the hot zone of the furnace tube by a Kanthal wire (A1, Fe−Cr−Al alloy), as shown in Fig. 1. The furnace temperature was regulated by a PID controller with an overall accuracy of ±5 °C. The actual temperature of the sample was measured using a calibrated B-type thermocouple placed next to the sample inside the working tube.

The $p(O_2)$ and $p(S_2)$ at $p(SO_2)$ of 10 kPa and 1300 °C for target matte grades were calculated by FactSage 7.1, as listed in Table 1. The $p(O_2)$, $p(S_2)$, and $p(SO_2)$ in the furnace were controlled by mixing different volume ratios of CO (99.90 vol.%), CO_2 (99.99 vol.%), SO_2 (99.90 vol.%), and Ar (99.999 vol.%) gases provided by Saizhong Gas Co., Ltd., China. The gas flowrates were regulated by digital mass-flow controllers (Sevenstar, Huachuang, China) and introduced into the furnace after being premixed in a guiding pipe.

The $CO+CO_2+SO_2+Ar$ mixture gas was put into the furnace tube for approximately 10 min to remove the residue air and stabilize the atmosphere. And then, the initial samples were equilibrated at 1300 °C and $p(SO_2)$ of 10 kPa for the required time.

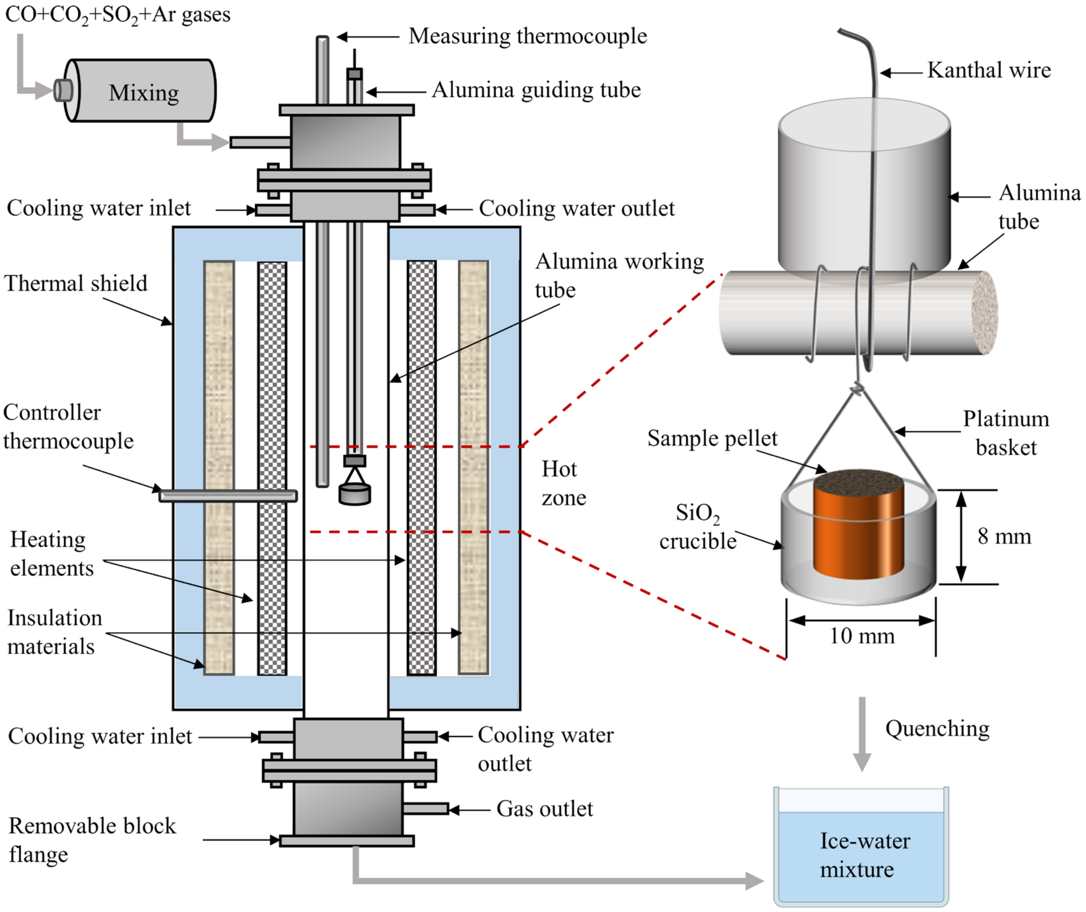

Fig. 1 Schematic diagram of reaction device

Table 1 Gas flowrates for target matte grades at 1300 °C and $p(SO_2)$ of 10 kPa

Target matte grade (Cu)/wt.%	Target $\lg[p(O_2)/p^{\ominus}]$	Target $\lg[p(S_2)/p^{\ominus}]$	Gas flowrate/(mL·min^{-1})			
			CO	CO$_2$	SO$_2$	Ar
55	−8.14	−2.11	27	67	47	259
60	−8.07	−2.26	22	68	45	265
65	−7.96	−2.48	16	71	43	270
70	−7.80	−2.79	11	72	42	275
75	−7.58	−3.23	8	74	41	278

$p^{\ominus}$ is 101.325 kPa

After equilibration, the bottom end of the furnace tube was immersed in the ice-water mixture, and the block flange was removed. When pulling up the wire, the samples would drop into an ice-water mixture and be quenched within seconds.

2.3 Characterization

The quenched samples were dried and mounted in epoxy resin. The sample surfaces were ground, polished, and carbon-coated by a carbon vacuum evaporator (JEE−20, Japan). The microstructures of the samples were observed by a scanning electron microscope (SEM, MIRA4 LMH, Czech Republic) coupled with an energy dispersive X-ray spectrometer (EDS).

The elemental compositions of the samples were measured by EPMA (JXA−8530F, Japan) using a wavelength dispersive spectrometer (WDS). The accelerating voltage and the beam current were 15 kV and 20 nA, respectively. The beam diameter was set to be 20 μm for the matte and liquid slag phases and 5 μm for the solid tridymite. At least eight points were randomly selected from each phase for statistical reliability. The standard materials used for EPMA were metallic Cu for Cu K_α, metallic Fe for Fe K_α in matte and hematite for Fe K_α in liquid slag and tridymite, FeS_2 for S K_α, quartz for Si K_α, quartz for O K_α in matte, obsidian for O K_α in liquid slag and tridymite, and MgO for Mg K_α. The average elemental detection limits of EPMA are listed in Table 2. As EDS and EPMA are not sensitive to the oxidation valence of iron, the total iron concentration in the slag was recalculated to "FeO" for ease of presentation in the results.

Table 2 Elemental detection limits (EDL) of EPMA

Material	EDL/(mg·kg^{-1})					
	Cu	Fe	S	O	Si	Mg
Matte	280	174	90	251	66	48
Liquid slag	226	146	74	339	69	47
Tridymite	182	116	71	365	80	47

2.4 Thermodynamic calculation

The isotherms of the FeO_x−SiO_2−MgO slag system at fixed $p(SO_2)$ of 10 kPa and 1300 °C were predicted by FactSage 7.1 using "PhaseDiagram" module. The databases of "FactPS" and "FToxide" and the solutions of "FToxid-SLAGA", "FToxid-SPINA", "FToxid-MeO", "FToxid-cPyrA", "FToxid-oPyr", "FToxid-pPyrA", and "FToxid-OlivA" were selected to calculate the isotherms of the slags.

The $p(O_2)$, $p(S_2)$, and required flowrates of $CO+CO_2+SO_2+Ar$ gases for target matte grades at the fixed $p(SO_2)$ of 10 kPa and 1300 °C were calculated by FactSage 7.1 using the "Equili" module [11]. The selected databases were "FactPS", "FToxide", and "FTmisc". The solutions selected in the calculations were "FTmisc-Matte", "FToxid-SLAGA", "FToxid-SPINA", "FToxid-MeO", "FToxid-cPyrA", "FToxid-oPyr", "FToxid-pPyrA", and "FToxid-OlivA".

3 Results

3.1 Equilibration time

A series of experiments were carried out to determine the equilibration time at 1300 °C and $p(SO_2)$ of 10 kPa. The initial samples for the target matte grade of 60 wt.% Cu were annealed at 1300 °C and $p(SO_2)$ of 10 kPa for 4, 6, 8, and 10 h. The equilibration time was defined based on the stabilization of the matte and liquid slag compositions measured by SEM−EDS, as shown in Fig. 2. The concentrations of Cu, S, and Fe in the matte became homogeneous in 8 h. The concentrations of "FeO" and SiO_2 in the slag also reached equilibrium in 8 h. Therefore, all samples in the following experiments were annealed in the furnace for at least 8 h to obtain uniform phase compositions.

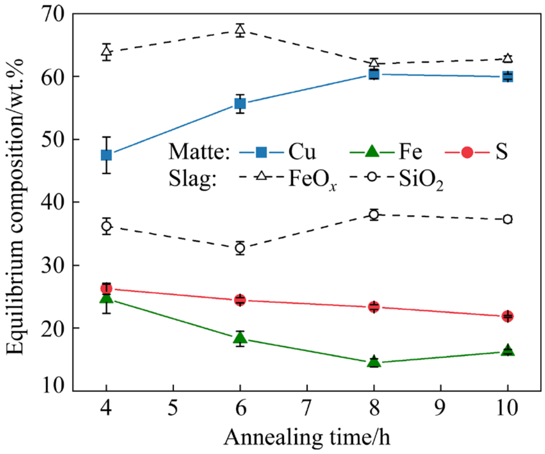

Fig. 2 Compositions of matte and liquid slag as function of annealing time for target matte grade of 60 wt.% Cu

3.2 Microstructures and equilibrium compositions of matte, slag, and tridymite

The typical microstructures of the matte−slag systems at 1300 °C and $p(SO_2)$ of 10 kPa for the matte grades of 55 wt.% Cu and 75 wt.% Cu are shown in Fig. 3. It can be confirmed that the copper matte was in equilibrium with liquid slag and solid tridymite in all experimental conditions.

The equilibrium phase compositions were measured and summarized in Table 3. The major components of the matte were Cu, Fe, S, and O, while the concentrations of Si and Mg in the matte were below the detection limit. Thin Cu-rich veins (90−99 wt.% Cu) existed in the matte phase due to the insufficient quenching rate [8]. The total concentrations of the elements of in matte measured by EPMA were 99.41−101.25 wt.%.

The slag phase included liquid slag and solid tridymite, as shown in Fig. 3(b). The compositions of the liquid slag and solid tridymite are listed in Table 4. The liquid slag phase consisted of "FeO", SiO_2, MgO, and a small amount of Cu and S. The experimentally measured MgO concentration in the liquid slag was 3−5 wt.% over the matte grade range investigated in this study.

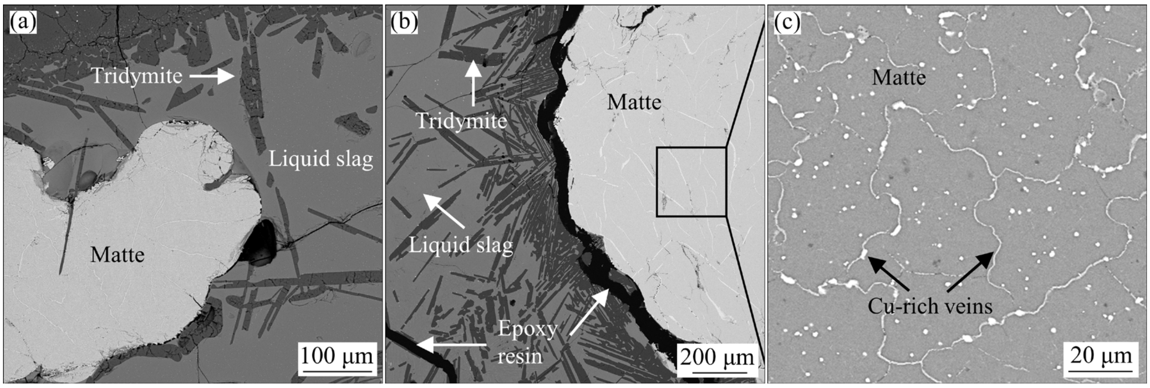

Fig. 3 Back scattered electron micrographs of copper matte and tridymite-saturated FeO_x−SiO_2−MgO slags at 1300 °C and $p(SO_2)$ of 10 kPa: Tridymite, liquid slag, and matte with 55 wt.% Cu (a), 75 wt.% Cu (b) and Cu-rich veins (c)

Table 3 Measured equilibrium compositions of copper matte at 1300 °C and $p(SO_2)$ of 10 kPa obtained by EPMA

Sample No.	$\lg[p(O_2)/p^\ominus]$	Matte composition/wt.%			
		Cu	Fe	S	O
1	−8.14	57.75 ± 0.94	15.66 ± 0.45	24.75 ± 0.31	0.78 ± 0.16
2	−8.14	56.71 ± 0.78	16.58 ± 0.35	24.67 ± 0.44	0.77 ± 0.20
3	−8.07	60.44 ± 0.70	13.99 ± 0.60	24.28 ± 0.86	0.84 ± 0.39
4	−8.07	62.60 ± 1.70	12.37 ± 0.97	23.63 ± 0.51	0.79 ± 0.42
5	−7.96	65.98 ± 0.14	10.54 ± 0.13	22.01 ± 0.04	1.22 ± 0.07
6	−7.96	67.82 ± 0.53	8.96 ± 0.41	22.56 ± 0.23	0.58 ± 0.29
7	−7.8	70.11 ± 0.80	6.42 ± 0.24	21.02 ± 0.15	1.18 ± 0.15
8	−7.8	70.35 ± 0.43	6.38 ± 0.16	21.23 ± 0.16	0.71 ± 0.09
9	−7.58	73.44 ± 0.88	4.00 ± 0.56	20.35 ± 0.30	0.53 ± 0.09
10	−7.58	74.52 ± 0.36	2.81 ± 0.37	19.70 ± 0.33	0.64 ± 0.20

The black rod-like crystals were secondary tridymite recrystallized by the excessive silica in the slag. At 1300 °C, the SiO_2 crucible dissolved in the molten slag until the SiO_2 concentration in the liquid slag reached the maximum solubility. The excessive SiO_2 from the dissolution of the SiO_2 crucible and excessive silica in the initial slag mixtures recrystallized as separate solid particles. The tridymite tended to precipitate on the slag−crucible interfaces, while some discrete crystals were dispersed randomly in the liquid slag [13]. The composition of tridymite was close to the stochiometric value of SiO_2. The concentrations of Cu and S in the tridymite were below the detection limit.

4 Discussion

4.1 Effect of MgO on matte

Figure 4 displays the concentrations of Cu, Fe, S, and O in matte as a function of oxygen partial pressure or matte grades in the present study. The experimental data from Refs. [7,9,12] were presented in the graphs for comparison.

As can be seen in Fig. 4(a), the copper concentration in matte increased with increasing the $p(O_2)$ in the present study, similar to the measurements obtained by ROGHANI et al [9] and CHEN et al [12] at 1300 °C and $p(SO_2)$ of 10 kPa. At the fixed $p(O_2)$, increasing the MgO concentration

Table 4 Measured equilibrium compositions of liquid phase and solid tridymite phase of FeO_x−SiO_2−MgO slags at 1300 °C and $p(SO_2)$ of 10 kPa obtained by EPMA

Sample No.	Slag phase	Slag composition/wt.%					Fe/SiO_2 mass ratio in slag
		MgO	SiO_2	“FeO”	Cu	S	
1	Liquid	3.98 ± 0.72	39.35 ± 0.74	56.67 ± 0.75	0.53 ±0.07	0.86 ± 0.08	1.12
	Tridymite	0.03 ± 0.00	98.88 ± 0.67	1.10 ± 0.67	−	−	−
2	Liquid	3.97 ± 0.66	38.96 ± 0.73	57.07 ± 0.99	0.50 ±0.14	0.76 ± 0.12	1.14
	Tridymite	0.01 ± 0.02	98.95 ± 0.43	1.04 ± 0.43	−	−	−
3	Liquid	4.42 ± 0.52	40.43 ± 0.86	55.15 ± 0.77	0.68 ±0.14	0.64 ± 0.07	1.06
	Tridymite	0.00 ± 0.00	98.62 ± 0.31	1.38 ± 0.31	−	−	−
4	Liquid	4.67 ± 0.59	40.89 ± 0.79	54.44 ± 0.63	0.71 ±0.17	0.65 ± 0.09	1.04
	Tridymite	0.01 ± 0.01	98.71 ± 0.19	1.29 ± 0.19	−	−	−
5	Liquid	4.23 ± 0.52	40.83 ± 0.69	54.94 ± 0.46	0.62 ±0.10	0.53 ± 0.06	1.05
	Tridymite	0.02 ± 0.01	98.16 ± 0.12	1.82 ± 0.13	−	−	−
6	Liquid	4.37 ± 0.54	40.10 ± 0.53	55.54 ± 0.94	0.72 ±0.18	0.56 ± 0.06	1.08
	Tridymite	0.01 ± 0.01	98.53 ± 0.22	1.46 ± 0.23	−	−	−
7	Liquid	4.17 ± 0.45	40.98 ± 0.62	54.85 ± 0.70	0.69 ±0.17	0.44 ± 0.08	1.04
	Tridymite	0.01 ± 0.00	98.66 ± 0.16	1.33 ± 0.16	−	−	−
8	Liquid	4.26 ± 0.59	39.93 ± 0.69	55.81 ± 0.63	0.73 ±0.15	0.47 ± 0.14	1.09
	Tridymite	0.01 ± 0.01	98.84 ± 0.17	1.15 ± 0.17	−	−	−
9	Liquid	3.95 ± 0.46	41.28 ± 0.92	54.77 ± 0.93	0.83 ±0.12	0.29 ± 0.09	1.03
	Tridymite	0.01 ± 0.01	98.79 ± 0.15	1.19 ± 0.15	−	−	−
10	Liquid	4.33 ± 0.21	41.07 ± 0.76	54.60 ± 0.63	0.85 ±0.09	0.31 ± 0.13	1.03
	Tridymite	0.02 ± 0.01	98.75 ± 0.18	1.23 ± 0.18	−	−	−

led to an increase in matte grade. Compared with the predicted matte grade by FactSage, the experimentally determined matte grade in this study was slightly lower in the same conditions with 4 wt.% MgO in the SiO_2-saturated FeO_x−SiO_2−MgO slags. A similar relationship between $p(O_2)$ and matte grade was observed by ABDEYAZDAN et al [7] at 1300 °C and $p(SO_2)$ of 25 kPa with 0.8 wt.% or 2.4 wt.% MgO in the slags, while the matte grade was less sensitive to the MgO concentration compared with the data obtained at $p(SO_2)$ of 10 kPa in this study.

The MgO addition decreased the FeO activity of the slags, promoting the oxidation of FeS into the slag. Subsequently, the decreasing iron activity of the matte leads to an increase in the matte grade, corresponding to Reactions (1) and (2) suggested by FALLAH-MEHRJARDI et al [14] and YAZAWA [15], respectively. The basic addition like CaO had similar effects on the copper concentration of the matte, as reported in literature [12].

$$FeS_{(matte)}+1/2O_2=FeO_{(slag)}+1/2S_2(g) \tag{1}$$

$$FeS_{(matte)}+3/2O_2=FeO_{(slag)}+SO_2(g) \tag{2}$$

Figure 4(b) indicated that iron concentration in matte decreased with the increasing matte grade, and it was independent of the MgO concentration in slags. The current results agreed well with the FactSage predictions and available measurements in the literature with a MgO concentration range of 0−10 wt.% at 1300 °C and $p(SO_2)$ of 10 kPa [9,12,16] and 25 kPa [7]. Moreover, the observations in the literature suggested that the iron concentration in matte was not sensitive to the prevailing $p(SO_2)$ in the system.

The sulfur concentration in the matte decreased from approximately 25 wt.% to 20 wt.% within the matte grade range at 1300 °C and $p(SO_2)$ of 10 kPa, as shown in Fig. 4(c). The sulfur concentration in the matte of the MgO-free systems measured by CHEN et al [12] had the same trend

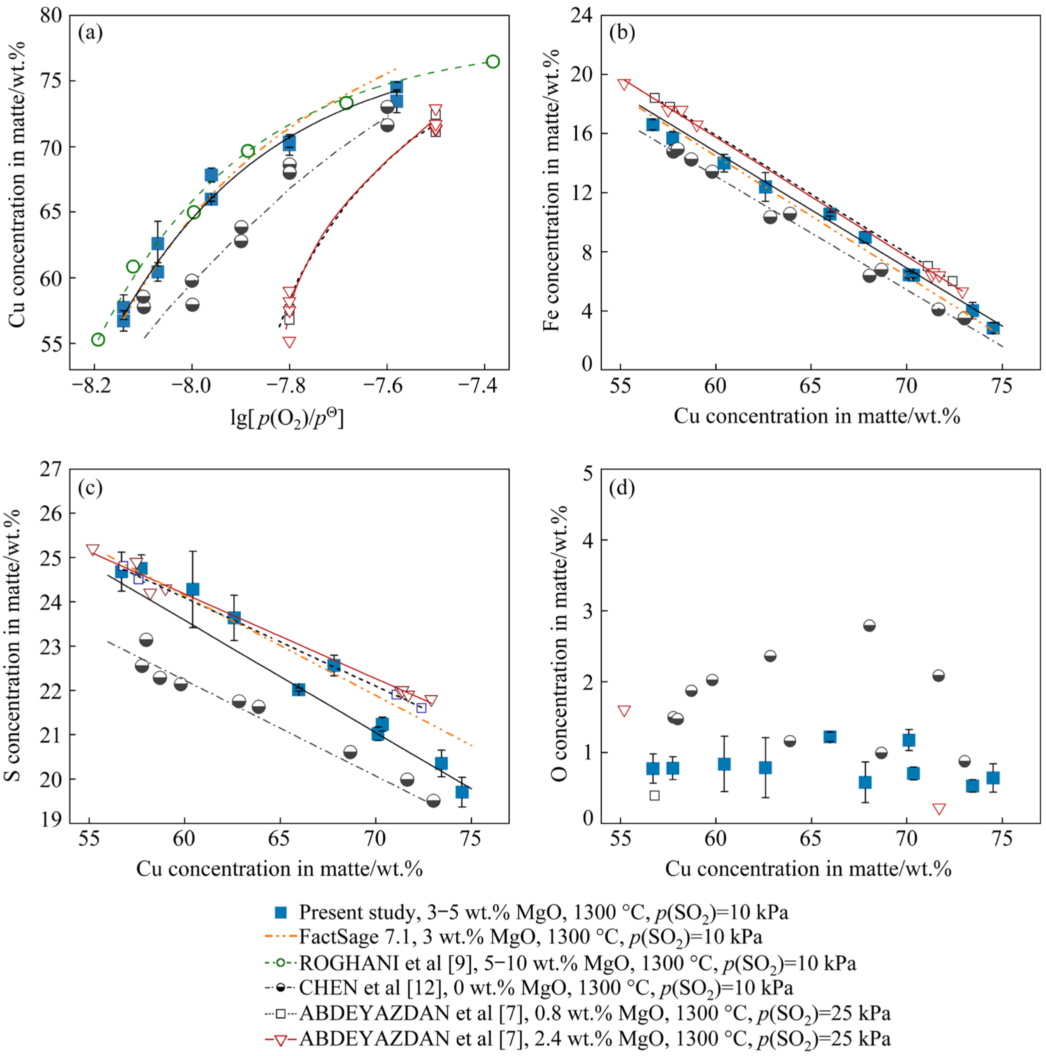

Fig. 4 Concentrations of Cu (a), Fe (b), S (c), and O (d) in matte in equilibrium with SiO_2-saturated FeO_x−SiO_2−MgO slags as function of oxygen partial pressure or matte grade in present study and Refs. [7,9,12]

though a little lower values than that of the current study. The experimental data obtained by ABDEYAZDAN et al [7] at 1300 °C and $p(SO_2)$ of 25 kPa with 0.8 wt.% or 2.4 wt.% MgO in the slags were on the higher side of the current results, with similar decreasing trends. For the range of matte grades investigated, the $p(SO_2)$ and MgO concentration had no apparent effect on the sulfur concentration in the matte.

Figure 4(d) shows that the dissolved oxygen concentration in the matte observed in this study was not sensitive to the matte grade and the MgO addition in slag. CHEN et al [12,13] reported that the oxygen concentration in matte decreased with increasing the matte grade, independently from $p(SO_2)$. As the oxygen in matte was not included in the existing FactSage matte database [17], ABDEYAZDAN et al [7] calculated the dissolved oxygen in matte from the differences between 100 wt.% and sums of all measured elements in matte. The calculated oxygen concentration showed a downward trend with increasing the matte grade, which appeared to be related to a stronger ability of iron to form an oxy-sulfide liquid solution in matte at low matte grades [18]. However, the MgO concentration had no obvious effect on the oxygen solubility in the matte, which agreed with the observations by ABDEYAZDAN et al [7] and SINEVA et al [8].

4.2 Effect of MgO on slag

4.2.1 Cu concentration in slag

Figure 5(a) displays the Cu concentration in the SiO_2-saturated FeO_x−SiO_2−MgO slags against matte grade in the present study and available data from the literature [7,9,12]. The experimental

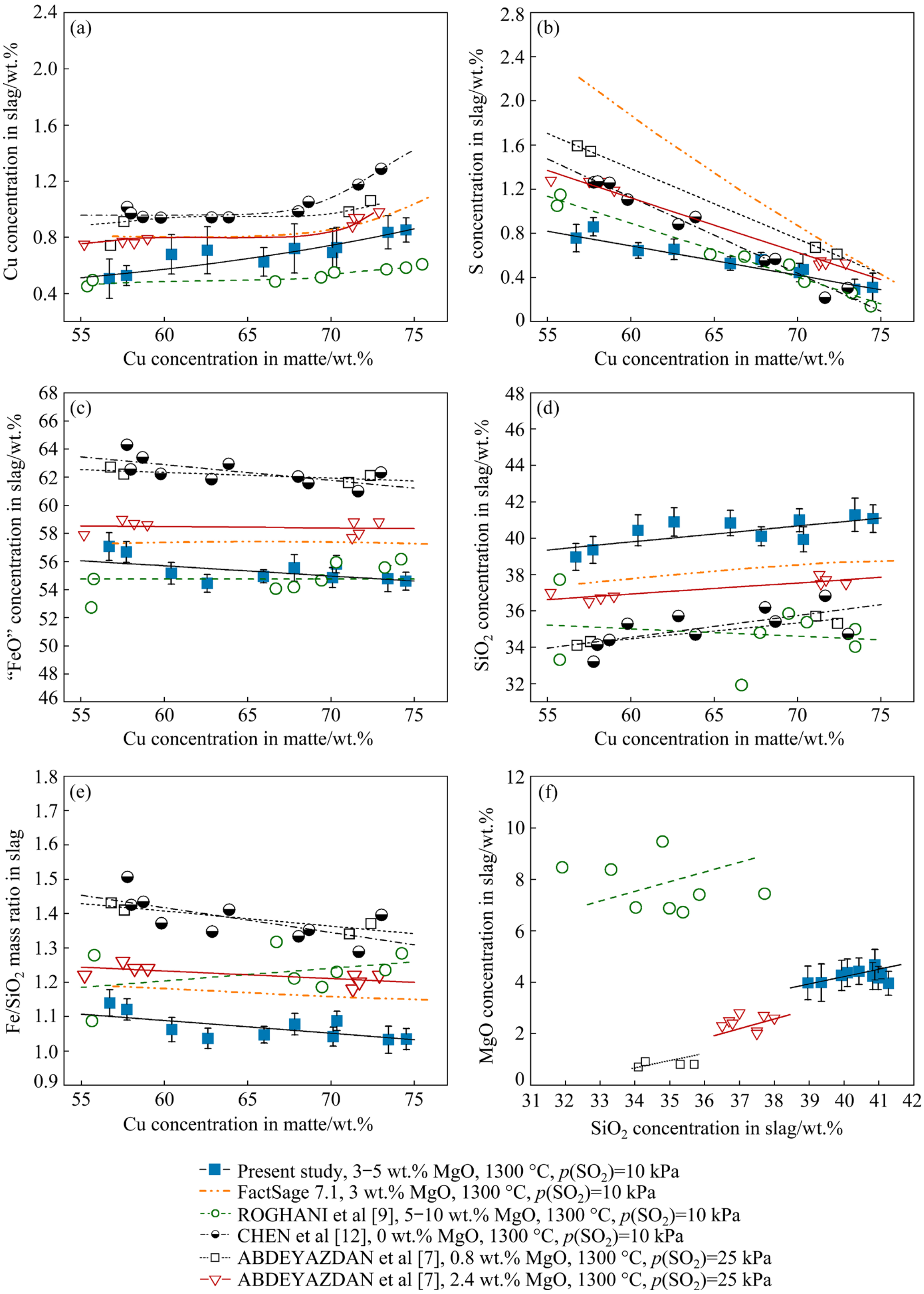

Fig. 5 Compositions of SiO_2-saturated FeO_x−SiO_2−MgO slags in present study and literature [7,9,12]: (a) Cu concentration; (b) S concentration; (c) "FeO" concentration; (d) SiO_2 concentration; (e) Fe/SiO_2 mass ratio; (f) MgO concentration

conditions in the literature [6−10,19−25] are listed in Table 5 for comparison. In the industrial copper smelting process, the Cu loss in the smelting slag originated from both the mechanical suspension of sulfide copper particles and the chemical dissolution of Cu constitutes, as suggested by YAZAWA [15]. In the present study and the experimental data by ABDEYAZDAN et al [7] and CHEN et al [12], the slag compositions were directly measured by EPMA, ruling out the presence of entrained matte droplets in the slag. Therefore, the Cu loss in the slags of the present study and those observations in Refs. [7,12] resulted from the chemical dissolution.

Table 5 Data for MgO-containing iron silicate slags in present study and literature

System	Type of slag	MgO concentration	Gas pressure/kPa	Temperature/°C	Source
Matte and FeO_x−SiO_2−MgO slags	SiO_2 sat	3 wt.%	$p(SO_2)$=10	1300	Present study
	SiO_2 sat	0.8, 2.4 wt.%	$p(SO_2)$=25	1200, 1300	[7]
	SiO_2−MgO sat	5−10 wt.%	$p(SO_2)$=10, 50, 101	1300	[9]
	Spinel sat	0−1.5 wt.%	$p(SO_2)$=25	1200	[19]
	Spinel sat	~2 wt.%	$p(SO_2)$=30, 60	1180−1250	[6]
	SiO_2 sat	10−15 wt.% MgO−CaO	$p(SO_2)$=10, 50, 101	1300	[10]
	SiO_2 sat	0.9 wt.% MgO−Al_2O_3−CaO	$p(SO_2)$=25	1200, 1300	[8]
Copper alloy and FeO_x−SiO_2−MgO slags	SiO_2 sat	4.4 wt.% MgO	$p(O_2)=10^{-10}-10^{-4}$	1250	[20]
	Al_2O_3−spinel sat	0−6 wt.% MgO−Al_2O_3	$p(O_2)=10^{-9}-10^{-6}$	1300	[21]
	SiO_2 or spinel sat	0.5 wt.% MgO−Al_2O_3−CaO	$p(O_2)=10^{-6.5}$	1150−1350	[22]
Oxide slags	Isotherms	FeO−Fe_2O_3−MgO	$p(O_2)$=21	1400−1800	[23]
	Phase diagram	FeO/Fe_2O_3−MgO−SiO_2	$p(O_2)$=21	>25	[24]
	SiO_2 or spinel sat	MgO−FeO−CaO−SiO_2	$p(O_2)=10^{-7}-10^{-3}$	1300	[25]

“sat” stands for saturated

Figure 5(a) shows that experimentally measured Cu loss in the slag as a function of the matte grade in this study was lower than calculations by FactSage. The concentration of dissolved copper in the SiO_2-saturated FeO_x−SiO_2−MgO slags increased from approximately 0.5 wt.% to 0.85 wt.% as the matte grade increased from 55 wt.% to 75 wt.% at 1300 °C and $p(SO_2)$ of 10 kPa in this study. However, ROGHANI et al [9] reported that the Cu loss in the SiO_2-saturated FeO_x−SiO_2−MgO slags increased with increasing matte grade up to 20 wt.% Cu, and then decreased slightly between the matte grade of 30 wt.% and 60 wt.%, and increased again in the region of higher matte grade. As for the Cu concentration in the iron silicate slags obtained at higher $p(SO_2)$, the dissolved Cu in slag stayed almost constant up to the matte grade of 65 wt.% Cu at $p(SO_2)$ of 50 kPa [13] and 70 wt.% Cu at $p(SO_2)$ of 25 kPa [7], and then it started to increase with increasing matte grade.

The Cu concentration in slags decreased with the addition of MgO. At 1300 °C and $p(SO_2)$ of 10 kPa, the dissolved Cu in slag decreased from 1.0 wt.% for MgO-free FeO_x−SiO_2 slag [12] to 0.7 wt.% for the FeO_x−SiO_2−MgO slag with approximately 4 wt.% MgO under the matte grade of 70 wt.% Cu. Similarly, ABDEYAZDAN et al [7] found that the dissolved Cu decreased from 0.9 wt.% to 0.7 wt.% when the MgO concentration in slags increased from 0.8 wt.% to 2.4 wt.% at 1300 °C and $p(SO_2)$ of 25 kPa. In iron silicate slags, silicate can sustain complex three-dimensional polymeric networks [26]. Adding basic oxides such as MgO and CaO could decrease the chemically dissolved copper in slags by replacing Cu^{2+} with Mg^{2+} and Ca^{2+} within the silica structures [20].

The Cu loss in slags has been extensively studied for the industrial interest of recovering copper values from smelting slags. Some researchers [15,27,28] suggested that the Cu loss in the smelting slags occurred due to oxidic and sulfidic copper dissolution when producing matte of different grades. MACKEY [26] proposed that the sulfidic dissolution was responsible for Cu solubility in slag when the matte grade was up to about 60 wt.% Cu, while oxidic dissolution accounted for the Cu loss at the matte grade higher than 70 wt.% Cu. SRIDHAR et al [4] constructed a relationship between the Cu concentration in slag and that in matte during copper sulfide smelting using industrial data from 42 commercial plants. It was shown that the Cu solubility in the slag was caused by the oxidation of Cu at different oxygen pressures while producing mattes of various grades. Additionally, they supposed that assuming the sulfidic copper dissolution in the slag was unnecessary to explain Cu loss.

The oxidic copper solubility in the slag increased with increasing $p(O_2)$ [26] and increasing temperature [7,8] but decreased with the additional amounts of the additives such as MgO, CaO, and Al_2O_3 in the slag [26,27]. For a fixed matte grade, the oxygen partial pressure of the slag decreased with increasing the MgO, CaO, and Al_2O_3 concentrations [7,18,26,29]. The oxygen partial pressure of the system appears to be related to the proportions of the ferric iron (Fe^{3+}) and ferrous iron (Fe^{2+}) in slag, as represented by Reaction (3). The equilibrium constant (K_{eq}) of the reaction at 1300 °C could be calculated by Eq. (4) [18]. At a fixed matte grade and fixed partial pressures of SO_2, the FeS activity ($a_{(FeS)}$) and $p(SO_2)$ remain constant. The addition of MgO decreases the FeO activity ($a_{(FeO)}$) in the SiO_2-saturated FeO_x−SiO_2−MgO slags, which subsequently results in the decrease of Fe_2O_3 activity ($a_{(Fe_2O_3)}$) in the MgO-containing slags. By adding MgO in the slag at a given matte grade, the proportion of Fe^{3+} tends to decrease with decreasing the oxygen partial pressure of the system [7,30]. Consequently, the oxidic copper dissolution in the SiO_2-saturated FeO_x−SiO_2−MgO slags decreases as oxygen partial pressure is reduced by adding MgO.

$$FeS_{(matte)}+3Fe_2O_{3(slag)}=7FeO_{(slag)}+SO_2(g) \tag{3}$$

$$K_{eq}=\frac{a_{(FeO)}^{7}a_{(FeS)}}{a_{(Fe_2O_3)}^{3}[p(SO_2)/p^{\Theta}]} \tag{4}$$

For the sulfidic copper dissolution in the slags, FALLAH-MEHRJARDI et al [31] found that raising the Cu concentration in matte from 49 wt.% to 55 wt.% would reduce the Cu solubility in the FeO_x−SiO_2 slags from 0.8 wt.% to 0.7 wt.%, as the sulfur concentration in the slag declined from 2.6 wt.% to 1.8 wt.%. These results supported that the Cu loss in slag at low matte grades was mainly derived from the sulfidic copper dissolution. Opposite to FALLAH-MEHRJARDI et al [31], other studies [7,12] have shown that the Cu solubility in the SiO_2-saturated fayalite slags increased with increasing the matte grade, while the sulfur concentration in the slags decreased. Therefore, the concept of sulfidic and oxidic copper dissolution in the slags helps explain the chemically dissolved mechanism of Cu in the slags, while further investigation is needed to clarify the overall behavior of Cu and sulfur in the slags.

Above all, the chemically dissolved Cu in the SiO_2-saturated fayalite slags increases with increasing the matte grade and decreases with higher MgO. By adding the MgO into the slag, the Mg^{2+} replaces the Cu^+ in the silica structure, and the lower FeO activity in MgO-containing slags leads to a decrease in $p(O_2)$ over the slag, which in turn reduces the Cu solubility in the slags.

4.2.2 Sulfur concentration in slag

The sulfur concentration in all slags decreased with increasing the matte grade, as shown in Fig. 5(b). The dissolved sulfur concentration in slag predicted by FactSage was higher than the experimental values in this study at 1300 °C and $p(SO_2)$ of 10 kPa. The pure SiO_2-saturated FeO_x−SiO_2 slag exhibited the highest sulfur solubility [12], and MgO additions remarkably reduced it. The dissolved sulfur in MgO-free fayalite slag [12] decreased from 1.2 wt.% to 0.68 wt.% by adding 4.42 wt.% of MgO to the liquid slag at the matte grade of 60 wt.% Cu, 1300 °C and $p(SO_2)$ of 10 kPa. Similarly, ABDEYAZDAN et al [7] found that increasing the MgO concentration decreased the sulfur solubility in SiO_2-saturated fayalite slag at 1300 °C and $p(SO_2)$ of 25 kPa. The sulfur solubility in slag decreased by about 50% when the MgO concentration of the slag increased from 0 to 2.4 wt.% at a fixed matte grade. This trend was stronger at lower matte grades but decreased as the matte grade increased [7].

In fayalite slags, the presence of MgO could decrease the sulfur capacity in the slag [7,26]. SHIMPO et al [27] proposed that Fe^{2+} had a stronger affinity for sulfur than Ca^{2+} and Al^{3+}, whereas the addition of CaO or Al_2O_3 decreased the concentration of total Fe^{2+}; consequently, the slag lost part of the ability to dissolve sulfur. Similarly, MgO could also reduce the sulfur solubility in slag.

4.2.3 "FeO" concentration in slag

Figure 5(c) indicates that the "FeO" concentration in the SiO_2-saturated FeO_x−SiO_2−MgO slag is inversely proportional to the matte grade. In current study, iron existed as Fe^{2+} and Fe^{3+} in the slags. As the valence state of the iron could not be measured by EPMA, the total iron concentration in the slags was recalculated as "FeO" for ease of presentation. Within the range of matte grade studied in this work, the "FeO" concentration in the liquid slag decreased by 1−2 wt.% as the matte grade increased from 55 wt.% to 75 wt.% Cu. This trend agreed well with the FactSage predictions and the experimental data in the literature [7,9].

Adding MgO decreased the "FeO" concentration in the liquid slag phase. At the matte grade of 75 wt.% Cu, the "FeO" concentration in slag decreased from 62.5 wt.% [12] to 54.60 wt.% when the MgO concentration increased from 0 to approximately 4.33 wt.%. Similar trends were found by ABDEYAZDAN et al [7] for FeO_x−SiO_2−MgO slags with 0.8−2.4 wt.% MgO at 1300 °C and $p(SO_2)$ of 25 kPa. The results indicated that the MgO concentration in slag strongly impacted the liquid composition of the SiO_2-saturated FeO_x−SiO_2−MgO slags.

4.2.4 SiO_2 concentration in slag

As shown in Fig. 5(d), the SiO_2 concentration in the SiO_2-saturated FeO_x−SiO_2−MgO slags slightly increased over the matte range investigated in the present study, similar to the trend reported in the literature [7,13] and predicted by FactSage. However, ROGHANI et al [9] found that the SiO_2 concentration in the slag tended to decrease with increasing the matte grade, which could be attributed to the increasing Cu solubility in the slag at higher matte grade [20] and silica analysis error due to the inclusion of the solid silica floating on the top of the slag layer [9]. A comparison of the MgO-free [13] and MgO-containing systems in this study indicated that adding MgO could slightly increase the SiO_2 concentration in slag. Similar trends were reported by ABDEYAZDAN et al [7] for iron silicate slags at silica saturation with 0.8 wt.% or 2.4 wt.% MgO at 1300 °C and $p(SO_2)$ of 25 kPa.

4.2.5 Fe/SiO_2 mass ratio in slag

Figure 5(e) indicated that the Fe/SiO_2 mass ratio in all slags slightly decreased with increasing the matte grade. The slight changes in SiO_2 and total iron concentration in slags were contributed to the limited effect of matte grade on the Fe/SiO_2 mass ratio in the slag [13]. At a given matte grade, the increase of MgO concentration decreased the Fe/SiO_2 mass ratio in slag. The Fe/SiO_2 mass ratio in fayalite-based slags at silica saturation decreased from approximately 1.4 [12] to 1.03 when the MgO concentration increased from 0 to 4.33 wt.% at the matte grade of 75 wt.% Cu. The Fe/SiO_2 mass ratio is an essential parameter for regulating industrial operations as it is highly related to the viscosity and liquidus temperature of the slag [26]. Therefore, in the copper concentrates smelting processes, silica is a crucial flux to control the liquidus of the iron silicate slag. The current results implicated that with the addition of MgO in SiO_2-saturated iron silicate slag, more SiO_2 should be added as a flux to maintain the slag under fully liquid conditions [20].

4.2.6 MgO concentration in slag

As shown in Fig. 5(f), the experimentally measured SiO_2 concentration of the SiO_2-saturated FeO_x−SiO_2−MgO slags in this study slightly increased with the addition of MgO. The SiO_2 concentration in the slags of the literature [7,9] exhibited a similar upward trend within a narrow range as the MgO concentration in the slags increased, indicating that adding MgO into the FeO_x−SiO_2−MgO slags enhanced the SiO_2 solubility in the slags. The maximum solubility of MgO in SiO_2-saturated iron silicate slag was relatively low due to the formation of the olivine phase (Mg_2SiO_4−Fe_2SiO_4 solid solution) [30].

4.3 Isotherm of FeO_x−SiO_2−MgO slag at 1300 °C

The experimentally measured slag compositions were plotted onto the 1300 °C isotherms of FeO_x−SiO_2−MgO system, as shown in Fig. 6. The superimposed phase diagrams of FeO_x−SiO_2−MgO system were predicted by FactSage. The prevailing $p(O_2)$ of 10^{-6} and 10^{-5} kPa in the calculations presented middle points of the oxygen partial pressure ranges investigated in this study and the literature [7], respectively. The experimental data in Table 4 were calculated as molar fractions because the mole number of FeO_x was always the same even if the mass fraction of Fe^{2+} and Fe^{3+} varied [20].

As shown in Fig. 6, the present experimental results of the FeO_x−SiO_2−MgO slags fitted well with the predicted tridymite (SiO_2) primary phase field at 1300 °C and $p(O_2)$ of 10^{-6} kPa. The experimental data in FeO_x−SiO_2 systems observed by CHEN et al [12] at 1300 °C and $p(O_2)$ of 10^{-6} kPa agreed well with the predicted tridymite−slag phase boundary. The liquid slags of the FeO_x−SiO_2−MgO system obtained by ROGHANI et al [9], which coexisted with solid SiO_2 and Mg_2SiO_4 (Olivine), were located at the olivine−slag phase boundary. The MgO solubility in the slag was limited by the formation of the solid olivine phase [30]. The liquidus compositions obtained at 1300 °C and $p(SO_2)$ of 25 kPa by ABDEYAZDAN et al [7] showed a good agreement with the predicted tridymite−slag phase boundary at $p(O_2)$ of 10^{-5} kPa. It was noticed that the computational

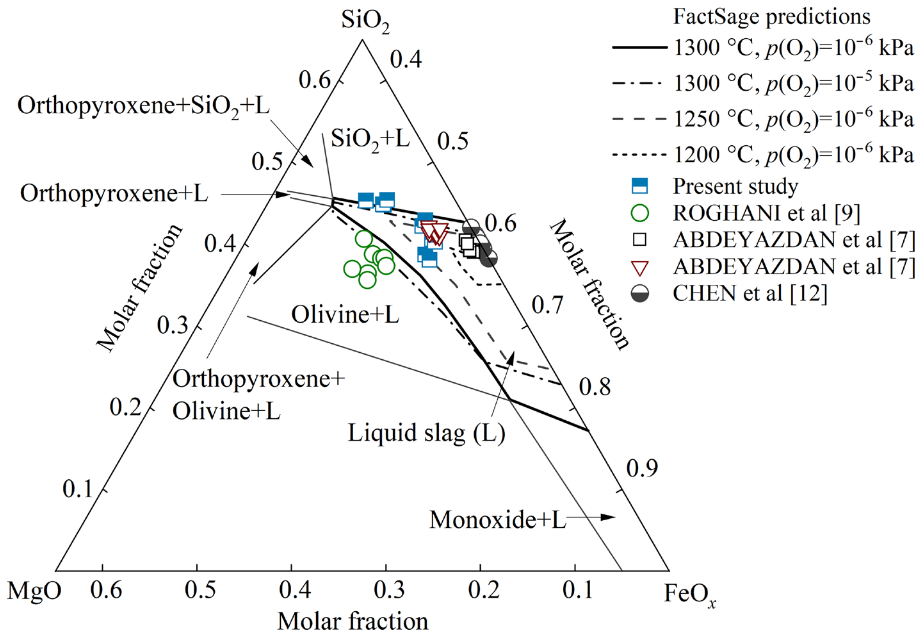

Fig. 6 Isothermal section of superimposed phase diagrams of FeO_x−SiO_2−MgO system with experimental data in present study and literature [7,9,12]

modeling was executed for "pure" FeO_x−SiO_2−MgO slags [13], while the slags in this study and the literature [9,12] included additional elements, such as Cu, S, and other minor elements [10]. Therefore, the experimental data for the FeO_x−SiO_2−MgO systems had minor discrepancies with the calculated results.

A comparison of the 1300 °C isotherms obtained at $p(O_2)$ of 10^{-6} and 10^{-5} kPa indicated that $p(O_2)$ had a significant impact on the spinel primary phase field but a limited effect on the SiO_2 and MgO primary phase fields. With increasing the $p(O_2)$, the SiO_2 primary phase field slightly moved to a lower SiO_2 but higher "FeO" concentration area. While the spinel primary phase field considerably shifted to a higher SiO_2 but lower FeO concentration area, indicating that the lower oxygen partial pressure could help decrease the proportions of the solid silica and spinel in the slag. The maximum MgO solubility in the FeO_x−SiO_2−MgO slag almost stayed constant at around 8 wt.% when the $p(O_2)$ increased from 10^{-6} to 10^{-5} kPa at 1300 °C.

In Fig. 6, the isotherms of 1200, 1250, and 1300 °C were predicted for the FeO_x−SiO_2−MgO system at $p(O_2)$ of 10^{-6} kPa to reveal the influence of the temperature. The predicted liquid slag domain was enlarged when the temperature raised from 1200 to 1300 °C at the fixed $p(O_2)$ of 10^{-6} kPa. With increasing the temperature, the predicted tridymite primary phase field moved to a higher SiO_2 but lower FeO_x concentration region, while the spinel primary phase field exhibited a lower SiO_2 but higher FeO_x concentration. Meanwhile, the olivine primary phase field was extended to a much higher MgO concentration region. Therefore, the solid silica, spinel, and olivine particles that recrystallized by the excessive SiO_2, FeO, and MgO could be dissolved in the liquid slag by increasing temperature.

The current data provide guidance for designing the fluxing strategies of the FeO_x−SiO_2−MgO slag system in copper smelting processes. As given in Fig. 6, with increasing the temperature and decreasing the $p(O_2)$, the liquid slag domain for the FeO_x−SiO_2−MgO system got wider, and its extent was limited by the formation of tridymite or spinel, depending on the Fe/SiO_2 mass ratio [12]. For the olivine−liquid equilibria, the maximum MgO solubility in the liquid slag increased with increasing the temperature while it was not sensitive to $p(O_2)$. When the slag reached the saturation of the solid phase, the slag viscosity got enhanced, consequently increasing the loss of the valuable metals in the slag due to the physical entrainment [20].

In industrial copper smelting processes, the slag compositions should be adjusted to the liquid area for good slag fluidity and low metal losses in slag. At 1300 °C and $p(O_2)$ of 10^{-6} kPa, when the MgO concentration in SiO_2-saturated FeO_x-SiO_2 slags raised from 0 to 8 wt.%, SiO_2 concentration in the liquid oxides increased from around 38 wt.% to 45 wt.%, indicating that more SiO_2 should be added to maintain a fully molten slag. The maximum solubility of MgO in the liquid slag increased from approximately 3 wt.% to 8 wt.% as the temperature raised from 1200 to 1300 °C at a fixed $p(O_2)$ of 10^{-6} kPa under copper smelting conditions. Therefore, the higher temperature and lower oxygen partial pressure would promote the dissolution of the solids in the liquid phase of FeO_x-SiO_2-MgO slags. Moreover, the MgO concentration in raw materials should be limited to reduce the introduction of MgO into the smelting system [7].

4.4 Distribution of Cu, Fe, and S between matte and slag

The distribution behavior of elements between matte and slag governs the recovery efficiency of valuable metals [26]. The distribution coefficient is crucial thermodynamic data to describe the deportment of elements between matte and slag [32], as calculated by Eq. (5):

$$L^{\mathrm{m/s}}(\mathrm{Me})=\frac{w(\mathrm{Me})_{\mathrm{matte}}}{w(\mathrm{Me})_{\mathrm{slag}}} \tag{5}$$

where $L^{\mathrm{m/s}}(\mathrm{Me})$ is the distribution coefficient of elements (Me) in matte and liquid slag. $w(\mathrm{Me})_{\mathrm{matte}}$ and $w(\mathrm{Me})_{\mathrm{slag}}$ refer to the experimentally measured concentrations of the element Me in matte and liquid slag, respectively.

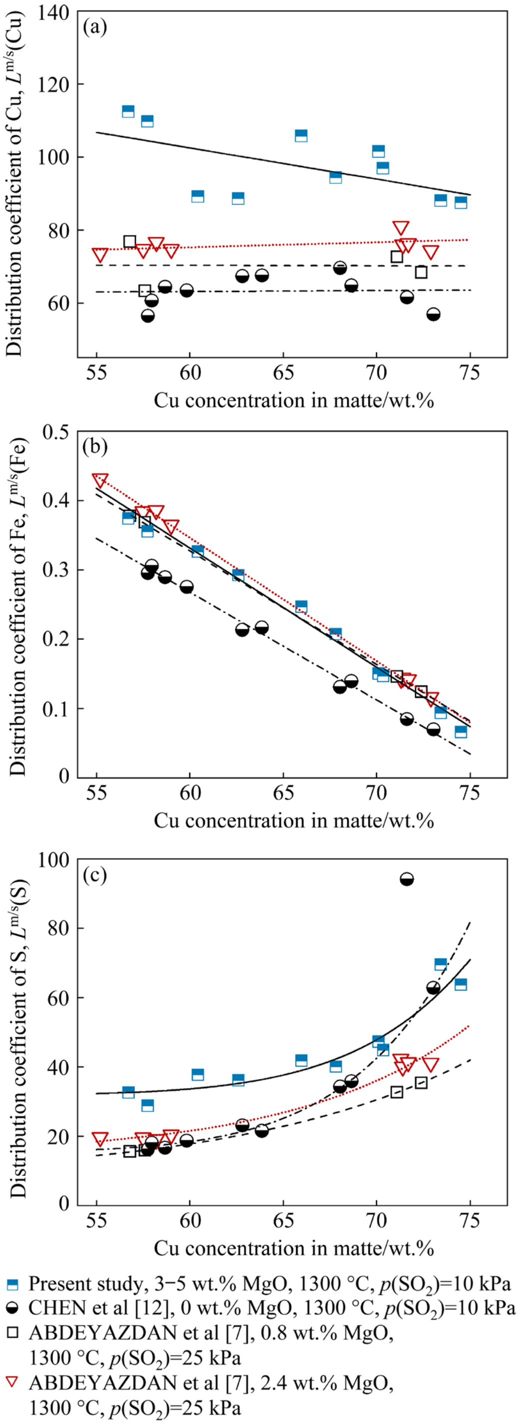

Fig. 7 Distribution coefficients of Cu (a), Fe (b), and S (c) between matte and slag at 1300 °C as function of matte grade in present study and literature [7,12]

Figure 7 presents the distribution coefficients of Cu, Fe, and S between matte and SiO_2-saturated fayalite-based slags as a function of matte grade in this study and the literature [7,12]. As shown in Fig. 7(a), the distribution coefficient of Cu between the matte and FeO_x-SiO_2 slag stayed relatively constant at around 60 at 1300 °C and $p(SO_2)$ of 10 kPa [12]. As the MgO concentration in slag increased to 4 wt.% in this study, the Cu distribution coefficient increased up to about 110 at 55 wt.% matte grade. When the matte grade increased from 55 wt.% to 75 wt.%, the Cu distribution coefficient between the matte and iron silicate slags with approximately 4 wt.% MgO decreased from around 110 to 90. ABDEYAZDAN et al [7] reported that the Cu distribution coefficient increased with the addition of MgO in slags, while it had no noticeable changes with increasing the matte grade at 1300 °C and $p(SO_2)$ of 25 kPa. The results indicated that the addition of MgO and lower matte grade highly favored the deportment of Cu into the matte phase.

As shown in Fig. 7(b), the Fe distribution coefficient between matte and FeO_x−SiO_2−MgO slags was less than 1 and decreased with the increasing matte grade. The results indicated that most of the iron was distributed into the slag phase, and a higher matte grade could improve its deportment to the slag. Contrary to the distributions of Cu and Fe, the deportment of S into matte was highly favored by increasing the matte grade, as displayed in Fig. 7(c). At the matte grade of 60 wt.% Cu, the S distribution coefficient increased from 20 to 37 by increasing the MgO concentration of the slag from 0 to 4 wt.%. Similar increasing trends were also obtained by ABDEYAZDAN et al [7] at 1300 °C and $p(SO_2)$ of 25 kPa. The Fe distribution coefficient observed in this study was higher than that in the literature [7] due to the differences in $p(SO_2)$ and MgO concentration used in the experiments.

In general, the copper and sulfur tend to deport in matte, and their distributions into the matte phase could be improved by adding MgO in fayalite-based slags. The distribution of copper in the matte phase preferred lower matte grade, whereas the enrichment of precious metals in the matte phase, such as Au, Ag, Pt, and Te [16,33], was highly favored by higher matte grade. The experimental measurements provide reliable fundamental data for regulating industrial operations and improving the integrated recovery efficiency of valuable metals.

5 Conclusions

(1) The effect of MgO concentration in slag on the phase equilibria of matte and SiO_2-saturated iron silicate slag at 1300 °C and $p(SO_2)$ of 10 kPa was clarified. The presence of MgO in the FeO_x−SiO_2−MgO slags increased the matte grade under a fixed $p(O_2)$ by decreasing the activity of FeO in the slag and promoting the oxidation of FeS into the slag.

(2) The chemically dissolved copper in the SiO_2-saturated FeO_x−SiO_2−MgO slags increased with increasing the matte grade. While the Cu loss in the slags decreased by adding MgO due to the decreasing $p(O_2)$ over the slag caused by the lower FeO activity in the MgO-containing slags and the replacement of Cu cations by Mg^{2+} in the silica structure. In industrial copper smelting processes, the Cu loss in the slags could be lowered by adding basic oxides and controlling the matte grade.

(3) The slag composition of the FeO_x−SiO_2−MgO system could be optimized by limiting the MgO concentration in raw materials and adding SiO_2 flux to obtain a fully molten slag or slag with a low solid fraction. The crystallized solid particles of SiO_2, spinel, and olivine can be dissolved in the liquid slag by increasing the smelting temperature and decreasing the oxygen partial pressure.

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铜复杂资源造锍熔炼过程中 MgO 对铜锍和二氧化硅饱和铁硅渣相平衡的影响

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摘　要：采用高温平衡实验及电子探针微区分析方法研究铜复杂资源中 MgO 对造锍熔炼平衡体系铜锍及熔炼渣成分(FeO_x−SiO_2−MgO)的影响。结果表明，在 1300 ℃、$p(SO_2)$=10 kPa 熔炼条件下，增加熔炼渣中 MgO 含量可降低渣中 FeO 的活度，进而降低渣中氧分压($p(O_2)$)、减少铜在渣中化学溶解损失量；同时，渣中 FeO 活度降低可促进铜锍中 FeS 氧化进渣，提高铜锍品位。在高硅渣型中，过量 MgO 易在渣中形成固相夹杂颗粒(Mg_2SiO_4−Fe_2SiO_4)，导致渣黏度升高、增加渣中铜损失。当熔炼温度由 1200 ℃升至 1300 ℃及 $p(O_2)$为 10^{-6} kPa 时，FeO_x−SiO_2−MgO 渣中 MgO 的最大溶解量由 3%增至 8% (质量分数)；渣中 MgO 含量增加时，可通过添加 SiO_2 熔剂调整渣型、升高熔炼温度，进而降低渣中固相析出物含量，改善熔渣性质。

关键词：氧化镁；铁橄榄石渣；铜锍熔炼；相平衡；元素分布

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