Thermochemical Calculations of Fayalite Type Slags After Addition of Fluxing Agents During Smelting and Converting Stages

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Abstract

In recent years, secondary resources (slags, scraps, etc.) have become a very important source for all valuable metals like copper due to the depletion of high grade ores and increasing the demand of this metal. Since copper is lost to slag between 0.7 and 2.3 wt. % during copper smelting process and 4 to 8 wt.% during the converting stage, the theoretical consideration with physical properties of slags should be investigated to minimize the copper losses via achievement of good separation between matte and slag. Therefore, in this study, thermochemical calculations of the fayalite type slags with the addition of some fluxing agents such as CaO, B₂O₃, and calcined colemanite (CC) were carried out by using the Equilib and Phase Diagram modules of the FactSage thermochemical software.

1. Introduction

In the world, copper losses to the slag in the pyrometallurgical copper production constitute a major problem [1]. Studies [2-4] on this problem indicated that mainly there are two types of copper losses to slag namely mechanical and physico-chemical losses. Former originates from mechanically entrapped particles or floating unstable droplets of matte which do not find enough time to reach to the matte layer. Mechanical losses are mainly related to the viscosity of the slag. When slag viscosity increases, mechanical copper losses also increase. Latter is related to solubility of copper in sulphide and oxide forms in slag. In other words, copper losses are present in the slag melt as copper ions. During smelting of charge, silica is being widely used as a fluxing agent to promote well separation of matte and slag. However, excessive silica usage results in high viscosity and strong acidity, which causes the loss of valuable metals. For these reasons, beside silica, limestone (CaCO₃) is usually added to balance slag viscosity and basicity. Several authors [5-8] have investigated other fluxing agents aside from CaO such as colemanite or boric acid for certain metallurgical industries.

Therefore, this study has aimed to investigate the effect of some fluxing agents (CaO, colemanite or B₂O₃) on copper losses to slag for the copper matte smelting process in order to reduce copper losses in the slag phase. By this way, comparative results could be obtained for all fluxing agents used in the experiments and the changes in liquidus temperature could be estimated by computer software (FactSage) [9].

2. Experimental Method

Industrial smelting and converting slags frequently based on fayalite contain mainly iron oxide (as FeO and Fe₃O₄) and SiO₂ as well as low amount of CaO, Al₂O₃, ZnO, PbO, MgO and so on. When minor oxides such as CaO, Al₂O₃, ZnO are ignored, the slags can be identified by the components of FeO-SiO₂. As seen from Figure 1 calculated by FactSage, the liquid slag phase (Fe₂SiO₄ called as fayalite) is bordered by γ-Fe, SiO₂, Fe₂O₃ and FeO. In addition, it is seen that the composition of the condensed phases is strongly dependent on the partial pressure of oxygen of the gas phase. Furthermore, these figures verify that Fe₂O₃/FeO ratio increases with increasing partial pressure of oxygen from too low levels (for equilibrium with solid iron, ~10⁻¹¹ atm at 1250 °C) to relatively high values (for equilibrium with solid magnetite, ~10⁻⁷ atm at 1250 °C) [10].

Therefore, in this study, thermochemical calculations were carried out and plotted as ternary phase diagrams by using the Phase Diagram module of the FactSage thermochemical software to analyze the effects of fluxing agents (CaO, B₂O₃ and CC) in the FeO-Fe₂O₃-SiO₂ system at different conditions (different temperatures and partial pressure of oxygens). In addition, the precipitate target phase was determined 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.
3. Results and Discussions

As it is known the industrial flash smelting furnaces generally operate with slags near the silica saturation region between 1200 and 1300 °C. According to the ternary diagram FeO-Fe₂O₃-SiO₂ with isobars for oxygen (in Figure 1), the oxygen partial pressure varies from $10^{-7}$ to $10^{-11}$ atm. on the line of silica saturation. Therefore, initially, the additions of fluxing agents (CaO, B₂O₃ and CC) and temperature effects on the iron silicate slags were investigated theoretically by calculating with FactSage software.

Figure 2 shows the change in the liquid slag regions with the 10 wt.% addition of B₂O₃, CaO and Calcined Colemanite at different temperature on the phase diagram of FeO-Fe₂O₃-SiO₂ calculated by “Phase Diagram” module of FactSage. According to the results, it is seen that B₂O₃ addition to the FeO-Fe₂O₃-SiO₂ slag system tended to larger the liquid slag region with increasing temperature due to forming a eutectic with very low melting point. However, as temperature increases, CaO addition to the fayalite slag results in limited expanding the liquid slag region. On the other hand, as seen in Figure 2, after the addition of CC the liquid slag region expands considerably by increasing temperature from 1200 to 1300 °C [11].

Figure 1: The stability diagram of Fe-O-SiO₂ with O₂ isobars at 1250 °C under 1 atm.

Figure 2: Change in the liquid slag region with the 10 wt.% addition of a) B₂O₃, b) CaO and c) CC at different temperature on the phase diagram of FeO-Fe₂O₃-SiO₂ calculated by “Phase Diagram” module of FactSage 6.2. (Redrawn from Rusen et. al. 2016)
Another study was realized with Fe-SiO$_2$-O$_2$-Ca$_2$B$_6$O$_{11}$ in order to understand the melting behaviour of slags after addition of CC. The calculated first precipitation phase under different partial pressures of oxygen and temperatures is shown in Figure 3. According to FactSage model calculations, whereas SiO$_2$ is the first precipitate for low CC additions under all atmosphere (10$^{-7}$ to 10$^{-11}$ atm), after 8% CC addition spinel is the first precipitate phase for 10$^{-7}$ and 10$^{-9}$ atm, and olivine is the first precipitate for 10$^{-11}$ atm after 4% CC addition.

Figure 3. First precipitate phase in Fe-O$_2$-SiO$_2$ – Ca$_2$B$_6$O$_{11}$ under 1 atm.

4. Conclusions

In this work, thermochemical calculations on the effects of several fluxing agents (CaO, B$_2$O$_3$ and CC) additions to the fayalite type slag were theoretically studied under different conditions. From the FactSage calculations, it is concluded that by increasing temperature the liquid slag region expands with different ratios for all fluxing agents. The largest liquid slag region expansion is observed after B$_2$O$_3$ addition, but it is limited for CaO addition. On the other hand, as the calcined colemanite adds to the system, liquid slag region expands both lower and higher Fe/(Fe+SiO$_2$) ratios. In addition, after calculations it is noted that SiO$_2$ is the first precipitate phase up to 5% CC addition to slag for all different oxygen partial pressures.

References


