EFFECTS OF CLAY MINERALS ON VISCOSITY AND COPPER ENTRAINMENT LOSSES IN SMELTING SLAGS

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Introduction

Hydrous aluminium phyllosilicate group minerals, often broadly classified as ‘clays’, exist as common gangue components in most copper porphyritic ore deposits. In the case of Chile, the most frequently clays correspond to kaolinite, montmorillonite and illite, which weight content in the deposit, ranging from 4 to 22 wt\%.\textsuperscript{1} The processing of these ores has been problematic; with difficulties, such as reduced production performance, complex tailings treatment, and pumping challenges arising.\textsuperscript{2} Generally, clays minerals contained in primary copper sulphide deposit move directly to mineral pulp through the processing circuit as their fine sizes and flat shapes make them virtually unavoidable to be dragged since they are entrained by the pulp and bubbles, and continue to the concentrate during froth flotation stage of hypogenous sulphurised pulps even reaching pyrometallurgical process generating inefficiencies in practically all unit operations.

The characteristics of cooper smelting slag are strongly related with its composition affecting for example its viscosity,\textsuperscript{3} which turn to be unpredictable because, additional iron and minor alkali oxides from clay minerals contained into concentrates and dissolution of refractory bricks, are also collected by the slag, making complex the operation. The viscosity of the slag represents one of the most relevant variables in the process since its direct impact on copper mechanical entrapment\textsuperscript{4} and refractory bricks wear.\textsuperscript{5} Clay minerals effect on slag viscosity lies in its decomposition at high temperatures giving to the melt: i) ions which support construction and polymerisation of crystal lattice and structural network, and ii) alumina that actively participates on thermodynamic equilibrium promoting magnetite generation.

Geometallurgical research that allows to identify and analyse the presence and behaviour of phyllosilicate as gangue minerals on ore mineral processing and extractive metallurgy is an area of increasing interest, particularly in the context of copper metallic production. Empirical studies had been conducted in order to clarify the effect of different oxides on slag viscosity,\textsuperscript{3} and also theoretical models had been developed. Nevertheless, there is no model that allows to estimate the viscosity and copper entrainment losses of slag based on fundamentals and experimental results which consider type and concentration of clay minerals contained into copper concentrates fed to smelting stage.

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Experimental

In this study, a mixture of synthetic fayalite slag doped with 2, 5 or 8% of either kaolinite or montmorillonite was charged into a high alumina crucible but keeping the total SiO$_2$ in the charge, then it was melted at temperatures of 1275, 1300, 1325 and 1350°C in an electric furnace under controlled atmosphere using CO/CO$_2$/N$_2$ gas to fix the oxygen partial pressure of $10^{-9}$ atm. After 8 hours to reach the equilibrium, rheometry tests were performed while maintaining the above conditions, in order to determine the effect of the type and concentration of clay minerals on viscosity and shear stress of the molten phase. The rheometer had a modified spindle of stainless steel AISI 310 which allows to resist the high temperature inside of furnace. Three viscosity measurements at three different samples were performed at the same temperature and composition to compare results and ensure measurements reproducibility. During the viscosity measurements, a thermocouple Pt-Pt/Rh (10%) was used to record the temperature.

Furthermore, equilibrium tests at 1275 and 1300°C and the same experimental conditions described above were carried out to characterise the compositional changes of the molten phase while clay mineral was added. Once experiments were finished, the crucible was quenched into cold water, and samples were taken and characterised by using optical microscopy, XRD, XRF and ICP.

Results and Discussion

Slag viscosity

According to the study, after the equilibrium, the presence of kaolinite in copper sulphide concentrates, results in its thermal decomposition and the rupture of its structure providing oxidised and silicate species to the melt, as consequence, the amount of fayalite decreased while the formation of an aluminium spinel of hercynite (FeO·Al$_2$O$_3$) and magnetite (Fe$_3$O$_4$) were promoted. The increase of the magnetite content increases the viscosity of the slag since the formation of ferric complexes that interact with the slag structural network, at the same time the formation of hercynite leads to increase the slag viscosity since alumina behaves as acid oxide when its content is greater than 5 wt% into the slag$^6$.

On the other hand, when synthetic fayalite slag was doped with Montmorillonite the matrix changes from fayalite to olivine since the decomposition of that clay mineral at high temperatures provides magnesium to the melt which interacts with the iron of the fayalite structure and becomes part of the solution. The degree of polymerisation of the slag increase because more SiO$_4^{4-}$ ions were available for the construction of slag structure. The formation of hercynite and magnetite were promoted as well.
Figure 1: Viscosity of the fayalite slag when it was doped with 2, 5 and 8 wt% of kaolinite in the charge at different temperatures

Figure 2: Viscosity of the fayalite slag when it was doped with 2, 5 and 8 wt% of Montmorillonite in the charge at different temperatures

Copper entrainment losses
Regarding copper entrainment losses, the main factor to affect the rate of matte settling results to be the slag viscosity at the same time, a significant effect for viscosity of fayalite slag is the magnetite content. Table 1 shows the magnetite content into the obtained slag doped with clay minerals in the charge at 1275°C. A direct relationship between the magnetite and clay minerals content in the slag is observed.

Table 1: Magnetite content into the obtained slag at 1275°C determined by XRD

<table>
<thead>
<tr>
<th>Doped clay in the charge (wt%)</th>
<th>Kaolinite</th>
<th>Montmorillonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>6.7</td>
<td>8.9</td>
</tr>
<tr>
<td>5</td>
<td>7.7</td>
<td>10.4</td>
</tr>
<tr>
<td>8</td>
<td>12</td>
<td>15</td>
</tr>
</tbody>
</table>

As a result, a relation between clay minerals contents and cooper entrainment losses in slag could be inferred through data obtained from the smelting operation. The correlation between the copper matte grade, with the magnetite content and the
corresponding copper entrainment losses into the slag at the equilibria for different copper smelting operations is illustrated in Figure 3.

![Figure 3](image_url)

**Figure 3:** Relation between the copper matte grade with magnetite and copper losses into the slag for different industrial copper smelters. (Collection data)

According to Figure 3 and compositions for the slags that were experimented in this study, the presence of clay minerals contained into the copper sulphide concentrates contributes to strongly increases the content of magnetite and then the copper entrainment losses, as an example, 8 wt% of montmorillonite in the charge results in 15 wt% of magnetite and copper losses over 3 wt% into the slag in comparison to 8 wt% of magnetite and 1.2 wt% of copper losses, respectively, for the case without clay minerals under the same experimental conditions.

**References**