Distribution of Bi Between Slags and Liquid Copper

CHUNLIN CHEN and STEVEN WRIGHT

The distribution of Bi between liquid copper and calcium ferrite slag containing 24 wt pct CaO, iron silicate slag with 25 wt pct SiO_2, and calcium iron silicate slags was measured at 1573 K (1300 °C) under controlled $CO-CO_2$ atmosphere. The experimental results showed that bismuth distribution is affected by the oxygen partial pressure, and bismuth is likely to exist in slags in the 2+ oxidation state, i.e., as BiO. The distribution ratio between calcium ferrite slag and metal was found to be close to that of iron silicate slag. The Bi distribution ratio was found to decrease with increasing SiO_2 and Al_2O_3 content in slag. Increasing temperature was found to decrease the Bi distribution ratio between slag and metal. Using the measured equilibrium data on Bi content of the metal and slag and composition dependence of the activity of Bi in liquid copper, the activity and hence activity coefficient of BiO in the slag was calculated. The close value of activity coefficient of BiO in both slags at the same oxygen partial pressure indicates that the CaO-BiO and SiO_2-BiO interactions are likely to be at the same level, or the FeO_x-BiO interaction is the predominant interaction for BiO in the slag. Therefore at a constant FeO_x content in the slag, the CaO-BiO and SiO_2-BiO interactions doesn't affect γ_{BiO} significantly.

I. INTRODUCTION

TOXIC elements such as bismuth, arsenic, antimony, cadmium, mercury, selenium, and tellurium are naturally found in base metal ores at low to sometimes significant concentrations. Ore bodies where the concentrations of these elements are low are becoming depleted, while ore bodies of potential for exploitation are more complex, finer grained, and contain increasing amounts of toxic elements. World-wide, the industry mines and processes hundreds of million tons of base metal ores each year; the accumulated mass of minor elements introduced into the biosphere is large and one could expect a significant environmental impact to result. Research at CSIRO is aimed at gathering the required data for developing predictive models to account for the dispersion of minor elements in various solid, liquid, and gaseous streams. The present paper describes a component of the work for development of predictive tools for studying the deportment of minor elements between different phases during high temperature processing of base metal ores.

Accurate accounting of Bi in copper smelting processes is a challenging task and mathematical tools are used to assist in bridging gaps in data and for reconciling uncertainties arising for non-representative sampling and characterization of inhomogeneous samples from commercial processes. Predictive models are required so that the effects on the deportment of minor elements such as bismuth between phases by potential changes of process conditions can be fully evaluated. This understanding can be used to develop alternative practices for controlling the deportment of minor elements between different product streams and the safe storage/disposal of such toxic elements.

The thermodynamics of Bi, such as its equilibrium distribution between slag and copper, oxidation state in the slag and activity coefficient in the various slags have been the subject of some studies[1–12] over the last four decades. Nagamori et al.[1] measured the distribution of Bi between liquid copper alloys and iron silicate slags at oxygen potentials (P_{O_2}) in the range of 10^{-11} to 10^{-6} atm at 1473 K and 1573 K (1200 °C and 1300 °C). They proposed the following equilibrium:

$$\text{Bi} + \frac{v}{2}\text{O}_2 = \text{BiO}_v \qquad [1]$$
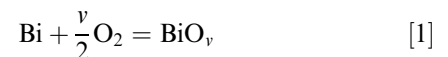
for which the equilibrium constant is

$$K = \frac{a_{\text{BiO}_v}}{a_{\text{Bi}} \cdot p_{O_2}^{v/2}} = \frac{(\gamma_{\text{BiO}_v})(X_{\text{BiO}_v})}{[\gamma_{\text{Bi}}][X_{\text{Bi}}]p_{O_2}^{v/2}} = \frac{[n_\text{T}](\gamma_{\text{BiO}_v})(\text{pct Bi})}{(n_\text{T})[\gamma_{\text{Bi}}][\text{pct Bi}]p_{O_2}^{v/2}} \qquad [2]$$

The distribution coefficient $L_{\text{Bi}}^{\text{S/C}}$ is defined as

$$L_{\text{Bi}}^{\text{S/C}} = \frac{(\text{pct Bi})}{[\text{pct Bi}]} = \frac{K(n_\text{T})[\gamma_{\text{Bi}}]p_{O_2}^{v/2}}{[n_\text{T}](\gamma_{\text{BiO}_v})} \qquad [3]$$

Rearranging Eq. [3] yields

$$\log L_{Bi}^{S/C} = \log \frac{K(n_T)[\gamma_{Bi}]}{[n_T](\gamma_{BiO_v})} + \frac{v}{2}\log P_{O2}, \qquad [4]$$

where [] refers to bismuth in metal, () refers to oxidic bismuth in slag, n_T is the total mole number of constituents in 100 g of each phase when all constituents

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are expressed with mono-nuclear metal atom base such as $FeO_{1.5}$, $CuO_{0.5}$, etc. Provided that n_T and the activity coefficients are kept constant, the plot of $\log L_{Bi}^{S/C}$ against $\log P_{O_2}$ could give a linear relationship with a slope of $v/2$, which suggests the oxidation state of the dissolved species in the slag. However, γ_{BiO_v} in the slag may not be constant and could change with oxygen partial pressure due to a change of slag chemistry (Fe^{3+}/Fe^{2+} ratio). The dependency of $\log \gamma_{BiO_v}$ on oxygen partial pressure may not be strong, since oxygen partial pressure only changes the Fe^{3+}/Fe^{2+} ratio, while the other major components of the slag maintain the same concentration. The previous study shows that the logarithm of the activity coefficient of arsenic oxide in slag is close to a linear function of the logarithm of the oxygen partial pressure.[13] Therefore, it is assumed in this study that the activity coefficient of bismuth oxide is to be a function of oxygen partial pressure as described in Eq. [5]

$$\log \gamma_{BiO_v} = a \cdot \log P_{O_2} \qquad [5]$$

Equation [4] can be rearranged as

$$
\begin{aligned}
\log L_{Bi}^{S/C} &= \log \frac{K(n_T)[\gamma_{Bi}]}{[n_T]} + \frac{v}{2}\log P_{O_2} - \log(\gamma_{BiO_v}) \\
&= \log \frac{K(n_T)[\gamma_{Bi}]}{[n_T]} + \frac{v}{2}\log P_{O_2} - a\log P_{O_2} \quad [6] \\
&= \log \frac{K(n_T)[\gamma_{Bi}]}{[n_T]} + (v/2 - a)\log P_{O_2}
\end{aligned}
$$

The "a" term in this Equation is expected to be much smaller than $v/2$ and the slope of $\log L_{Bi}^{S/C}$, would still be close to $v/2$, which indicates the oxidation state of Bi in slag.

The experimental results of Nagamori et al.[1] showed that $L_{Bi}^{S/C}$ in the oxygen potential range of 10^{-6} to 10^{-11} atm was virtually constant and independent of temperature. Therefore, they concluded that Bi dissolves in the slag in atomic form rather than as an oxide. Jimbo et al.[2] experimentally found that the dissolution of Bi in an iron silicate slag was dependent on the oxygen partial pressure. Plots of Bi solubility expressed as $\log L_{Bi}^{S/C}$ vs $\log P_{O_2}$, suggested that Bi could exist in slag as Bi, BiO, and $BiO_{1.5}$, in which the BiO is the predominant species.

The distribution ratio of Bi between iron silicate slag and copper at 1573 K (1300 °C) measured by See and Rankin[3] show large scatter, and was reported to be independent of oxygen partial pressure. Marschman and Lynch[4] measured the Bi dissolved in iron silicate slag at the fixed Bi partial pressure in the gas phase using an isopiestic technique at oxygen partial pressures of 10^{-12} to 10^{-8} atm. The results showed that the Bi entered the silicate slag in both neutral and oxidic molecular forms and the oxidic form identified was BiO.

Takeda et al.[5] measured the distribution of Bi between molten copper and both iron silicate slag and calcium ferrite slags at 1523 K (1250 °C) at various oxygen partial pressures. They found that Bi exists in the slag as $BiO_{1.5}$, and the measured distribution ratio of Bi

between the two slags and liquid copper are similar at the oxygen partial pressure range of 10^{-9} to 10^{-6} atm, which indicates that the Bi activity coefficients in both types of slags are of the same magnitude. Eerola et al.[6] also studied the distribution behavior of Bi between molten copper and calcium ferrite slags under copper fire-refining conditions. The $L_{Bi}^{S/C}$ they measured at oxygen partial pressures between 10^{-8} and 10^{-6} atm agrees with the results of Takeda et al.,[5] which suggests that Bi exists in the slag as $BiO_{1.5}$ in calcium ferrite-based slags. When the oxygen partial pressure was higher than 10^{-6} atm, the $L_{Bi}^{S/C}$ reported by Eerola et al.[6] was greater than that of Takeda et al.,[5] and indicated that $BiO_{2.5}$ and $BiO_{1.5}$ could coexist in the slag at high oxygen potentials. Kim and Sohn[7] investigated the effects of CaO, Al_2O_3, and MgO additions to silica-saturated iron silicate slags on the Bi distribution ratio between molten copper and slag at 1523 K (1250 °C) and oxygen partial pressure in the range of 10^{-12} to 10^{-6} atm. They found that the Bi distribution ratio was independent of oxygen partial pressure, supporting the atomic dissolution hypothesis of Bi in the slag. They also found that the Bi distribution ratio was not significantly affected by the additions of basic oxides such as CaO and MgO to the silicate-saturated slags.

Roghani et al.,[8,9] measured the Bi distribution between calcium ferrite slag and copper matte, and also iron silicate slag and copper matte under various SO_2 partial pressure at 1573 K (1300 °C). It was found that when the matte grade was fixed (the Bi activity coefficient in the matte was fixed), the Bi distribution ratio increased with increasing SO_2/O_2 partial pressure, and the Bi existed in the slag predominantly as BiO. The Bi distribution ratio between iron silicate slag and matte was about one magnitude higher than for bismuth in calcium ferrite slag, which means the Bi activity coefficient in iron silicate slag was about one magnitude lower than calcium ferrite slag and contradicted the findings of Takeda et al.[5]

Font et al.[10, 11] measured the Bi distribution between the iron silicate or calcium ferrite slags and Ni mattes at 1573 K (1300 °C). They found that the Bi distribution ratio between calcium ferrite slag and matte was about one magnitude higher than that of iron silicate slag which was contrary to the findings of Roghani et al.[8, 9]

Paulina et al.[12] investigated the distribution of Bi between copper and FeO_x-CaO-SiO_2 slag under oxygen partial pressure of 10^{-6} atm at 1573 K (1300 °C). It was found that the slag/metal bismuth distribution ratio decreased as the CaO content of the slag increased but was much less affected by the Fe/SiO_2 (wt/wt) ratio.

There are considerable discrepancies on the oxidation state of Bi in slags. Furthermore, the magnitude of distribution ratios obtained for similar slag chemistries equilibrated under comparable conditions show large variations. The previous studies[1–7] show that liquid copper alloys have much high bismuth than slags and could readily "contaminate" the slags through suspension/emulsification. The Bi-level in the slags reported or estimated from previous studies[1–7] could go down to a

few ppm, which would have been a great challenge for the chemical analysis, due to the difficulties of slag digestion and not loosing volatile bismuth, and then with the accuracy of the measurement technique. It is highly likely that the discrepancies are due to (1) suspended copper–bismuth micro-droplets in the slag and (2) limitation and large uncertainties of the chemical analysis of the low Bi in the slag. The primary objective of the present study was to resolve the discrepancy in the published studies on the oxidation state and solubility of bismuth in slags and then deduce the effect of slag chemistry and its oxidation state on the activity and activity coefficient of most stable form of bismuth species in slags. The approach of this investigation was to measure the equilibrium distribution of Bi between the liquid copper and two types of slags under various oxygen partial pressures and temperatures using the classic equilibration and quench technique.

II. EXPERIMENTAL

The previous experimental work has shown that the distribution ratio of Bi between slag and copper is low so that the majority of Bi will report to the liquid copper phase during gas/slag/alloy equilibrium experiments. Therefore, use of a Cu-Bi alloy as the Bi source in the experiments should reduce the reaction time required for the Bi in slag and alloy phases to distribute between each other and reach equilibrium. Another benefit of using Cu-Bi alloy as the Bi source is that the vaporization of Bi may be minimized since the liquid copper phase is fully covered by the slag during the equilibration experiments.

Master copper alloy with approximately 3 wt pct Bi was synthesised by adding Bi metal granulates to molten copper contained in a magnesia ceramic crucible at 1423 K (1150 °C) under flowing N_2 in an induction furnace. The molten alloy was extracted by suction into silica glass tubing and allowed to cool to room temperature inside the tubing. The cold copper alloy was then removed from the tubing.

In order for the analytical department to establish a reliable procedure to determine very low Bi levels by inductively coupled plasma mass spectrometry (ICP-MS), a number of copper alloy samples containing Bi in the range of 30,000 to 0 ppm were prepared and submitted for analysis. These samples were then used as standards in the equilibrium studies. The standard sample with 2000 ppm of Bi was prepared by doping the master alloy into molten copper at 1423 K (1150 °C) under flowing N_2 in a tube furnace with sealed end caps for atmosphere control. Further samples containing 100, 25, and 5 ppm of Bi were prepared using the previously made high Bi-level standards, with the same procedure to control the targeted Bi levels. The analytical results of the standard samples by ICP-MS are listed in Table I. There is a good agreement between the analytical value and the prepared value and therefore there is, a high degree of confidence in the analytical procedures used.

Approximately 150 g of well-mixed FeO_x and SiO_2 powders (25 wt pct SiO_2) and 50 g of master Cu-Bi alloy

Table I. Comparison of the Measured Bi Concentration in Cu-Bi Alloy with the Targeted Value

Sample ID (Cu-Bi Alloy)	Target Concentration	ICP-MS Results
Mater alloy	30,000	29,600 (ICP)
High purity copper		0.8 ppm
SA1	2260 ppm	2100 ppm
SA2	104 ppm	102 ppm
SA3	27 ppm	25 ppm
SA4	5.8 ppm	5 ppm

was added to a magnesia crucible of 59 mm internal diameter and 100 mm tall. The FeO_x had been previously prepared from commercial grade Fe_2O_3 by reduction at 800 °C in a small vibrating bed reactor with a 45 pctCO-55 pctCO$_2$ gas mixture for several hours. The crucible containing the powders and the copper alloy was positioned at the hot zone of a vertical tube furnace with a 110 mm diameter working tube. The work tube had water-cooled end caps for atmosphere control. The furnace was then sealed and a mixture of carbon monoxide and carbon dioxide gases (CO/CO_2 ratio = 7.16) with a total flow of 400 ml/min was introduced into the working tube. The furnace temperature was increased to 1573 K (1300 °C). After 16 h, the furnace power was switched off and the crucible was allowed to cool to room temperature with gas flowing through the work tube. The cooled crucible containing the master slag was removed from the furnace. The slag and alloy were then carefully separated from the crucible and from each other. The master slag was then pulverized using a Tema ring mill, for use in equilibrium tests. A representative sample was submitted for analysis by inductively coupled plasma (ICP). Table II lists the compositions of iron silicate and calcium ferrite master slags prepared at 1573 K (1300 °C) with a gas mixture of CO and CO_2 with ratio of 7.16.

A vertical tube furnace fitted with an alumina working tube of 60 mm diameter and water-cooled brass end caps to isolate the atmosphere was used for the equilibrium study. Reaction gases entered the furnace from bottom and exited through an alumina tube connected to gas bubblers. The flow rates of the CO_2 and CO gases, were regulated by mass flow controllers for each gas with total combined flow rate of 400 cm^3/min maintained in the furnace over the duration of each experiment. The required CO_2:CO ratio for the desired P_{O2} for an experiment was determined using Eq. [7] of Yazawa and Takeda.[14]

$$\log P_{O_2} = 2 \log \left(\frac{CO_2}{CO} \right) - \frac{29,510}{T} + 9.05 \qquad [7]$$

In each experiment, approximately 5 grams of Cu-Bi alloy and 7 grams of slag were placed in a cylindrical-shaped magnesia crucible of 20 mm diameter and 30 mm height. The crucible was suspended from an alumina tube from which the reaction gases exited. The crucible containing the alloy and slag mixture was suspended in the upper cold zone initially, while the gas mixture purged air from the working tube. The crucible

	Cu (Wt Pct)	Fe (Wt Pct)	Mg (Wt Pct)	Ca (Wt Pct)	Si (Wt Pct)
Iron silicate slag	1.26	50.1	2.36	0	12.2
Calcium ferrite slag	1.5	49.5	2.06	17.0	0

was then slowly lowered into the test position (hot zone) over a 10-minute period. Although it was found that the time required for establishing equilibrium for both iron silicate slag and calcium ferrite slag system was around 16 hours, the experimental time was extended to 24 hours. The equilibration time was determined by monitoring the Fe^{3+}/Fe^{2+} ratio in the slag and the Bi distribution ratio between the slag and copper.

After the required reaction time, the crucible and its contents were removed from the furnace and quickly quenched in the cold water. The slag and metal phases were then removed from the crucible and separated from each other by physical means. The slags were ground manually using a mortar and pestle, and then passed through a 75-micron sieve to remove any small copper droplets present in the slag. Representative samples of the metal and slag were then analyzed by ICP techniques following acid digestion. Silicon in the slag was digested using a borate fusion technique according to an Australian standard.[15] Ferrous oxide and total iron content of the slag samples were determined by the digestion and titration technique adapted from Young.[16] The low Bi concentration in the slag was analyzed by ICP-MS.

III. RESULTS AND DISCUSSIONS

Through a series of experiments, the distribution of bismuth between slag and metal was measured under different experimental conditions that include variations in slag chemistry, oxygen partial pressure, and the temperature. The experimental conditions as well as the compositions of slag and alloy after equilibration are listed in Table III. The distribution of Bi $L_{Bi}^{S/C}$ was defined as Eq. [3].

A. Copper Solubility

Figure 1 shows that the solubility of Cu in the iron silicate slags increases with increasing oxygen partial pressure. There is general agreement between the results of this study and the published data.[1,3,7,14] The SiO_2 content in the iron silicate slag of this study and the previous studies by Nagamori et al.[1] and See and Rankin[3] was about 25 wt pct, while silica-saturated slag was used in the other studies.[7,14] The crucibles used by Nagamori et al.[1] and by See and Rankin[3] were Al_2O_3, therefore, the slags should have been saturated with Al_2O_3. The slags in this study are magnesia saturated. The differences of the slag chemistry due to the silica content and the saturating phase are responsible for the difference of Cu solubility shown in Figure 1. Figure 2 shows that the measured Cu content in the calcium ferrite slag of this study agrees very well

with Yazawa and Takeda's data,[14] except for the point at the oxygen partial pressure of 10^{-6} atm. The measured Cu content in the calcium ferrite slag at PO_2 of 10^{-6} atm is 6.88 wt pct, whereas the value reported by Yazawa and Takeda is 5.15 wt pct. This could be due to the contamination of this slag sample with tiny copper droplets in the current study, even though the slag was crushed and screened to remove copper prills. It is clear from Figures 1 and 2 that the dependency of the Cu content in both types of slags on the oxygen partial pressure is close to the slope expected for that of Cu_2O existing in the slag in the oxide form.

B. Fe^{3+}/Fe^{2+} Ratio in the Slags

The variation of the Fe^{3+}/Fe^{2+} ratio in the iron silicate slag are plotted as a function of log PO_2 in Figure 3. As is shown, except for the data at PO_2 of 10^{-10} atm, the Fe^{3+}/Fe^{2+} ratio determined in the iron silicate slag of this study is in good agreement with that from previous study,[13] which demonstrates that the slag and gas in this study are in equilibrium. It was reported that the Fe^{2+} measured in the current study at PO_2 of 10^{-10} atm was subject to error due to the presence of residue after the digestion of the slag sample during the titration analysis.

For the iron silicate slag, the slope of the ratio is close to that of the silica-saturated iron silicate slag given by Michal and Schuhmann.[17] The Fe^{3+}/Fe^{2+} ratio was approximately doubled by decreasing the SiO_2 content to 25 pct. This observation was supported by Michal and Schuhmann's[17] finding that the Fe^{3+}/Fe^{2+} ratio increases with a decrease in SiO_2 in the slag. There is good agreement on the Fe^{3+}/Fe^{2+} ratio in the calcium ferrite slag with 25 wt pct CaO at 1573 K (1300 °C) between this study and literature data.[13,18]

C. MgO Solubility

The MgO in the iron silicate slags is about 10 wt pct, which is higher than the 6 wt pct given in previous work[13] and 5 to 10 wt pct reported by Roghani et al.,[8] This indicates that the slag was possibly contaminated by the MgO-FeO solid solution and the $MgFe_2O_4$ spinel that forms between the crucible and the slag. The higher MgO content may then be due to the difficulties encountered in the separation of thin layer slag from those solid solution phases. This suspicion was supported by the SEM analysis of the slag sample. It was found that the MgO content in the bulk slag is about 5 wt pct, while the MgO in the layer close to the crucible is about 30 wt pct. Similar to the iron silicate slags, the MgO content in the calcium ferrite slags was 6 to 7 wt pct and was higher than the literature value of

Table III. Slag and Metal Chemistry After Equilibrium

| ID	Slag	T (K)	P_{O_2} (atm)	Al$_2$O$_3$	CaO	SiO$_2$	MgO	FeO	Fe$_2$O$_3$	Cu$_2$O	Bi (ppm) Slag	Bi (ppm) Alloy	$\frac{FeO+CaO+MgO}{Fe_2O_3+SiO_2+Al_2O_3}$	$L_{Bi}^{S/C}$
S27	FeO$_x$-SiO$_2$	1573	10^{-10}	0	0	26.68	8.97	51.61	15.88	0.97	72	27,100	1.42	0.0027
S17	FeO$_x$-SiO$_2$	1573	$10^{-9.2}$	0	0	26.76	9.53	51.61	8.15	1.45	121	29,600	1.75	0.0041
S16	FeO$_x$-SiO$_2$	1573	$10^{-8.5}$	0	0	26.77	9.88	50.58	9.87	1.62	141	29,000	1.65	0.0049
S21	FeO$_x$-SiO$_2$	1573	10^{-8}	0	0	25.25	9.29	49.29	15.02	2.25	161	27,600	1.45	0.0058
S3	FeO$_x$-SiO$_2$	1573	$10^{-7.5}$	0	0	25.67	11.11	46.07	14.59	2.47	189	21,300	1.42	0.0089
S2	FeO$_x$-SiO$_2$	1573	10^{-7}	0	0	25.03	10.50	45.17	15.59	3.75	144	20,600	1.37	0.0070
S15	FeO$_x$-SiO$_2$	1573	10^{-7}	0	0	25.70	11.52	42.6	17.88	2.86	185	22,600	1.24	0.0082
S4	FeO$_x$-SiO$_2$	1573	$10^{-6.5}$	0	0	25.46	10.5	41.57	18.17	5.13	311	23,400	1.19	0.013
S19	FeO$_x$-SiO$_2$	1573	10^{-6}	0	0	25.03	9.97	37.97	22.89	4.80	355	27,300	1.00	0.013
C20	FeO$_x$-CaO	1573	$10^{-9.2}$	0	23.67	0	7.13	33.98	28.18	1.18	134	28,000	2.30	0.0048
C11	FeO$_x$-CaO	1573	$10^{-8.5}$	0	23.65	0	6.78	30.63	32.98	1.57	72	18,400	1.85	0.0039
C6	FeO$_x$-CaO	1573	10^{-8}	0	23.79	0	6.77	26.77	37.34	2.34	185	27,800	1.54	0.0067
C8	FeO$_x$-CaO	1573	$10^{-7.5}$	0	22.95	0	6.37	25.87	38.34	2.60	184	26,900	1.44	0.0068
C10	FeO$_x$-CaO	1573	10^{-7}	0	22.25	0	8.12	23.29	39.48	3.17	156	16,700	1.36	0.0093
C9	FeO$_x$-CaO	1573	$10^{-6.5}$	0	22.53	0	6.75	18.02	44.92	3.85	266	21,500	1.05	0.0124
C18	FeO$_x$-CaO	1573	10^{-6}	0	21.85	0	5.75	16.86	43.63	7.53	682	19,500	1.02	0.0350
S12	FeO$_x$-SiO$_2$	1573	10^{-8}	0	0	31.05	11.03	47.23	9.44	2.15	121	25,800	1.44	0.0047
S13	FeO$_x$-SiO$_2$	1573	10^{-8}	0	0	35.33	11.02	41.83	9.16	2.55	128	29,300	1.19	0.0044
S22	FeO$_x$-SiO$_2$	1533	10^{-8}	0	0	24.36	5.25	47.10	23.03	3.19	290	28,600	1.10	0.01
S23	FeO$_x$-SiO$_2$	1623	10^{-8}	0	0	23.30	11.23	43.24	27.18	1.90	100	28,400	1.08	0.0035
S26	FeO$_x$-SiO$_2$	1673	10^{-8}	0	0	25.47	18.83	43.75	12.59	1.26	51	30,700	1.64	0.0017
S24	FeO$_x$-SiO$_2$-Al$_2$O$_3$	1573	10^{-8}	4.87	0	22.89	10.3	43.76	20.89	2.34	120	27,600	1.11	0.0043
S25	FeO$_x$-SiO$_2$-CaO	1573	10^{-8}	0	5	25.46	13.02	35.52	20.17	1.78	44	6300	1.17	0.007
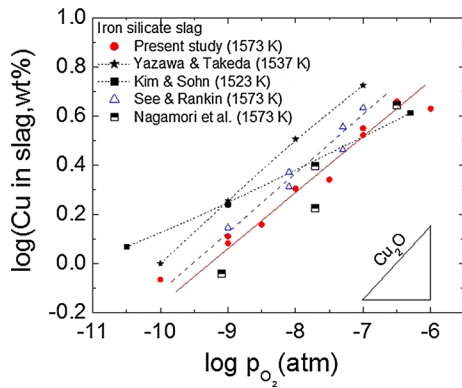
Fig. 1—Variation of the copper content in iron silicate slags with oxygen partial pressure at 1573 K (1300 °C). Literature data from Refs. [1, 3, 7, 14].

Fig. 2—Variation of the copper content in calcium ferrite slags with oxygen partial pressure at 1573 K (1300 °C). Literature data from Ref. [14].

three percent, which indicates the contamination of the slag with magnesiowustite and spinel solid phases. Previous study by Takeda et al.[5] shows that bismuth oxide has neutral behavior, and similar solubility in both acidic iron silicate slag and basic calcium ferrite slag. Therefore, the Bi in MgO-rich solid solution is expected to be in the similar level of Bi in slag. As a result, the solid solution contamination in both types of slags in the current study is not expected to impact the Bi distribution significantly.

D. Bi Distribution Ratio Between Slag and Copper

The measured distribution ratio of Bi between slag and metal are plotted against the oxygen partial pressure in Figure 4. The distribution of Bi is affected strongly by
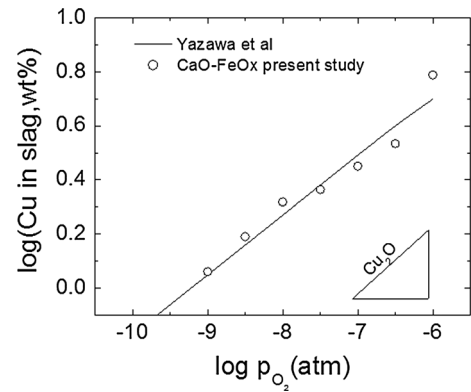
the oxygen partial pressure over the range studied, which supports the concept of oxidic dissolution of Bi in the slag. All the experimental data from this study on the iron silicate slag and the calcium ferrite slag have fallen on one line except for a point from the calcium ferrite slag series at a pO$_2$ of 10^{-6} atm. This slag could have been contaminated with metallic Cu, which resulted in higher analysis results for Bi content of the slag. When the copper contamination was accounted for using the relationship in Figure 2, the corrected/recalculated Bi distribution ratio for this experiment falls on the line in Figure 4. The slopes obtained in the present study for both iron silicate slag and calcium ferrite slag are 0.22, which does not agree with the literature[1,3,5,7] where a range of slopes are reported (see Table IV) and
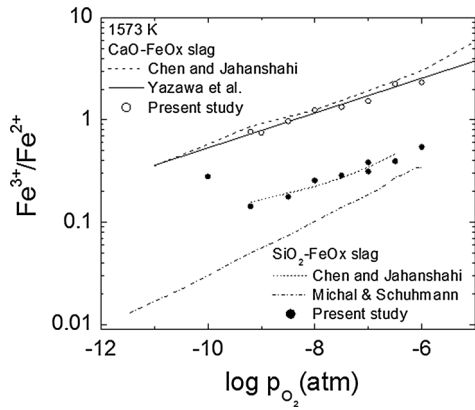
Fig. 3—Comparison of the Fe^{3+}/Fe^{2+} ratio in the slags under varied oxygen partial pressure with the literature data.[13,14,18]
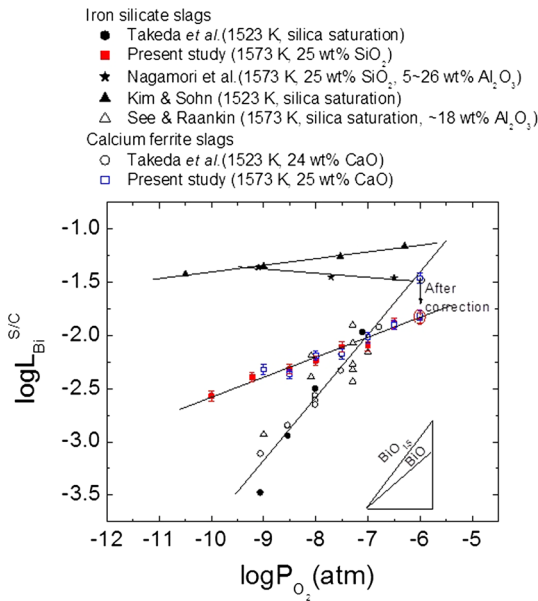

Fig. 4—Variation of the equilibrium distribution of Bi between iron silicate slags and the liquid copper with oxygen partial pressure at 1573 K (1300 °C) compared with literature data.[1,3,5–7]

plotted in Figure 4. The slope $\left(\frac{v}{2} - a\right)$ of 0.22 observed in this study tends to suggest that Bi was more likely to be existing as BiO in the slag under oxygen partial pressure of 10^{-10} to 10^{-6} atm. The dependency of BiO activity coefficient on the oxygen partial pressure a in Eq. [5] of about 0.28 was likely due to the change of the Fe^{3+}/Fe^{2+} ratio with increasing oxygen partial pressure.

The literature on Bi distribution between slag and copper are not consistent. The results by Kim and Sohn[7] and by Nagamori et al.,[1] show that the dependency of the Bi distribution ratio on the oxygen partial pressure was weak. However, the experiments by Nagamori et al.,[1] were carried out using an alumina crucible, and the slags should have been alumina saturated. At 1573 K (1300 °C), the alumina content of the slags varied from 5.8 to 26.3 wt pct. The large

compositional changes could mask the variation of the distribution ratio with the oxygen partial pressure, making it difficult to compare with other studies. In Kim and Sohn's work,[7] the slopes obtained for Pb and Cu are much less than the values expected for PbO and Cu_2O, which indicates that the dependency of the distribution ratio of minor elements including Bi on the oxygen partial pressure was somehow underestimated. Marschman and Lynch[4] used an isopiestic technique under various oxygen partial pressures and the slope of the relationship between the Bi solubility in slags and the oxygen partial pressure varied from 0.32 to 0.52.

The derived slopes $\left(\frac{v}{2} - a\right)$ of the experimental data on iron silicate slag by Jimbo et al.[2] and by Roganhni et al.[8] were 0.4 and 0.38, respectively, less than 0.5, the slope expected of BiO. Takeda et al.[5] and Eerola et al.[6] report the slope to be larger than 0.5, which suggests that Bi exists in slag as Bi_2O_3. However, the equilibration time used in Eerola's experiments[6] was only an hour, and the oxygen partial pressure was not controlled. The oxygen partial pressure was derived from the measured O content in the metal. If the slag and metal were not in equilibrium, the derived oxygen partial pressure did not represent the true oxidation state of the slag.

As stated above, the slopes obtained for both iron silicate slag and calcium ferrite slag were 0.22, which does not agree with the literature data. Reasons for the poor agreement are not apparent. One possible reason is that the entrained copper droplets were not removed from the slags before chemical analysis for the early studies. As the concentration of Bi in copper is 100 times larger than that in slag, the mechanically dispersed copper contains of the same order of magnitude of Bi as the chemically dissolved Bi, hence resulted in large uncertainty in their results. It is known that dissolved copper in copper-saturated slag precipitates as metallic copper from the slag during cooling. The size of the precipitated copper droplets in slag was reported to be around 1 μm during quenching in water, <10 μm during quenching in nitrogen flow, and 50 to 100 μm during slow cooling in furnace.[19] In this study, the samples are quenched in water. Therefore, the precipitated cu droplets are expected to have a size of less than 10 μm, which can easily pass 75 μm sieve used for screening the entrained copper in slag in the current study. Therefore, screening and removing the copper droplets out of the slag will minimize the contamination of the slag with mechanically entrained copper, but has little impact on chemically dissolved copper.

Another possible source of difference for the early studies could be because Bi is very volatile at high temperature, which leads to low concentration of Bi in the slag. The concentration of Bi in the slag could be less than 100 ppm, which brings the challenge for the chemical analytical technique and may result with a large uncertainty for the analytical results contributing to the scatter of the published data. An ICP-MS was used in the present study for measuring the trace amount of Bi in the slag, which has much higher

Table IV. Dependence of the Bi Distribution Ratio on the Oxygen Partial Pressure

Investigators	System	Temperature [K (°C)]	PO_2 (atm)	Slope ($v/2 - a$)	Analytic Method
Nagamori *et al.*	slag-Cu	1473 to 1573 (1200 to 1300)	10^{-9} to 10^{-6}	−0.04	AAS
See and Rankin	slag-Cu	1573 (1300)	10^{-9} to 10^{-7}	0	AAS
Marschman and Lynch	slag-Gas	1458, 1523 (1185, 1250)	10^{-12} to 10^{-8}	0.32 to 0.52	AAS
Jimbo *et al.*	slag-Cu	1473, 1523 (1200, 1250)	10^{-11} to 10^{-7}	0.4	colorimetry
Roganhni *et al.*	slag-Matte	1573 (1300)	10^{-9} to 10^{-6}	0.38	ICP
Kim and Sohn	slag-Cu	1523 (1250)	10^{-11} to 10^{-6}	0.063	DCP
Takeda and Yazawa	slag-Cu	1523 (1250)	10^{-9} to 10^{-6}	0.60	AAS
Eerola *et al.*	slag-Cu	1523 (1250)	10^{-8} to 10^{-4}	0.75	AAS
Present study	slag-Cu	1573 (1300)	10^{-10} to 10^{-6}	0.22	ICP-MS

Table V. Comparison of Bi Analytical Results of the Same Samples by Various Laboratory[20]

	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5
Analytical method	ICP-MS	AAS	ICP-MS	ICP-MS	ICP-MS
Sample	Bi (ppm)	Bi (ppm)	Bi (ppm)	Bi (ppm)	Bi (ppm)
Enviro slag	<0.1	3.238	0.109	<1	0.25
Sarm Ore	0.125	3.99	0.365	<1	0.385
Converter matte 1	10.7	5.8	11.7	12	13.77
Converter matte 2	12.8	8.6	13	14	15.45
Converter slag	0.67	4.21	0.547	<1	0.66
Furnace slag	0.28	4.5	<0.3	<1	0.2

accuracy than the other analytical techniques such as Atomic absorption spectroscopy (AAS), Colorimetry, and ICP.

McKenzie and Seechoonparsad[20] conducted a round-robin analysis study where slag and matte samples were analyzed by laboratories around the world for minor elements including Bi. The results for Bi are summarized in Table V. Analysis by ICP-MS from Labs 1, 3, 4, and 5 are in reasonably good agreement, whereas the result by AAS from Lab 2 has a large difference to other Labs. This suggests that the results by ICP-MS from this study are most likely to be more accurate than the analytical results by AAS used by the majority of other studies.[1, 3–6]

In this study a series of metal samples at various Bi concentration were made by diluting the master alloy with high purity copper (containing <1 ppm Bi) to concentrations between 30,000 ppm Bi and 5 ppm. Table I shows, there was good agreement between the targeted Bi concentrations and the analyzed Bi concentrations by ICP-MS, providing a high degree of confidence in the analytical results.

To examine the effect of temperature on the bismuth distribution, experiments were carried out at the range of 1533 K to 1673 K (1260 °C to 1400 °C) at the oxygen partial pressure of 10^{-8} atm with iron silicate slag and Cu alloy. Loss of Bi through volatilization was not significant as concentrations in the slag remained well within the detection limits for ICP-MS analysis. Figure 5 shows that, at a given oxygen partial pressure, distribution of Bi to the slag was increased at lower temperature, which agrees with the findings by Takeda *et al.*[5] The copper content of the slag followed the same trend, at fixed oxygen partial pressure, where the Cu loss to the slag decreased with increasing temperature.

Figure 4 shows that distribution ratios of Bi of both iron silicate slag and calcium ferrite slag were very close at the fixed oxygen partial pressure and 1573 K (1300 °C), indicating that the interaction between Bi oxide and CaO was about the same as the interaction between Bi and SiO_2, or the interaction between iron oxide and Bi oxide predominated and was much stronger than the interaction between CaO or SiO_2 and Bi oxide. Consistent with this observation, Figure 6 shows that the Bi distribution ratio is relatively constant with change of slag basicity defined as Eq. [8].

$$\text{Basicity} = \frac{\text{FeO} + \text{CaO} + \text{MgO}}{\text{SiO}_2 + \text{Fe}_2\text{O}_2 + \text{Al}_2\text{O}_2} \qquad [8]$$

Addition of 5 wt pct Al_2O_3 to the iron silicate slag lowered the Bi distribution ratio. Similar to the effect observed for Al_2O_3, an increase in SiO_2 concentration in the slag leads to the slight decrease of Bi distribution ratio, which suggests that Bi oxide behavior was slightly more acidic than basic.

E. Activity Coefficient of BiO in the Slag

The slope of the line of distribution ratio vs oxygen partial pressure from this study was 0.22, which suggests that Bi was more likely to be existing as BiO in the slag. Rearranging Eq. [3] yields:

$$\gamma_{\text{BiO}} = \frac{K[\gamma_{\text{Bi}}][X_{\text{Bi}}]p_{\text{O}_2}^{1/2}}{X_{\text{BiO}}} \qquad [9]$$

Thus for a given activity coefficient of Bi in the metal, concentrations of Bi in the metal and slag, the oxygen partial pressure, and the activity coefficient of bismuth oxide (γ_{BiO}) can be readily calculated from this equation.
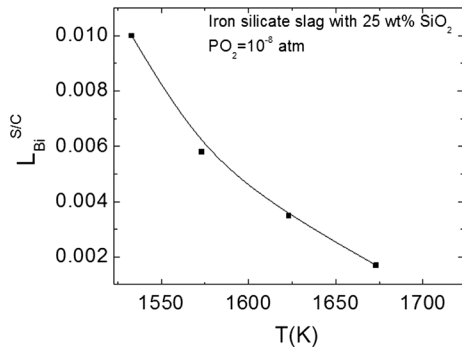
Fig. 5—Variation of the equilibrium distribution of Bi between iron silicate slags and the liquid copper with temperature.
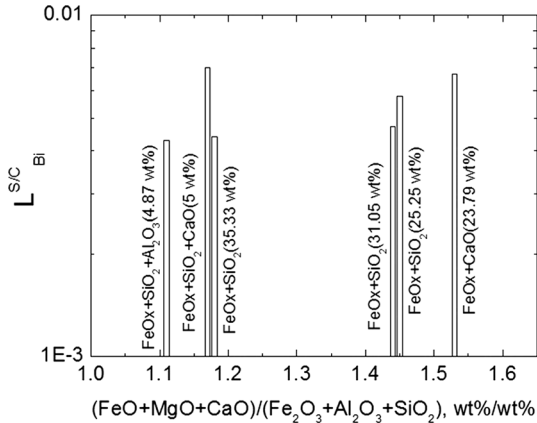

Fig. 6—Variation of the equilibrium distribution of Bi with slag basicity at 1573 K (1300 °C) and oxygen partial pressure of 10^{-8} atm.
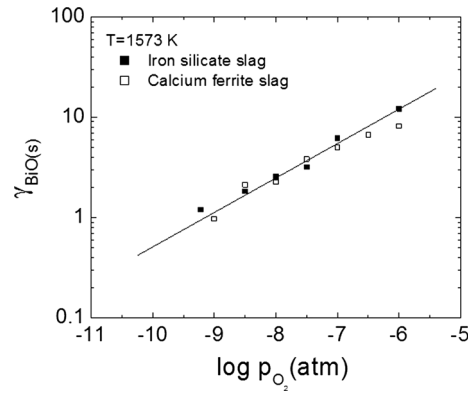

Fig. 7—Variation of the activity coefficient of BiO in both iron silicate slags and calcium ferrite slags with oxygen partial pressure at 1573 K (1300 °C).
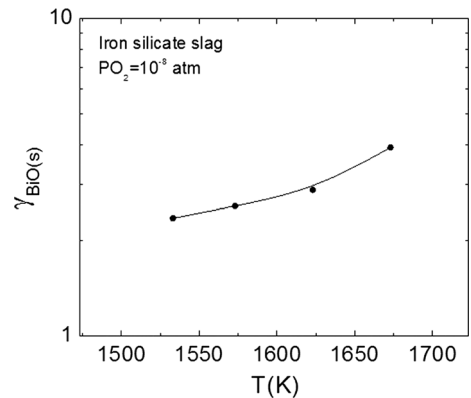

Fig. 8—Variation of the activity coefficient of BiO in iron silicate slag with varied temperature at oxygen partial pressure of 10^{-8} atm.

The activity of Bi in the alloy from the present work was calculated using γ_{Bi}^{o} of 2.22.[1] Based on the calculated Bi activity in the alloy and the distribution ratio of Bi between slag and metal, the activity and hence activity coefficient of BiO was calculated from Eq. [9]. For these calculations the Gibbs free energy change of the reaction [10] was taken from the literature[1]

$$Bi(l) + 0.5O_2(g) = BiO(s), \qquad [10]$$

where the free energy change of the reaction is:

$$\Delta G = -212254 + 99.79T \quad J/mol \qquad [11]$$

Figure 7 shows that the activity coefficient of BiO in both iron silicate and calcium ferrite slags increases by an order of magnitude with increasing pO_2. Based on the iso-activity data of Takeda et al.,[18] for a calcium ferrite slag with a fixed CaO content, as the pO_2 is increased, the activity of FeO decreased. Thermodynamic calculation using the structurally based cell slag model in the thermodynamic package Multi-Phase Equilibrium[21] also shows that the activity of FeO in iron silicate slag with fixed SiO_2 content decreases with increasing PO_2. As a result, the interactions between BiO and FeO in the slags decreases, leading to the increase of γ_{BiO} in both types of slag. Figure 8 shows

that the γ_{BiO} in the slag increases with increasing temperature at fixed oxygen partial pressure.

IV. CONCLUSIONS

A study of the equilibrium distribution of bismuth between CaO-FeO$_x$-SiO$_2$ slags and liquid copper at 1573 K (1300 °C) under varied oxygen partial pressures showed that bismuth distribution is affected by the oxygen partial pressure, and bismuth is most likely to exist in slags in the 2+ oxidation state, i.e., as BiO.

The distribution ratio between calcium ferrite slag and liquid copper was found to be close to that of magnesia-saturated iron silicate slag in equilibrium with liquid copper. The Bi distribution ratio was found to decrease with increasing SiO_2 and Al_2O_3 content in slag. Increasing temperature was found to decrease the Bi distribution ratio between slag and metal.

This work could not reconcile the apparent discrepancies in the behavior of Bi in slags reported in the literature. However, the work was found to be consistent with previous studies with respect to Cu in slag, Fe^{3+}/Fe^{2+} ratio, etc. The Bi analysis was performed by ICP-MS, and low concentration standards were prepared and the analytical results were in good agreement

with these. The previous studies used older analysis techniques which have less sensitivity, and this may contribute significantly to the apparent discrepancies.

The activity and hence activity coefficient of BiO in the slag was calculated from the measured distribution ratio of Bi. The close value of activity coefficient of BiO in both types of slags at the same oxygen partial pressure indicates that the CaO-BiO and SiO_2-BiO interactions are likely to be at the same level, or the FeO_x-BiO interaction is the predominant interactions for the BiO in the slag, and the CaO-BiO and SiO_2-BiO interactions doesn't affect the γ_{BiO} significantly at the fixed FeO_x level.

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