Original Article

Minimizing of copper losses to converter slag by a boron compound addition

Mehmet Ali Topçu a, Aydin Rüsen a,*, Bora Derin b

a Karamanoglu Mehmetbey University, Dept. of Metallurgical and Materials Eng., 70100, Karaman, Turkey
b Istanbul Technical University, Dept. of Metallurgical and Materials Eng., 34469, Istanbul, Turkey

ARTICLE INFO

Article history:
Received 11 July 2019
Accepted 8 October 2019
Available online 6 November 2019

Keywords:
Converter slag
Calcined colemanite
Copper loss
FactSage

ABSTRACT

In copper production, the concentrate obtained after ore-flotation follows by pyrometallurgical route; Smelting, Converting and Fire Refining stages to obtain the anode pyrometallurgical route. In this product process, a significant amount of copper (4–8 %Cu) goes to converter slag (CS) which is the most serious problem facing the copper sector. Therefore, in this study, it was aimed to minimize the copper losses to CS in converter stage by adding calcined colemanite (CC) which is a boron compound. After characterization of CS in detail, effect of the reaction temperature and CC addition were experimentally investigated. Then, thermochemical calculations of the slag with the addition of CC were carried out by using the Equilib and Phase Diagram modules of the FactSage thermochemical software. Experimental results show that the amount of copper losses to the CS can be decreased from 4.45% to 1.2% by adding 2% CC to the converter slag at the temperature of 1250 °C for 3 h reaction time.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Copper is an important nonferrous metal which has been used for thousands of years because of its superior physical properties, and its cost are increasing day by day due to the depletion of copper ore reserves [1]. Today, most of the metallic copper is generally produced from sulphidic ores with pyrometallurgical routes including concentration, smelting, converting and refining stages. In converting stage, unmixed two different liquid phases occurs namely, a blister copper with high copper content (98.5%) and a slag phase including oxidised materials with high amount of copper (4–8%). Considering that total copper slag (formed in smelting and converting stages) generation in the world is more than 30 million tons [2], it is very important to produce the copper with minimum losses to slag in copper sector. Converter slag (CS) based on the fayalite (2FeO·SiO2) type is formed by combining the silica (SiO2) as a fluxing agent with iron oxide (FeO) which arising from oxygen blowing to copper matte (Cu2S – FeS). By forming the fayalite phase (according to the Reaction 1), a good separation between blister copper and slag is provided in the converter stage. Except of fayalite phase, CS also contains a small amount of other oxides such as CaO, Al2O3, etc. [3–5]

\[
2\text{FeS}_{\text{immatte}} + 3\text{O}_2(\text{in blast}) + \text{SiO}_2(\text{flux}) + \text{2FeO} \cdot \text{SiO}_2(\text{slag}) + 2\text{SO}_2(\text{off-gas}) + \text{heat} 
\]

(1)

It is well known that there are two main copper losses mechanisms to slag which are physicochemical and mechan-
ical losses in converting stage. [6,7] According to the previous studies [8-10], physicochemical losses are related with dissolution of copper as in sulphide or oxide form (Cu₂S and Cu₂O). This type of losses is associated with thermodynamic conditions of converting stage such as temperature, partial pressure of oxygen, slag composition, and chemical activity of metals. On the other hand, the viscosity of the slag is highly effective over copper losses. Studies [11-16] on copper losses to the smelting slag showed that most of the copper losses arise from mechanically entrained matte and metallic copper especially at lower matte grades. But, for only more than 70 wt.%Cu matte grades, the majority of the copper losses result from physico-chemical losses. As pointed out before, SiO₂ added as flux, increases the viscosity and decreases the surface tension by formation magnetite phase and so copper losses to slag increase in viscous layer. Previous studies [15,17] stated that CS contains a lot of magnetite which enhances the slag viscosity and so increases the mechanical copper losses to slag.

The evaluation of huge amount converter slag with substantial copper value will prevent the continuous reduction of metal reserves and eliminate the negative effects on the environment. Therefore, even if hydrometallurgical recovery treatments for industrial copper slags [18-20] have become very important, new improvements in pyrometallurgical processes are also seen useful and effective to reduce the copper losses [21,22]. On the other hand, copper losses to slag could be decreased by adding some fluxing agents in the system to balance the slag viscosity and basicity. In other words, it is one of the best ways to break down the magnetite structure by adding a flux to the slag and so forming a slag with a lower viscosity could be achieved. For example, by adding CaO as a flux to the slag, the magnetite present in the slag can combine with CaO to produce new formations such as Calcium ferrite with low melting temperature [3]. Several authors have investigated other fluxing agents aside from CaO such as colemanite or boric acid for certain metallurgical industries; Iron-Steel and copper in smelting stage. The studies [23,24] showed that colemanite usage as flux in iron and steel industry decreases the viscosity and the melting temperature of the steelmaking slag. Other studies on usage of borate compounds as a fluxing agent in the copper smelting stage conducted by Rüsen et al. [11,25,26], showed that copper losses to flash furnace slag in laboratory conditions can be reduced from 1% to 0.28%. Previous studies improved that production efficiency can be increased by minimizing the copper losses during the production process by addition of colemanite to the system which leads to decrease in viscosity of slag. These results showed that colemanite could be added in both primary and secondary copper production steps in order to decrease the copper losses to slag. It can be added either together with charging materials in smelting furnace or directly added to the converter furnace. It can also be added to the secondary smelting furnace or to the electric slag cleaning furnaces during settling of the matte.

Considering that the converter slag contains a high proportion of copper, decreasing of copper losses in this type of slags by the addition of flux will provide considerable gains in industrial terms. For this reason, in this study, it was aimed to reduce the copper losses to converter slag by the addition of calcined colemanite. Also, this study includes characterization of converter slag and its thermochemical calculations in the copper converter stage.
2. Materials and method

2.1. Materials

The converter slag used in this study was obtained from Eti Copper Co. (EBI), which is the only plant producing copper from sulphidic ore in Turkey. The material was provided as a powder (lower than 200 µm) form which is taken from the waste site and subjected to crushing - grinding processes. Chemical analysis of CS was performed by coupled plasma mass spectroscopy (ICP-MS) and X-Ray Fluorescence Spectrometer (XRF) at EBI Analysis Laboratory and Middle East Technical University (METU), respectively. The CS mainly contains 23.8 wt.% SiO₂, 44.3 wt.% Fe₂O₃, 4.45 wt.% Cu, 1.09 wt.% S, 3.39 wt.% Zn. Remaining part of the CS consists of the other oxides (Al₂O₃, PbO, CaO, Na₂O, K₂O, MgO etc.) given in Table 1.

The raw colemanite supplied by Eti Mine Co. Bigadı/ Turkey. Before experimental studies, the raw colemanite with—75 μm particle sizes was calcined at 400 °C for 24 h in muffle furnace to remove chemically bonded water. The calcined colemanite (CC) with 51.7 wt.% B₂O₃, 27.7 wt.% CaO, 8.6 wt.% CaCO₃, 7.9 wt.% SiO₂ and 4.1 wt.% other oxides such as Al₂O₃, MgO and SrO labelled as CC [11].

In previous study [17], mineralogical structure of CS was determined a Bruker Advance D8 model X-ray powder diffraction (XRD) instrument with Cu Kα radiation at 30 kV at a scanning rate of 0.4 min⁻¹ existing at Karamanoğlu Mehmetbey University. According to the X-ray of CC sample, Fayalite (Fe₂SiO₄) and Magnetite (Fe₃O₄) are main phases. In addition, it was determined that the CS contains some amorphous structure. As stated before, it is known that copper found in the CS is in metallic copper, matte and copper oxide forms [3,12,27]. However, due to the high intensity of the fayalite and magnetite phases which forming the main structure of the CS, the known forms of copper cannot be effectively detected on the XRD pattern. For this reason, more detailed mineralogical analysis was performed with the help of Field Emission Scanning Electron Microscopy (FE-SEM) device. SEM analysis was performed by using Hitachi SU5000 model with energy dispersive X-Ray (EDX) spectroscopy to identify other mineralogical structure in CS without any coating.

In particular, as a result of the analysis performed with SEM, the structure of the particles in the CS is clearly defined. The colour mapping method obtained by using SEM and EDX data is a method which used frequently by the researchers to determine the possible phases in the examined sample and to see the elemental distribution. In this study, colour mapping method was also applied for converter slag. Thus, the distribution of Cu, Zn, Fe, Si, O and S elements within the slag was determined. The results of SEM-BSE image taken from converter slag with elemental colour mapping are shown in Fig. 1.

According to the SEM analyses, fayalite and magnetite phases known from XRD analyses and the matte which corresponds to mechanically entrapped in converter slag causing the copper losses were observed. Also, elemental colour mapping by SEM for converter slag was performed. In the colour mapping (Fig. 1); Copper (Cu) is presented by red, Iron (Fe) by blue, Oxygen (O) by green, Silicon (Si) by purple, Sulphur (S) by yellow, Zinc (Zn) by orange, Aluminium (Al) by white and Calcium (Ca) by turquoise. The colour mapping method results showed that, apart from the matte form (labelled as y), there are two separate copper-containing structures in the converter slag. The particle which does not overlap with oxygen and sulphur indicates the metallic copper as labelled in Fig. 1-A by x. The higher magnification and elemental colour mapping of the x-structure shown in red square was illustrated in Fig. 1-B. According to this figure, a complex (Cu – Zn – S) structure was existed in the CS. On the other hand, other oxides such as CaO and Al₂O₃ are dispersed in the CS. All of chemical and mineralogical analysis results of CS are consistent with the previous study [17].

2.2. Experimental method

Each experiment was conducted by using a high temperature vertical tube furnace which is equipped with gas cleaning system, gas flowmeter and water circulating system that provides external cooling of the furnace. An inert atmosphere was generated by using nitrogen gas and sent to system to prevent oxidation of the samples during the test period. In order to keep the moisture in the nitrogen gas, it was passed through moisture holders containing silica gel and sent to the system by flowmeter in order to be sent to the system at a certain flow rate (0.2 L min⁻¹).

The main objective of this study is to investigate the usability of colemanite addition in the converter furnace in primary copper production. Therefore, all the experiments were carried out with the addition of adequate amount of calcined colemanite (CC) to 60 g of converter slag (CS) as well as 10 g of pure copper chips (as a blister phase) were added to the system in order to provide the converter furnace conditions. After the filling of mixture in an alumina crucible, it was placed to hot zone of the furnace and heated to the desired temperature. The tube furnace was heated and cooled at a rate of 10 °C min⁻¹ in all experiments.

In melting experiments, the reaction temperature and CC addition were selected as variables in the range of 1200, 1250, 1300 °C and wt. 0%, 2%, 4%, respectively to investigate the copper losses to CS. In this study, the reaction time was chosen as 3 h since the converter process generally was carried out for 3–4 h in copper plants. After separation and grinding processes, the samples were subjected to chemical and mineralogical analyses (ICP-MS, XRF, SEM, and XRD) and evaluated for copper losses to slag.

2.3. Model

In the present study, in order to reveal the effects of CC addition in the ternary system at different temperatures, phase diagrams were calculated and plotted by using the Phase Diagram module of the FactSage thermochemical software. The precipitate target phase was also specified by calculating the temperature when a second phase first starts to form (activity is 1, and 0 mol) from the precipitate target phase using FACT-SLAG solution phase. FToxide solution database was selected for the liquid and solid solutions in the system, whereas all gas, liquid and other stoichiometric solid phases were selected from the FactPS database.
Table 1 – Chemical analysis of converter slag.

<table>
<thead>
<tr>
<th>Element (wt. %)</th>
<th>SiO₂</th>
<th>Cu</th>
<th>FeΣ</th>
<th>S</th>
<th>ZnO</th>
<th>PbO</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>MgO</th>
<th>Bal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount</td>
<td>23.84</td>
<td>4.45</td>
<td>44.32</td>
<td>1.09</td>
<td>4.20</td>
<td>0.50</td>
<td>1.49</td>
<td>0.91</td>
<td>0.72</td>
<td>0.69</td>
<td>0.98</td>
<td>16.81</td>
</tr>
</tbody>
</table>

The chosen FlOxid database in FactSage includes data for pure oxides and oxide solutions of 20 elements (also for dilute solutions of Si, Cl, I, PO₄, H₂O/OH, SO₄, CO₂, and F in the molten-slag phase). For the systems including ZnO, Mn₂O₃, PbO, NiO, MnO, CoO with the major oxide components FeO, SiO₂, CaO, Fe₂O₃, Al₂O₃, MgO most binary and many ternary sub-systems among these components and between these components and the major oxide components have been evaluated and optimized. Especially in the composition region of fayalite (Fe₂SiO₄) slags, extensive optimizations have been performed. For the systems including SnO, Cu₂O, As₂O₃ compounds, data have been optimized with the major oxide components (FeO, SiO₂, CaO, Fe₂O₃, Al₂O₃, MgO) generally for SiO₂-rich slags and in the composition region of fayalite slags. Sub-systems which have not been evaluated and optimized have been assumed ideal or have been approximated [28].

3. Results and discussions

3.1. Thermochemical calculation of converter slag with flux addition

In the present study, thermochemical calculations of CS were carried out with CC addition. As stated before, industrial CS frequently based on fayalite type slag which mainly contains iron oxide (as FeO and Fe₂O₃) and SiO₂ with low amount of CaO, Al₂O₃, ZnO, etc. According to the chemical analysis of CS, other oxides (CaO, Al₂O₃, PbO, MgO, K₂O and Na₂O) are present lower than 1% in the slag except for ZnO (4%). Therefore, the CS can be identified by the components of FeO-SiO₂ with a sum of ZnO and Cu (as oxide, sulphide and metal). Fig. 2 shows the FeO-Fe₂O₃-SiO₂ system with the presence of ZnO and Cu at 1250°C which is plotted as ternary phase diagrams by using the Phase Diagram module of the FactSage thermochemical software.

The liquid Cu and liquid slag phase is mainly bordered by γ-Fe₂O₃, FeO (Monoxide) and Fe₂O₃ (Spinel). As seen in Fig. 2, the composition of the condensed phases is strongly dependent on the partial pressure of oxygen (P₂O₅) of the gas phase. Also, this figure indicates that Fe₂O₃/FeO ratio increases with increasing P₂O₅ up to relatively high values (for equilibrium with spinel, 10⁻⁷ atm at 1250°C).

Fig. 2 also indicates the line of partial pressure of oxygen (P₂O₅ = 10⁻⁷ atm) highlighted with red colour in ternary phase diagram belonging to FeO-Fe₂O₃-SiO₂ system in the presence of ZnO and Cu. Four different SiO₂/(FeO+Fe₂O₃+SiO₂) ratios were selected in this line to investigate the formation percent of the Spinell and Liquid slag phases. According to the calculation results, spinel phase is formed in lower SiO₂ content region (solid black square and circle points) which includes slag liquid with solid spinel. As SiO₂ ratio increases in the slag, line goes to only liquid slag region (hollow circle), and so solid spinel phase disappears in the system.

As it is known, the industrial converter furnaces generally operate with slags near the magnetite saturation region around at 1250°C. According to the ternary diagram FeO-Fe₂O₃-SiO₂ with isobars for oxygen (in Fig. 2), the oxygen partial pressure varies from 10⁻⁶ to 10⁻⁹ atm. on the line of magnetite saturation. Therefore, initially, the effect of fluxing agent (CC) addition on the iron silicate slags in the presence of ZnO and Cu at 1250°C was investigated theoretically by calculating with FactSage software. Fig. 3 shows the change in the liquid slag regions with the different wt.% addition of CC at 1250°C on the phase diagram of Fe/(Fe + SiO₂) versus logP₂O₅ calculated by "Phase Diagram" module of FactSage.

According to the calculation results, slag liquid region could be obtained between 0.55 and 0.75 ratio of Fe/(Fe + SiO₂) about 10⁻⁷ atm P₂O₅ at 1250°C without CC addition. It is seen that from the Fig. 3 as the CC adds to the system, liquid slag region expands both lower and higher Fe/(Fe + SiO₂) ratios. This situation can explain as follows; CC addition to the system tended to larger the liquid slag region due to forming a eutectic with very low melting point [11].

3.2. Results of experimental studies

After thermochemical calculations, effects of CC addition and reaction temperature on copper losses to CS were investigated by performing pyrometallurgical experiments under different conditions. In the experiments, pure copper chips (as blister) and converter slag were mixed with different amount of CC in alumina crucible and they were melted together at various temperatures for 3 h. Experimental results are given Table 2 and summarized in Fig. 4.

The industrial converter furnaces generally operate with slags near the magnetite saturation region around at 1250°C which corresponds to between 10⁻⁶ and 10⁻⁹ atm oxygen partial pressure (Fig. 2). By using nitrogen gas (with lower than 3 ppm O₂), we could work close to the real furnace conditions. As seen from Table 2, Fe/(Fe + SiO₂) ratio varies from 0.54 to 0.6 which corresponds to Slag-liq. region for Po₂ of nearly 10⁻⁷ for only without CC addition. As Colemanite is added to system, these ratios become applicable over wider Po₂ ranges from 10⁻⁵ to 10⁻⁸.5 slag-liq. region (as shown in Fig. 3).

As it can be understood from Fig. 4a, in the absence of Colemanite, the increase in temperature led to a slightly increase in copper losses. With the addition of calcined Colemanite (2%) to the system, a remarkable decrease is observed in the copper losses to converter slag at 1250°C. However, in the addition of 4% calcined Colemanite, copper losses have increased considerably at 1300 degrees. Addition of excess Colemanite can change the slag structure by forming compounds with a lower melting point, and also by increasing the fluidity of the slag by the fluxing properties, resulting in an increasing in copper losses to the slag.

On the other hand, as seen in Fig. 4b, the addition of CC at 1200°C has slightly effect on the copper loss to the slag. How-
Fig. 2 – FeO-Fe₂O₃-SiO₂ system in the presence of ZnO and Cu at 1250 °C and under different oxygen partial pressures calculated by FactSage. The dotted lines represent isolines of oxygen partial pressures in log (P₀₂/atm), whereas the red line refers to isoline for log P₀₂ = −7 (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Fig. 3 – Change in the liquid slag regions with the different wt.% CC addition at 1250 °C in Fe-O₂-SiO₂-Cu-Zn system. (Solid line: 0 wt% CC, dashed line: 2 wt.% CC, dotted line: 4 wt % CC, and dash-dotted line: 8 wt % CC).

ever, copper losses could be decreased to a minimum level of 1.2% Cu with the addition of 2% calcined colemanite at 1250 °C. By increasing the addition of colemanite up to 4%, it was determined that the copper loss was gradually increasing. Similar effect is also observed in all tests performed at 1300 °C. Especially, the images of the experiments with the addition of 2% and 4% CC at 1300 °C prove this situation. Cross-sections of alumina crucibles obtained after the experimental studies
Table 2 – Chemical analysis findings of experiments with CS and various additions of CC as wt.% (under nitrogen atmosphere at different temperatures for 3 h).

<table>
<thead>
<tr>
<th>Exp. Code</th>
<th>Temp. (°C)</th>
<th>C.C. (%)</th>
<th>Cu</th>
<th>SiO₂</th>
<th>Fe</th>
<th>S</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>B₂O₃</th>
<th>Fe/(Fe + SiO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>with blister phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AC–1</td>
<td>1200</td>
<td>0</td>
<td>5.4</td>
<td>27.4</td>
<td>36.7</td>
<td>0.15</td>
<td>0.82</td>
<td>2.80</td>
<td>–</td>
<td>0.57</td>
</tr>
<tr>
<td>AC–2</td>
<td>1200</td>
<td>2</td>
<td>4.7</td>
<td>26.3</td>
<td>36.4</td>
<td>0.39</td>
<td>1.51</td>
<td>3.24</td>
<td>1.78</td>
<td>0.58</td>
</tr>
<tr>
<td>AC–3</td>
<td>1200</td>
<td>4</td>
<td>4.9</td>
<td>27.7</td>
<td>34.7</td>
<td>0.38</td>
<td>2.18</td>
<td>3.40</td>
<td>2.49</td>
<td>0.56</td>
</tr>
<tr>
<td>AC–4</td>
<td>1250</td>
<td>0</td>
<td>6.9</td>
<td>26.5</td>
<td>34.6</td>
<td>0.26</td>
<td>0.86</td>
<td>5.80</td>
<td>–</td>
<td>0.57</td>
</tr>
<tr>
<td>AC–5</td>
<td>1250</td>
<td>2</td>
<td>1.2</td>
<td>26.0</td>
<td>38.3</td>
<td>0.41</td>
<td>1.56</td>
<td>4.81</td>
<td>1.57</td>
<td>0.60</td>
</tr>
<tr>
<td>AC–6</td>
<td>1300</td>
<td>0</td>
<td>2.8</td>
<td>25.4</td>
<td>37.5</td>
<td>0.15</td>
<td>2.24</td>
<td>5.27</td>
<td>2.70</td>
<td>0.60</td>
</tr>
<tr>
<td>AC–7</td>
<td>1300</td>
<td>4</td>
<td>8.3</td>
<td>26.8</td>
<td>33.1</td>
<td>0.06</td>
<td>0.83</td>
<td>6.84</td>
<td>–</td>
<td>0.55</td>
</tr>
<tr>
<td>AC–8</td>
<td>1300</td>
<td>2</td>
<td>11.0</td>
<td>24.8</td>
<td>31.1</td>
<td>0.02</td>
<td>1.37</td>
<td>7.08</td>
<td>1.12</td>
<td>0.56</td>
</tr>
<tr>
<td>w/o blister phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AC–9</td>
<td>1250</td>
<td>0</td>
<td>2.4</td>
<td>28.5</td>
<td>38.5</td>
<td>0.08</td>
<td>0.88</td>
<td>3.54</td>
<td>–</td>
<td>0.57</td>
</tr>
<tr>
<td>AC–10</td>
<td>1250</td>
<td>2</td>
<td>2.48</td>
<td>29.6</td>
<td>37.1</td>
<td>0.07</td>
<td>1.67</td>
<td>3.86</td>
<td>1.29</td>
<td>0.56</td>
</tr>
<tr>
<td>AC–11</td>
<td>1250</td>
<td>4</td>
<td>2.25</td>
<td>26.9</td>
<td>37.3</td>
<td>0.08</td>
<td>2.23</td>
<td>5.08</td>
<td>1.63</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Fig. 4 – Effects of a) CC addition, b) reaction temperature on copper losses to CS.
with 2% and 4% CC addition are given in Fig. 5. It can be seen from Fig. 5 that the blister phase is not formed at the base of the crucible performed at 1300 °C because it is dispersed into the slag as small diameter copper particles with the increase of temperature. Therefore, in such a system, temperature should be limited to 1250 °C in the presence of the colemantine.

The presence of the blister forms a phase in which the mat and metallic copper particles in the slag can be descended and collected in it. With a small amount (2%) of colemantine addition to the slag at reasonable temperatures, fluidity of the slag can be increased and so very small copper-containing particles can reach to the blister phase (Fig. 5a–d). However, as colemantine addition and temperature increase, the slag has a more mobile structure, which leads to rising of the copper losses due to the distribution of copper in the blister phase into the slag (Fig. 5 e–f).

In the experiments, colemantine was used after calcination at 400 °C. However, as known from the thermal results of the ground colemantine [29], water vapor output continues up to 600 °C and CO₂ gas outlet continues up to 750 °C due to the structure of raw colemantine. Also, from the literature [30] it is known that B2O3 in colemantine was lost by evaporating as gaseous boric oxide at high temperature (>1000 °C) from the slag. Of course, their output does not stream up to the test temperature (1200–1300 °C), but they may result in some gaps in the macro structure in the resultant of the experiments. They can also result in moving up the copper particles from the slag. In this case, the coarse particles may glide downwards with the effect of gravity; the small particles may remain in the slag under the influence of bubbles and may even move upward.

The experiments continuous under the constant temperature (1250 °C) by mixing only the converter slag and predetermined boron compound (CC: 0%, 2%, 4%) without the addition of blister copper. The reason for the experiments without blister copper is to investigate the effect of CC addition on copper losses when the slag is placed in an externally heated pot (settling furnace). Experimental results of with and without blister phase for different CC additions at 1250 °C were compared and plotted in Fig. 6.

Considering the initial copper content (4.45% Cu) in converter slag, it can be deduced from the Fig. 6 that the loss of copper to the slag is decreased to very low levels (2.5% Cu) independently of CC addition. It is concluded that the copper losses can be significantly reduced by keeping the converter slag in the settling furnace. Fig. 6 also confirms that the addition of 2% CC makes a significant contribution to minimize the copper losses to slag (1.3%) in the experiments performed in converter furnace conditions (with blister at 1250 °C for 3 h).

Since CC is composed of CaO and B₂O₃, its addition to the converter slag should be considered in these two aspects when analysing the effect on copper losses. The former (CaO) is effective on magnetite. It is known that the converter slag contains large quantities of magnetite and this magnetite leads to an increase in the slag viscosity as well as copper losses. By adding CC to these slags, the magnetite present in the slag can be combined with CaO (in the CC) to produce new formations such as calcium ferrite which has lower melting temperature [3]. Some possible reactions with the melting points of these compounds are given in Reactions 2–4:

\[
\begin{align*}
\text{FeO} + \text{CaO} + \text{SiO}_2 &= (\text{CaO}.\text{FeO}.\text{SiO}_2)_{\text{TM}_1} = 1208 \degree \text{C} \\
2\text{FeO} + \text{SiO}_2 &= (2\text{FeO}.\text{SiO}_2)_{\text{TM}_2} = 1205 \degree \text{C} \\
\text{CaO} + \text{Fe}_2\text{O}_3 &= (\text{CaO}.\text{Fe}_2\text{O}_3)_{\text{TM}_3} = 1230 \degree \text{C}
\end{align*}
\]

![Fig. 5 – Cross-sections of alumina crucibles obtained after the experimental studies under different conditions.](image)

![Fig. 6 – Comparison of experimental results of with and without blister phase for different CC additions at 1250 °C.](image)
Considering that melting temperature of magnetite is 1508 °C, calcium ferrite structure with lower melting point (Tm3) is very beneficial to operate the converting furnace at reasonable temperatures by reducing the presence of magnetite. Since it has lower viscosity, lower specific gravity and more basic than that of fayalite slag [3], the viscosity of the slag could be decreased and settling rate could be improved by CC addition to the slag, which means mechanical copper losses could be prevented.

According to the chemical analysis, more than half of the colemite is composed of B₂O₃ (51.7% of CC). Therefore, after the addition of CC to the system, B₂O₃ also causes a significant effect on the structure of the slag. From the previous studies on metallurgical applications [11,23–26], it is known that B₂O₃ has the effect of decreasing the melting point, viscosity and density of the slag. As stated in previous studies [11,26] the liquidus temperatures of final slags decreased significantly with the increasing CC addition due to reaction of B₂O₃ with other oxides and forming the eutectics with low melting points, which results in the lowering of the melting temperature of slag. In addition, according to calculation results obtained by using FactSage Viscosity module [11], CC addition results in a slightly decrease in viscosity on smelting slags. In the light of these results, it could be concluded that a good separation the blister (Cu phase) from the slag can be achieved in the converter stage by means of B₂O₃, which prevents the mechanical copper losses to slag.

To sum up, by adding an appropriate amount of CC including CaO and B₂O₃, it will be possible to modify the physical and mineralogical properties of the slag, which resulted in reducing the copper losses. This was supported by the results of experimental studies. According to experimental results, after adding 2% CC at 1250 °C for 3 h, the copper losses to converter slag decreased from the initial content (4.45% Cu) to minimum level (1.2% Cu).

Since better results are obtained in the presence of blister phase, it can be deduced that calcined colemite addition could be applied especially in primary copper converter step (with blister phase in Fig. 6). Taking into account of experience obtained previous studies [11,25], it could be concluded that calcined colemite can be added either together with charging materials in smelting furnace or directly added to the converter furnace. It can also be added to the secondary smelting furnace or to the electric slag cleaning furnaces during settling of the matte. Slag settling in electric furnace is widely used to recover copper from slags during the copper production, which is operated immediately after smelting of concentrate to obtain a long settling duration for suspended matte droplets. Therefore, colemite can also be added in this step to reveal matte-slag separation by helping to adjust the viscosity of slag.

4. Conclusions

In this study, the effects of calcined colemite (CC) addition with silica as flux were investigated to reduce copper losses to slag in converter furnace which is important stage of pyrometallurgical copper production. For this purpose, a series of experiments were carried out in alumina crucible by adding a certain amount of CC to CS at different temperatures. As a result of experimental studies, copper amount in CS could be reduced to 1.2% by adding 2% of CC at 1250 °C for 3 h in an inert atmosphere. It was also determined that CC additions to the CS at higher temperature (more than 1250 °C) have a negative effect on copper losses due to the dispersion of the copper as small particles into the slag. In addition, the effect of CC addition on the iron silicate slags in the presence of ZnO and Cu at 1250 °C was investigated theoretically by calculating with FactSage software. Thermochemical results show that liquid slag region expands both lower and higher Fe/(Fe + SiO₂) ratios as the CC adds to the system.

Acknowledgements

The authors wish to thank the Karamanoglu Mehmetbey University Scientific Research Projects (BAP) Coordinating Office for support with grant number KMU-BAP-28-M-16. Also, we are grateful to Scientific and Technological Research Application and Research Center (BILTEM) for SEM images.

References


