INVESTIGATION OF PHASE EQUILIBRIA OF COPPER SMELTING SLAGS IN THE FeO-Fe$_2$O$_3$-SiO$_2$-CaO-MgO-Al$_2$O$_3$ SYSTEM AT FIXED OXYGEN POTENTIAL

Hector Henao, Peter Hayes & Evgueni Jak
The University of Queensland, Australia

David George-Kennedy & Collin Nexhip
Kennecott Utah Copper Corporation, USA

ABSTRACT

Since the start-up of their Flash Smelting Furnace (FSF) over a decade ago, the chemistry of copper concentrate being smelted by Kennecott Utah Copper Corporation (KUCC) has been gradually changing. Concentrate feed-stocks may on occasion contain higher than desired levels of SiO$_2$ and MgO. Increased levels of SiO$_2$ could potentially lead to an undesirably low Fe/SiO$_2$ in the settler slag, and this inturn can potentially compromise the furnace side-wall integrity due to less protective magnetite accretion formation. Increased levels of MgO can also potentially lead to slag skimming/tapping difficulties.

Optimal control of the slag chemistry in the copper smelting is therefore essential for high recovery and productivity and requires detailed knowledge of the slag phase equilibria. New experimental procedures have been developed by Pyrometallurgy Research Centre (PYROSEARCH) at the University of Queensland that have resolved a number of experimental difficulties associated with phase equilibria determination, in these systems. The techniques have been successfully applied to determine the slag liquidus temperature in a number of complex industrial slags. In the present study for KUCC, the experiments have been planned and conducted so as to be able to represent the liquidus information in the form of liquidus temperature vs Fe/SiO$_2$ ratio pseudo-binary phase diagrams. Each liquidus line has been constructed for a fixed combination of CaO, MgO and Al$_2$O$_3$ concentrations and at a fixed oxygen potential. The present work provides phase equilibrium experimental data in the FeO-Fe$_2$O$_3$-SiO$_2$-CaO-MgO-Al$_2$O$_3$ system at oxygen partial pressure of 10^{-8} atm in the range of temperatures and compositions directly relevant to the copper flash smelting. It was found that increase of MgO or CaO resulted in the significant decrease of the tridymite liquidus and change in the position of the tridymite liquidus in the direction

of higher silica concentration; however the spinel liquidus increases significantly with the increase of MgO or CaO.

The work has been used to support KUCC in their efforts to answer the following focus question: Would flash smelting of copper concentrate containing increased levels of SiO_2 and MgO adversely influence the operability and integrity of the Flash Smelter Furnace.

Key Words: *slags, copper smelting, liquidus, phase diagrams.*

INTRODUCTION

Optimal control of the slag chemistry in the copper Flash Smelter at Kennecott Utah Copper Corporation (KUCC) is one of the important issues influencing efficient and stable operation; and requires detailed knowledge of the slag phase equilibria.

This experimental work presents results of the phase equilibria of synthetic slags in the FeO-SiO_2-CaO-MgO-Al_2O_3 system at an oxygen partial pressure of 10^{-8} atm in the range of compositions and temperatures directly relevant to the KUCC –FSF operation.

Average smelting slag composition is given in Table 1 and the range of experimental conditions of interest is given in Table 2.

Table 1: Average compositions of the KUCC Flash Smelter slags [wt%]. (1315°C)

	PO_2	Cu	Fe	SiO_2	CaO	MgO	Al_2O_3	*Total*	Fe/SiO_2
Average	10^{-8} atm	0.7	40.0	30.0	3.0	2.0	3.0		1.33
	PO_2	Cu_2O	FeO	SiO_2	CaO	MgO	Al_2O_3	*Total*	Fe/SiO_2
Average (all oxides)	10^{-8} atm	0.8	51.5	30.0	3.0	2.0	3.0	90.3	1.33
Avg ox. normalised	10^{-8} atm	0.9	57.0	33.3	3.3	2.2	3.3	100.0	1.33

Table 2: Target Liquidus sections [wt%]

#	Comment	$logP_{O2}$	Cu_2O	FeO*	SiO_2*	CaO	MgO	Al_2O_3	Total	Fe/SiO_2	FeO+ SiO_2
1	Average	-8	0.9	57.0	33.3	3.3	2.2	3.3	100	0.8-1.5	90.3
2	Effect of MgO =6 wt %	-8	0.9	54.6	31.9	3.3	6.0	3.3	100	0.8-1.5	86.5
3	Effect of MgO = 9 wt %	-8	0.9	52.7	30.8	3.3	9.0	3.3	100	0.8-1.5	83.5
4	Effect of CaO =6 wt %	-8	0.9	55.3	32.3	6.0	2.2	3.3	100	0.8-1.5	87.6

* The FeO and SiO_2 concentrations in Table 2 are given for the average Fe/SiO_2 = 1.33 only as indication – the sum (FeO+SiO_2) is kept constant and the Fe/SiO_2 ratio is varied for each section

The experiments were planned and conducted with the aim to represent the information in the form $T_{liquidus}$ vs Fe/SiO_2. Each liquidus line has been constructed for fixed combinations of CaO, MgO and Al_2O_3 concentrations and fixed P_{O2}. In each case the change in a concentration of a minor component is offset by the sum of FeO and SiO_2 concentrations. For the average slag composition recalculated to oxides and normalised to 100% the sum of FeO and SiO_2 concentrations is equal to 90.3 wt% (see Table 2). For example, the Section #2 in Table 2 with MgO = 6.0% has 6.0-2.2 = 3.8 wt % higher than the average MgO=2.2 wt%, and therefore has (FeO+SiO_2)= 90.3 – 3.8 = 86.5 wt%.

Precipitation of solid phases (tridymite SiO_2 or spinel Fe_3O_4) results in the changes of compositions of liquid so that it is not possible to measure the liquidus at the exact concentration of minor components such as MgO, CaO and Al_2O_3. This means that multiple experiments are required for construction of each point on such liquidus sections with the exact concentration of minor components in the remaining liquid phase.

EXPERIMENTAL TECHNIQUES

There are a number of difficulties in obtaining accurate chemical equilibrium data for complex slag systems at controlled laboratory conditions. Experimental procedures have been developed that have resolved a number of experimental difficulties and have been successfully applied to a number of complex industrial slags by Pyrometallurgy Research Centre at the University of Queensland [1, 2, 3, 4].

The experimental technique could be explained with reference to Figures 1. The technique for phase equilibrium measurements is based on the high temperature equilibration of the synthetic slag samples in well controlled gas atmosphere and temperature followed up by quenching. The liquid slag phase is converted into glass on quenching, and crystalline solids (if present) are frozen in place. The quenched samples are then mounted, polished, and compositions of the liquid and solid phases are measured with EPMA - electron probe X-ray microanalyser JEOL JXA8200 equipped with wave-length dispersive detectors WDD. The accuracy of temperature is within 5 degrees Celsius, and the accuracy of phase composition measurements is within 1 wt%.
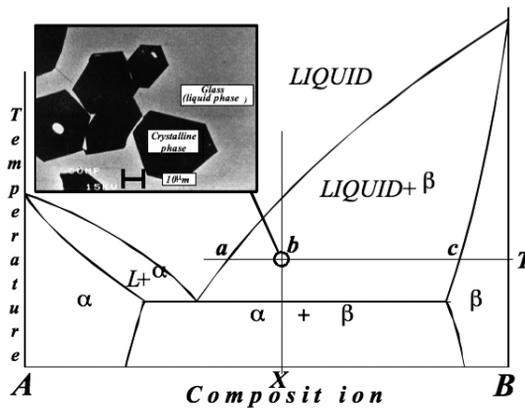

Figure 1: Experimental approach to phase equilibrium determination using sub-liquidus equilibration, quenching and EPMA

RESULTS OF PHASE EQUILIBRIA EXPERIMENTS

Examples of typical microstructures of equilibrated slags are given in Figure 2. Tridymite and spinel are the main crystalline phases observed in the samples. Note that Fe is present in both 2+ and 3+ states, but only the Fe cation concentration can be measured with EPMA. The iron was recalculated to FeO for presentation purposes.

As was explained above, the liquid composition changes as solid phases precipitate so that the exact MgO, CaO and Al_2O_3 concentrations could not be achieved from the first experiments. Multiple experiments were performed for construction of each point on the liquidus sections to obtain the liquidus at the target CaO, MgO and Al_2O_3 concentrations. Linear interpolation was then used to calculate positions of the liquidus as a function of Fe/SiO_2 ratio at exact values of CaO, MgO and Al_2O_3. At a given temperature, the position of liquidus point $(wt\%Fe)/(wt\%SiO_2)$ was expressed as a linear function of wt%CaO, wt%MgO and wt%Al_2O_3:

$$(wt\%Fe)/(wt\%SiO_2) = C1*(wt\%Al_2O_3) + C2*(wt\%MgO) + C3*(wt\%CaO) + C4 \qquad (1)$$
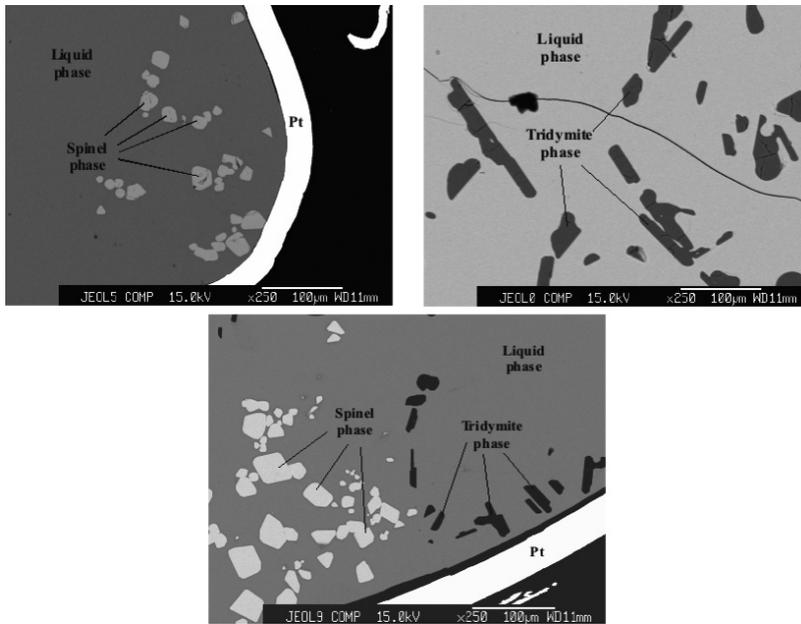
Figure 2: Examples of slag microstructures from phase equilibria experiments

The C1 through C4 coefficients were obtained for each Tridymite and Spinel primary phase field by minimising the sum of squared differences between calculated and experimental values to obtain the best fit. The obtained coefficients were then used to calculate the $(wt\%Fe)/(wt\%SiO_2)$ at the target compositions. Using the calculated values, the corresponding relationships between temperature and $(wt\%Fe)/(wt\%SiO_2)$ were obtained. The obtained equations can be used only to interpolate the liquidus temperature at slag composition between the obtained experimental values.

Effect of MgO Addition in Slag at Fixed Concentration of CaO and Al_2O_3

Figures 3 through 6 present results of the phase equilibria study on the CaO-*FeO*-SiO_2-MgO-Al_2O_3 system at $P_{O2}=10^{-8}$ atm. Figure 3 illustrates agreement between experimental $(wt\%Fe)/(wt\%SiO_2)$ values and the calculated values. This figure indicates the accuracy of the linear interpolation as well as the self- consistency of the experimental dataset. Figure 4 presents the tridymite liquidus for exact values of Al_2O_3 = 3.3 wt%, CaO = 3.3 wt% and MgO = 2.2, 6.0 and 9.0 wt% with experimental points close to the target composition.

Figure 5 presents the spinel liquidus for exact values of Al_2O_3 = 3.3 wt%, CaO = 3.3 wt% and MgO = 2.2, 6.0 and 9.0 wt%. Results of experiments with the Al_2O_3, CaO and MgO concentrations close to the targeted ones are also plotted in this figure.

Figure 6 is the final plot presenting the effect of MgO on liquidus temperatures for slags with Al_2O_3 = 3.3 wt% and CaO = 3.3 wt%.

The obtained phase diagram indicated that increase of MgO from 2.2 to 9 wt% results in the significant decrease of the tridymite liquidus temperatures – the tridymite liquidus moves toward higher-silica from values of $(wt\%Fe)/(wt\%SiO_2)$ of 0.8-0.9 at MgO = 2.2 to 0.6-0.65 at MgO = 9.0 wt%. The spinel liquidus, however, increases by approximately 30 degrees Celsius as MgO increases from 2.2 to 9 wt% at any given Fe/SiO_2 ratio.
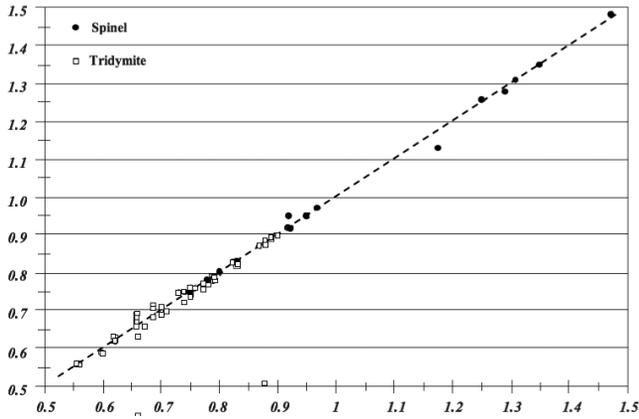
Figure 3: Comparison of experimental and calculated Fe/SiO_2 ratios for the tridymite and spinel liquidus for the series investigating effect of MgO at $P_{O2}=10^{-8}$ atm
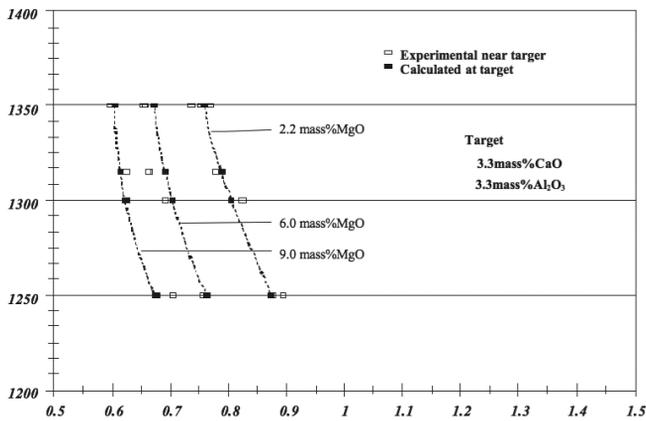

Figure 4: Effect of MgO on tridymite liquidus at target MgO, CaO and Al_2O_3 concentrations at $P_{O2}=10^{-8}$ atm
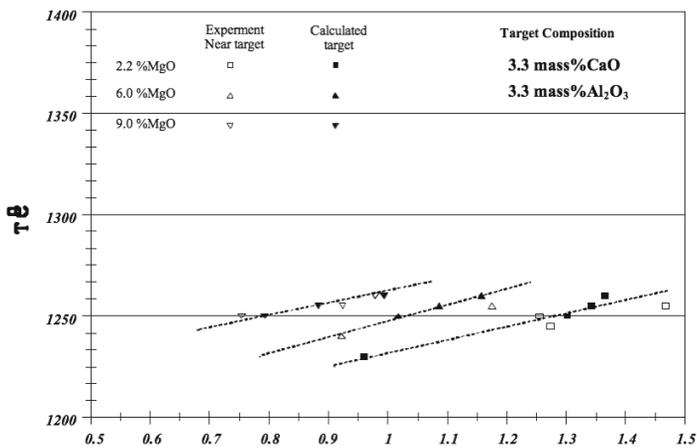

Figure 5: Effect of MgO on the spinel liquidus at target MgO, CaO and Al_2O_3 concentrations at $P_{O2}=10^{-8}$ atm
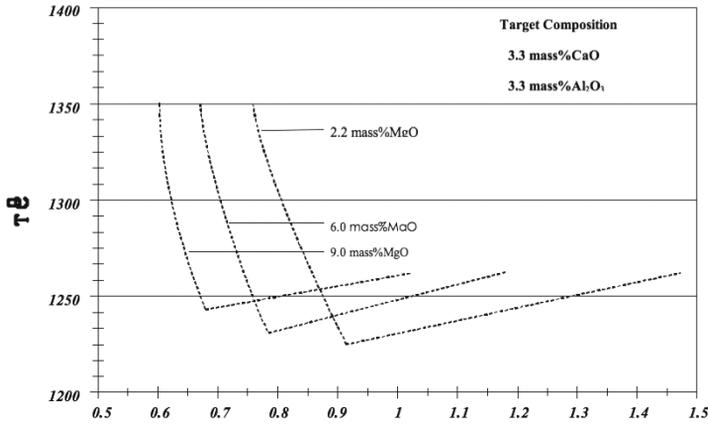
Figure 6: Effect of MgO on the tridymite and spinel liquidus at target MgO, CaO and Al_2O_3 concentrations at $P_{02}=10^{-8}$ atm

Effect of CaO Addition in Slag at Fixed Concentration of MgO and Al_2O_3

Figures 7 through 9 present results for the series of experiments aimed at the investigation of CaO effect on liquidus at a fixed concentration of MgO and Al_2O_3.

Figure 7 illustrates agreement between experimental and calculated data as well as self-consistency of the experimental dataset.

Figure 8 shows position of the tridymite liquidus lines at Al_2O_3 = 3.3 wt%, MgO = 2.2 wt% and CaO = 0%, 3.3% and 6.0% compared to the experimental points at Al_2O_3, MgO and CaO concentrations close to the targeted. Not enough experimental points were obtained to perform the correlation for the spinel liquidus region at high CaO concentrations, due to precipitation of olivine.

Figure 9 is the final summary plot presenting the effect of CaO on the tridymite and spinel liquidus lines. The results indicate that increasing CaO from 0 to 6 wt% results in the decrease of the tridymite liquidus –the increment tridymite position in the higher-silica direction from (wt%Fe)/(wt%SiO_2) of 0.90-0.95 at CaO=0 to 0.65-0.70 at CaO = 6.0 wt%.
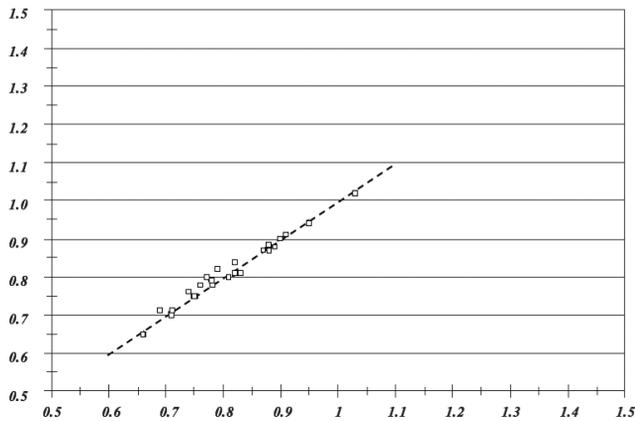

Figure7: Comparison of experimental and calculated Fe/SiO_2 ratios for the tridymite liquidus for the series investigating effect of CaO at $P_{02}=10^{-8}$ atm
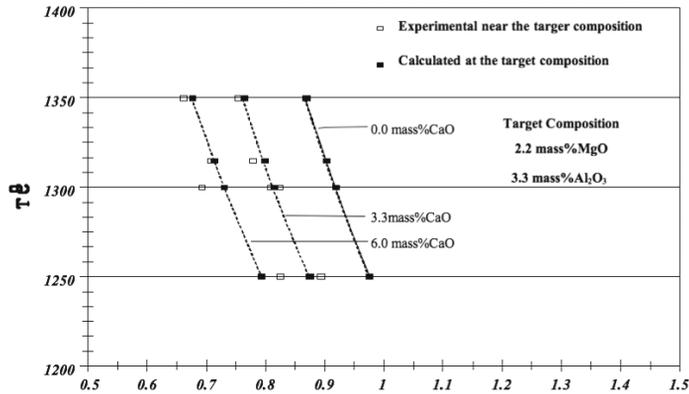
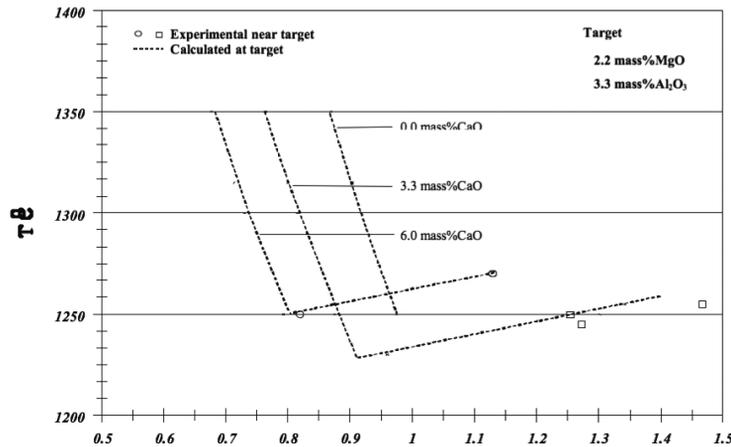Figure 8: Effect of CaO on tridymite liquidus at target MgO, CaO and Al$_2$O$_3$ concentrations at P$_{O2}$=10^{-8} atm

Figure 9: Effect of CaO on the tridymite and spinel liquidus at target MgO, CaO and Al$_2$O$_3$ concentrations at P$_{O2}$=10^{-8} atm

CONCLUSIONS

This paper presented results from a program to evaluate the phase equilibria of synthetic slags in the FeO-SiO$_2$-CaO-MgO-Al$_2$O$_3$ system, at an oxygen partial pressure of 10^{-8} atm. Over 150 melting and quenching experiments were completed in order to characterise liquidus temperatures in the range of temperatures and compositions of interest to KUCC-FSF operations. Here the Al$_2$O$_3$ concentration was fixed around 3.3%, the temperature was varied from ~1250-1350°C, CaO was varied from 0 to 6 wt%, whilst MgO was varied from 2.2 to 9.0%.

The resulting tridymite and spinel primary phase fields were identified within the range of conditions investigated. It was found that an increase of MgO results in the significant decrease of the tridymite liquidus, shifting the position of the tridymite liquidus in the direction of higher silica; however, the spinel liquidus increases significantly (~30°C) with the increase of MgO.

It was found that effect of CaO is similar to the effect of MgO - an increase of CaO

results in the significant decrease of the tridymite liquidus and shifts the position of the tridymite liquidus in the direction of higher silica; however, the spinel liquidus increases significantly with the increase of CaO.

Within the range studied, the phase equilibria results suggest that any (future) moderate increases in SiO_2 and MgO levels in FSF slag - as a result of changes in concentrate chemistry at KUCC - should not prove too problematic for maintaining furnace operability and integrity.

REFERENCES

Nikolic, S., Hayes, P. C. & Jak, E. (2008). Metall. Mater. Trans. B, Vol. 39B, pp. 179-188. [1]

Nikolic, S., Henao, H., Hayes, P. C. & Jak, E. (2008). Metall. Mater. Trans. B, Vol. 39B, pp. 189-199. [2]

Nikolic, S., Hayes, P. C. & Jak, E. (2008). Metall. Mater. Trans. B, Vol. 39B, pp. 200-209. [3]

Nikolic, S., Hayes, P. C. & Jak, E. (2008). Metall. Mater. Trans. B, Vol. 39B, pp. 210-217. [4]