Characterisation of the Effect of Al₂O₃ on the Liquidus Temperatures of Copper Cleaning Furnace Slags Using Experimental and Modelling Approach

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Most metallurgical smelting processes operate over a limited range of compositions and temperatures but generally, even with complex slag systems, within a given primary phase field. Knowledge of the sensitivity of the liquidus to changes in composition enables improved temperature control and stability of operation. The paper describes a general approach that was used to characterize the liquidus temperatures of the “CuO”−“FeO”−SiO₂−Al₂O₃ slags in an electric slag cleaning furnace operation as function of the principal chemical components using a combination of available computer based thermodynamic database descriptions of complex slags and targeted series of laboratory experiments. An approximate mathematical relationship, valid for a limited range of compositions and temperatures, has been developed describing the liquidus temperature of the slags as a function Fe/SiO₂ ratio, Cu, and Al₂O₃ concentrations in slag. [doi:10.2320/matertrans.M2018373]

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1. Introduction

The direct-to-blister copper smelting process is currently used commercially in three smelters, i.e. Olympic Dam (Australia), Glogow II (Poland), and Chingola (Zambia).¹ The process involves the oxidation of copper concentrates in a flash furnace to produce copper blister and high-copper, iron-silicate slag containing between 12–28 mass% Cu. Copper is subsequently recovered from the high-Cu containing slag by reduction using coke in an electric slag-cleaning furnace. Aluminum oxide is one of the impurities commonly found in the electric furnace slag. Variation in the Al₂O₃ concentration in the slag influences the stability of the electric furnace freeze lining and the slag fluidity. A quantitative description of the effect of Al₂O₃ on the slag liquidus is essential if operational stability and efficiency are to be improved.

The slag composition in the electric slag-cleaning furnace is commonly within the spinel primary phase field. Only a limited number of experimental studies²⁻⁴ have been reported defining the equilibria between iron-silicate slag, copper, and solid spinel. Most of the other studies⁵⁻¹⁰ have involved the investigation of the equilibria between iron-silicate slag, copper alloy, and tridymite. The measurements of the equilibria between iron-silicate slag and copper in alumina crucibles¹¹⁻¹⁶ have resulted in the uncontrolled dissolution of Al₂O₃ into the slag. To date, there is no study that systematically investigates the influence of Al₂O₃ on the iron-silicate slag, liquid copper, and spinel equilibria within the range of slag compositions of practical importance for slag cleaning or slag reduction processes was found in literature. In the present study, a combination of available computer based thermodynamic database descriptions of complex slags and targeted series of laboratory experiments have been used to develop an approximate polynomial description of the slag liquidus surface that is valid over the limited range of compositions and process conditions used in industrial practice.

2. Research Methodology

2.1 Outline of the general approach

The general approach used in the present study involves: i) performing predictions of liquidus temperatures for a selected range of chemical compositions using the FactSage computer program and a customised thermodynamic database;¹⁷ ii) development of a preliminary polynomial expression that provides an approximate description of the liquidus for the limited range of conditions of interest; iii) undertaking targeted experimental investigations to quantify the effect of selected chemical species on the liquidus of the slag; iv) adjustment of the polynomial expression to improve description of the experimental data; and finally, v) application of the polynomial expression to analyse the relationship between bulk slag composition and liquidus, or to control the operation of electric slag-cleaning furnace.

The liquidus surface describing the “CuO”−“FeO”−SiO₂−Al₂O₃ slags in equilibrium with liquid copper and solid spinel is determined at temperatures, Al₂O₃ concentrations, Cu concentrations, and Fe/SiO₂ ratios in slag of direct interest to the operation of electric slag-cleaning furnace within the direct-to-blister copper smelting process. The relationships between the slag liquidus temperature, mass%Al₂O₃, mass%Cu, and Fe/SiO₂ ratio in slag are expressed in the form of a polynomial equation. The FactSage computer package and a customised thermodynamic database¹⁷ were used to obtain the liquidus temperatures for over 400 compositional targets. These data were used to construct the initial polynomial equation. The polynomial equation was then corrected by optimizing the coefficients in the polynomial equation in order to fit the equation through all of the experimental data points.

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2.2 High-temperature experimental technique

The experimental methodology used in this study is based on the technique developed by the authors\textsuperscript{18,19} involving high temperature equilibration of pelletized metal and oxide powder mixtures on primary phase substrates under inert atmospheres, rapid quenching of the equilibrated samples, metallographic preparation of samples, and direct measurement of the compositions of equilibrium phases in samples with microanalysis technique.

High purity Cu$_2$O (99.99 mass\% purity), FeO (99.8 mass\% purity), SiO$_2$ (99.9 mass\% purity), and Al$_2$O$_3$ (99.99 mass\% purity) powders (supplied by Sigma-Aldrich, St Louis, USA) were used as starting materials. These powders were mixed in predetermined proportions using an agate mortar and pestle to produce different Fe/SiO$_2$ ratios, Cu concentrations, and Al$_2$O$_3$ concentrations in the final slags. An excess of Cu metal powder was used to ensure the presence of liquid Cu in final samples.

Magnetic/spinel (Fe$_3$O$_4$) substrates were used to hold the liquid containers for slag and metal mixtures. The spinel substrates were prepared from iron foil (99.5 mass\% purity, supplied by Goodfellow Cambridge Ltd., Huntingdon, England) folded into the required shape and then oxidized at 1200°C in a pure CO$_2$ atmosphere.

A vertical tube furnace was used for the equilibration experiments. The furnace temperature was controlled by a calibrated B type thermocouple placed immediately adjacent to the sample. The thermocouple was periodically tested against a standard thermocouple (calibrated by National Measurement Institute, Australia and manufactured in-house). The overall temperature accuracy was estimated to be within 5 K or better. Argon gas (>99.9 mass\% purity, supplied by Coregas Pty Ltd., Yennora, Australia) was used to achieve inert atmosphere in the furnace. The effective oxygen partial pressure the condensed phases of samples ($P(\text{O}_2)$) was controlled by the Cu metal gas atmosphere. The concentrations of metal cations in the phases were measured by EPMA. No information on the proportions of the same element having different oxidation states were acquired, all metal concentrations are recalculated to selected oxidation states, i.e. “Cu$_2$O”, “FeO”, SiO$_2$, and Al$_2$O$_3$, for convenience of presentation and to unambiguously report the compositions of phases. The accuracy of the EPMA measurement was estimated to be within 1 mass\%.

The EPMA measurements were performed only on areas where all equilibrium phases (slag/copper/spinel) were observed. Typical microstructures of the samples from the experiments are presented in Fig. 2. The samples obtained from experiments at 1200 and 1250°C were well-quenched (see Fig. 2(a)), while samples from experiments at 1300°C were not well-quenched (see Fig. 2(b)). For the “not-well quenched” slag, EPMA analysis with large probe diameter was carried out to minimise uncertainty in the measurement of the slag composition.

3. Experimental Results

The results of the EPMA measurements are summarized in Table 1. The experimental liquidus points are plotted in Fig. 3. The investigated area covers a wide range of compositions, i.e. Fe/SiO$_2$ ratio in slag = 1.27–2.62 mass/mass, Cu in slag = 1.1–6.5 mass\%, and Al$_2$O$_3$ in slag = 0.4–7.1 mass\%. The spinel phase was observed to contain between 0.9 and 31.1 mass\% Al$_2$O$_3$. The compositions of all metallic copper were close to a pure copper, with Fe concentration less than 0.5 mass\%.
Fig. 2 SEM back-scattered electron images of typical microstructures from slag/copper/spinel equilibrium in the Cu–Fe–O–Si–Al system under argon atmosphere at: (a) $T = 1200^\circ$C; and (b) $T = 1300^\circ$C.

Table 1 Measured compositions of "Cu$_2$O"–"FeO"–SiO$_2$–Al$_2$O$_3$ slag and spinel phases from slag/copper/spinel equilibria at 1473 K, 1523 K, and 1573 K (1200°C, 1250°C, and 1300°C).

<table>
<thead>
<tr>
<th>Exp#</th>
<th>Temp, °C</th>
<th>Time, h</th>
<th>Phase</th>
<th>Composition, mass%</th>
<th>Old Total*</th>
<th>Fe/SiO$_2$ mass/mass</th>
<th>Cu$_2$O mass/%</th>
<th>$T_{pol}-T_{exp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1200</td>
<td>18</td>
<td>Slag</td>
<td>Cu$_2$O: 74.6, FeO: 23.3, SiO$_2$: 0.7</td>
<td>98.6</td>
<td>2.49</td>
<td>1.4</td>
<td>-8</td>
</tr>
<tr>
<td>2</td>
<td>1200</td>
<td>6</td>
<td>Slag</td>
<td>Cu$_2$O: 72.9, FeO: 24.4, SiO$_2$: 0.9</td>
<td>98.3</td>
<td>2.32</td>
<td>1.6</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>1200</td>
<td>18</td>
<td>Slag</td>
<td>Cu$_2$O: 97.1, FeO: 0.9, SiO$_2$: 1.9</td>
<td>93.1</td>
<td>1.53</td>
<td>3.4</td>
<td>-8</td>
</tr>
<tr>
<td>4</td>
<td>1200</td>
<td>18</td>
<td>Slag</td>
<td>Cu$_2$O: 76.3, FeO: 30.2, SiO$_2$: 1.1</td>
<td>100.7</td>
<td>2.49</td>
<td>1.2</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>1200</td>
<td>6</td>
<td>Slag</td>
<td>Cu$_2$O: 72.4, FeO: 24.2, SiO$_2$: 2.1</td>
<td>99.3</td>
<td>2.33</td>
<td>1.2</td>
<td>-2</td>
</tr>
<tr>
<td>6</td>
<td>1200</td>
<td>18</td>
<td>Slag</td>
<td>Cu$_2$O: 73.1, FeO: 24.0, SiO$_2$: 1.4</td>
<td>99.4</td>
<td>2.37</td>
<td>1.3</td>
<td>-1</td>
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<td>7</td>
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<td>18</td>
<td>Slag</td>
<td>Cu$_2$O: 61.3, FeO: 32.2, SiO$_2$: 2.9</td>
<td>99.4</td>
<td>1.48</td>
<td>3.2</td>
<td>-10</td>
</tr>
<tr>
<td>8</td>
<td>1200</td>
<td>6</td>
<td>Slag</td>
<td>Cu$_2$O: 95.0, FeO: 4.2, SiO$_2$: 1.2</td>
<td>93.3</td>
<td>2.20</td>
<td>1.4</td>
<td>7</td>
</tr>
<tr>
<td>9</td>
<td>1200</td>
<td>6</td>
<td>Slag</td>
<td>Cu$_2$O: 89.7, FeO: 6.6, SiO$_2$: 4.6</td>
<td>95.0</td>
<td>2.93</td>
<td>0.3</td>
<td>*</td>
</tr>
<tr>
<td>10</td>
<td>1250</td>
<td>6</td>
<td>Slag</td>
<td>Cu$_2$O: 58.7, FeO: 31.2, SiO$_2$: 2.9</td>
<td>99.1</td>
<td>1.46</td>
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<td>11</td>
<td>1250</td>
<td>18</td>
<td>Slag</td>
<td>Cu$_2$O: 97.2, FeO: 2.3, SiO$_2$: 0.3</td>
<td>93.8</td>
<td>1.54</td>
<td>6.5</td>
<td>7</td>
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<td>12</td>
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<td>18</td>
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<td>Cu$_2$O: 60.0, FeO: 32.3, SiO$_2$: 2.3</td>
<td>99.4</td>
<td>1.42</td>
<td>7.0</td>
<td>10</td>
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<tr>
<td>13</td>
<td>1250</td>
<td>18</td>
<td>Slag</td>
<td>Cu$_2$O: 56.8, FeO: 31.1, SiO$_2$: 4.2</td>
<td>99.0</td>
<td>1.42</td>
<td>7.0</td>
<td>10</td>
</tr>
<tr>
<td>14</td>
<td>1250</td>
<td>18</td>
<td>Slag</td>
<td>Cu$_2$O: 56.8, FeO: 31.1, SiO$_2$: 4.2</td>
<td>99.0</td>
<td>1.42</td>
<td>7.0</td>
<td>10</td>
</tr>
<tr>
<td>15</td>
<td>1250</td>
<td>18</td>
<td>Slag</td>
<td>Cu$_2$O: 56.8, FeO: 31.1, SiO$_2$: 4.2</td>
<td>99.0</td>
<td>1.42</td>
<td>7.0</td>
<td>10</td>
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<tr>
<td>16</td>
<td>1250</td>
<td>6</td>
<td>Slag</td>
<td>Cu$_2$O: 57.3, FeO: 30.7, SiO$_2$: 6.9</td>
<td>99.6</td>
<td>1.45</td>
<td>4.6</td>
<td>-3</td>
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<tr>
<td>17</td>
<td>1250</td>
<td>6</td>
<td>Slag</td>
<td>Cu$_2$O: 90.7, FeO: 3.2, SiO$_2$: 0.4</td>
<td>94.3</td>
<td>1.85</td>
<td>3.9</td>
<td>9</td>
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<tr>
<td>18</td>
<td>1250</td>
<td>6</td>
<td>Slag</td>
<td>Cu$_2$O: 94.6, FeO: 4.9, SiO$_2$: 0.4</td>
<td>92.4</td>
<td>2.51</td>
<td>2.1</td>
<td>1</td>
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<tr>
<td>19</td>
<td>1300</td>
<td>6</td>
<td>Slag</td>
<td>Cu$_2$O: 70.0, FeO: 23.0, SiO$_2$: 2.3</td>
<td>98.2</td>
<td>2.15</td>
<td>2.9</td>
<td>5</td>
</tr>
<tr>
<td>20</td>
<td>1300</td>
<td>6</td>
<td>Slag</td>
<td>Cu$_2$O: 97.6, FeO: 1.7, SiO$_2$: 0.6</td>
<td>93.0</td>
<td>2.07</td>
<td>4.4</td>
<td>-2</td>
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<tr>
<td>21</td>
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<td>Slag</td>
<td>Cu$_2$O: 67.4, FeO: 2.3, SiO$_2$: 2.4</td>
<td>99.1</td>
<td>2.20</td>
<td>3.1</td>
<td>-9</td>
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<tr>
<td>22</td>
<td>1300</td>
<td>6</td>
<td>Slag</td>
<td>Cu$_2$O: 96.9, FeO: 3.2, SiO$_2$: 0.8</td>
<td>93.7</td>
<td>2.42</td>
<td>3.1</td>
<td>6</td>
</tr>
</tbody>
</table>

Note: Concentrations of elements below 0.1 mass% are below the detection limit of present EPMA measurement
† “Old total” is the sum of elements or oxides given by EPMA before it is normalized
‡ Significant difference between calculated and experimental liquidus temperatures
* Outside polynomial validity range
4. An Approximate Empirical Description of Slag Liquidus

Using the approach given above, the following polynomial equation describing the liquidus temperature of slag in equilibrium with metallic copper and solid spinel was derived:

\[
T_{\text{liquidus}} \quad ^\circ C = 972.04 + 8.13 \cdot \text{(mass\%Al}_2\text{O}_3 \text{ in slag)}
+ 82.53 \cdot \text{(Fe/SlO}_2\text{)} \cdot \text{(mass\%Cu in slag)}^{0.39}
\]

The polynomial equation is **approximate and valid only for limited range of slag compositions**, i.e. Fe/SlO\(_2\) ratio = 1.5–2.4 mass/mass, Cu = 1–8 mass\%, and Al\(_2\)O\(_3\) = 0.7–7.0 mass\%.

The polynomial equation was then used to construct slag liquidus compositions at fixed temperatures (isothermal liquidus compositions). The calculated slag liquidus compositions were represented on a “Cu\(_2\)O”-“FeO”-SiO\(_2\) pseudoternary diagram at fixed Al\(_2\)O\(_3\)/[“Cu\(_2\)O”-“FeO”-SiO\(_2\)-Al\(_2\)O\(_3\)”. This operation was carried out by projecting the slag composition in the Cu-Fe-O-Si-Al system at fixed Al\(_2\)O\(_3\) onto the Cu\(_2\)O-FeO-SiO\(_2\) plane from the O-corner as illustrated in Fig. 4.

Figure 3 shows the calculated slag liquidus compositions using the polynomial equation and the experimental liquidus data obtained in the present study. The slag liquidus compositions predicted by FactSage using the public database\(^{20-24}\) are also plotted in the figure. The labels next to the data points are Al\(_2\)O\(_3\) concentrations in slag in mass\%, experimental liquidus temperatures in Celsius, and the differences between liquidus temperatures calculated by the polynomial equation and from experiment (last column in Table 1). Based on the polynomial equation, the slag liquidus temperature appears to be sensitive to the Cu concentration in slag. A change in Cu concentration within ±1 mass\% leads to a change in the liquidus temperature by more than 8°C depending on the Fe/SlO\(_2\) and Al\(_2\)O\(_3\) in the slag.

The polynomial equation describes the experimental dataset within ±10°C for a limited range of slag compositions. Significant differences were observed between the isothermal lines from the polynomial equation and those from FactSage prediction using public database.\(^{20-24}\) The polynomial equation suggests higher liquidus temperatures.
than those predicted by FactSage using public database\textsuperscript{20–24} by more than 25°C for copper concentrations in the range between 3 and 8 mass% Cu in slag.

The relationships between Al\textsubscript{2}O\textsubscript{3} concentrations in slag and spinel phases for a given temperature and mass% Cu in slag are shown in Fig. 5. The Al\textsubscript{2}O\textsubscript{3} concentration in spinel can be expressed by the following polynomial equation:

\[
\text{mass}\% \text{Al}_2\text{O}_3 \text{ in spinel} = [0.10 \cdot (\text{mass}\% \text{Al}_2\text{O}_3 \text{ in slag})^2 \\
+ 0.88 \cdot (\text{mass}\% \text{Al}_2\text{O}_3 \text{ in slag})] \\
\times [8.69 \cdot 10^{-2} \cdot (\text{mass}\% \text{Cu in slag})^2 \\
- 1.06 \cdot (\text{mass}\% \text{Cu in slag}) + 9.04 \cdot 10^{-4}(T, \degree \text{C}) + 2.81] \\
\] (3)

The labels in Fig. 5 are Cu concentrations in slag and differences of Al\textsubscript{2}O\textsubscript{3} concentrations in spinel between calculated value by eq. (3) and experimental data. The absolute difference between the Al\textsubscript{2}O\textsubscript{3} in spinel from the polynomial equation and the experiments is less than 1.5 mass%.

The calculated lines of Al\textsubscript{2}O\textsubscript{3} in spinel at fixed Cu in slag = 4 mass% and different temperatures as a function of Al\textsubscript{2}O\textsubscript{3} in slag from eq. (3) are provided in Fig. 5. The major factor that influence the Al\textsubscript{2}O\textsubscript{3} solubility in spinel appears to be the Al\textsubscript{2}O\textsubscript{3} concentration in slag; the Al\textsubscript{2}O\textsubscript{3} in spinel increases with increasing Al\textsubscript{2}O\textsubscript{3} in slag. Temperature appears to give small effect on the solubility of Al\textsubscript{2}O\textsubscript{3} in spinel; the effect is less than the experimental uncertainty. The influence of Cu in slag on the Al\textsubscript{2}O\textsubscript{3} in spinel is non-linear and complex as shown in eq. (3).”

5. Discussion

The polynomial equation can now be used for the systematic analysis of the influence of Al\textsubscript{2}O\textsubscript{3} on the iron-silicate slag, liquid copper, and spinel equilibrium.

5.1 Effects of Cu, Al\textsubscript{2}O\textsubscript{3}, and Fe/SiO\textsubscript{2} in the slag on the slag liquidus temperature

The effects of Cu concentration, Al\textsubscript{2}O\textsubscript{3} concentration, and Fe/SiO\textsubscript{2} ratio in the slag on the slag liquidus temperature have been analysed based on the polynomial equation as shown in Fig. 6 and Fig. 7. A slag containing 4 mass% Al\textsubscript{2}O\textsubscript{3} in slag and Fe/SiO\textsubscript{2} ratio = 1.9 mass/mass was selected as a basis for comparison. The lines shows decreasing slag liquidus temperature with decreasing Cu in slag. A decrease of Cu level in the slag corresponds to decreasing oxygen partial pressure in the system. With decreasing oxygen partial pressure, the spinel phase is less stable and hence a decrease in the liquidus temperature in the spinel primary phase field is observed. In practice, the decrease of Cu concentration in the slag represents the progression of slag cleaning process, i.e.
reduction of Cu$_2$O in slag to Cu metal. At the base case composition, the decrease of Cu in slag from 5 mass\% to 1.8 mass\% lowers the slag liquidus by approximately 100°C.

Figure 6 demonstrates the effect of Al$_2$O$_3$ concentration in slag on the slag liquidus temperature at fixed Fe/SiO$_2$ ratio in slag = 1.9 mass/mass. In the investigated ranges of composition, a decrease of Al$_2$O$_3$ in slag by 2 mass\% at fixed Cu in slag leads to a decrease of liquidus temperature by approximately 16°C. Al$_2$O$_3$ is known as spinel forming component, its presence in the system can greatly increase the stability of the spinel phase.

Figure 7 illustrates the effect of changing Fe/SiO$_2$ ratio in the slag on the liquidus temperature. At fixed Cu in slag approximately 3 mass\%, a decrease of Fe/SiO$_2$ ratio in slag from 2.4 mass/mass to 1.9 mass/mass significantly decreases the slag liquidus temperature by approximately 60°C. The Fe/SiO$_2$ ratio reflects the extent of SiO$_2$ fluxing. Decreasing the Fe/SiO$_2$ ratio means increasing SiO$_2$ content in the system, which leads to an increase in the formation of liquid slag.

5.2 Mass\%solid as a function of dissolved copper concentration in bulk slag

The effects of Fe/SiO$_2$ ratio in the bulk slag (liquid + spinel) and temperature on mass\%solid have been calculated based on the polynomial equation describing the liquidus and spinel composition. The line of mass\%solid versus Cu in bulk was constructed by numerically solving the mass\%solid, mass\%“FeO” in slag, and mass\%Al$_2$O$_3$ in slag to achieve targets Fe/SiO$_2$ in bulk and Al$_2$O$_3$ in bulk at fixed temperatures and fixed Cu concentrations in slag. The mass\%“FeO” and mass\%Al$_2$O$_3$ in the liquid slag at fixed temperatures and fixed Cu concentrations in slag was calculated by eq. (2). The spinel composition corresponding to the liquid slag was calculated using eq. (3).

The mass\%solid was defined as 100-weight of spinel/ [weight of spinel + weight of liquid slag]. The Al$_2$O$_3$ in bulk was calculated as [(mass\%Al$_2$O$_3$ in slag × (1 – mass\%solid/100)) + (mass\%Al$_2$O$_3$ in spinel × mass\%solid/100)]. The Cu in bulk was calculated as [(mass\%Cu in slag × (1 – mass\%solid/100)) + (mass\%Cu in spinel × mass\%solid/100)], where mass\%Cu in spinel was assumed to be negligible.

The calculated mass\%solids at temperature 1250°C and 1200°C at fixed Al$_2$O$_3$ in bulk = 4 mass\% are provided in Fig. 8(a) and Fig. 8(b), respectively. It can be observed that the mass\%solid increases with decreasing temperature. The slope of the mass\%solid versus Cu concentration in bulk slag is steeper at 1250°C than that at 1200°C.

At T = 1250°C, Al$_2$O$_3$ in bulk = 4 mass\%, and Cu in bulk = 4 mass\% (Fig. 8(a)), Fe/SiO$_2$ in bulk = 1.9 mass/mass gives less than 8% solid while Fe/SiO$_2$ in bulk = 2.4 mass/mass gives more than 26% solid. The mass\%solid decreases as Cu concentration in bulk slag is lowered. The mass\%solid line at 1250°C, Al$_2$O$_3$ = 4 mass\%, and Fe/SiO$_2$ in bulk = 1.5 mass/mass does not appear in Fig. 8(a) since the slag is fully liquid at this condition.

At T = 1200°C, Al$_2$O$_3$ in bulk = 4 mass\%, and Cu in bulk = 4 mass\% (Fig. 8(b)), Fe/SiO$_2$ in bulk = 1.9 mass/mass and 2.4 mass/mass give approximately 19 and 31 mass\%solids, respectively. For the same condition, Fe/SiO$_2$ in bulk = 1.5 mass/mass gives significantly lower solid proportion below 5 mass\%solid.

The effect of Al$_2$O$_3$ in bulk at fixed temperature and Fe/SiO$_2$ in the bulk on the mass\%solid as a function of Cu in bulk has also been calculated using the polynomial equation. The calculated mass\%solids at different Al$_2$O$_3$ in bulk and at

![Fig. 7 Effect of Fe/SiO$_2$ in slag on the liquidus temperature as function of Cu in slag at fixed Al$_2$O$_3$ concentration in slag as predicted by the polynomial equation obtained in the present study.](image)

![Fig. 8 Mass\%solid as function of Cu in bulk for different Fe/SiO$_2$ ratios in the bulk at fixed Al$_2$O$_3$ in bulk = 4 mass\% and fixed temperature as predicted by the polynomial equation obtained in the present study: (a) T = 1250°C; and (b) T = 1200°C.](image)
fixed $T = 1200^\circ\text{C}$ and Fe/SiO$_2$ in bulk $= 1.5$ mass/mass are provided in Fig. 9. It can be observed in the figure that an increase of Al$_2$O$_3$ in bulk by 2 mass% results in an increase of mass% solid by approximately 6%.

The information on the effects of Al$_2$O$_3$ concentration in slag, Fe/SiO$_2$ ratio in slag, and Cu in slag on the liquidus temperature can be used to optimize the electric slag cleaning operation. Optimum furnace operating parameters, such as temperature and Fe/SiO$_2$ in slag, can be determined to obtain lower energy consumption and more stable freeze lining formation in the electric furnace. Improved control over slag fluidity enables improvement in physical separation of slag and blister to be achieved and decreased build up in the slag launder after slag tapping.

The approach outlined in the present paper demonstrates the advantage of developing computer-based tools to predict behaviour in complex chemical systems. The example given in the present study shows that these tools can be used even when complete descriptions of the chemical systems are not available, provided the behaviour over the selected range of compositions and process conditions is verified experimentally. The advantages of this approach are that simplified practical working models, based on sound thermodynamic principles, can be constructed and used in selected operations. The approach is preferable to the use of purely empirical models since the sensitivity of the predictions to the concentrations of different chemical species present in the system can be more easily identified. The simplified mathematical models and the results presented in terms of practical variables provides the opportunity to incorporate the models into automated control systems.

6. Summary

The effects of Al$_2$O$_3$ on the liquidus temperature of “Cu$_2$O”–“FeO”–SiO$_2$–Al$_2$O$_3$ slag have been determined through a combination of thermodynamic modelling and mathematical modelling, and have been further verified using selected experimental measurements. The resulting empirical relationship describes the liquidus temperature of the slag as a function Fe/SiO$_2$ ratio, Cu concentration, and Al$_2$O$_3$ concentration in slag. Although only accurate for a limited range of compositions, the polynomial model provides a useful approximation that can be used in industrial practice to improve the control and optimization of the slag cleaning furnace operation.

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REFERENCES