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Experimental approach to matte-slag reactions in the flash smelting process

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Abstract
Improving metal-slag separation in pyrometallurgical processes is increasingly important. Due to the harsh conditions, direct observations of the molten phases behavior in the settler of the Outotec Flash Smelting Furnace (FSF) are not possible and the ways to improve metal settling can only be studied by simulation and modelling. This study focuses on kinetics and mechanisms of the chemical reactions between matte droplets and slag, which were investigated in laboratory scale heat-quench equipment at typical smelting temperature of 1300 °C as a function of time in both air and argon atmosphere. The reaction mechanism in the FSF settler was formulated and results in argon atmosphere also indicate that the oxidation of cuprous sulfide by ferric ions in the slag contribute strongly to the copper losses in the slag.

Keywords: Matte-slag formation, settler, kinetics and mechanisms, copper losses
1. Introduction
Metallic copper is extracted from sulphide concentrates using pyrometallurgical processes. The flash smelting is the dominant technology which accounts for about 43% of global copper production (Wang S et al. 2019). Since introduction of the first Outokumpu Flash Smelting (FS) process in 1949, many academic and industrial research groups have contributed to the increased understanding as well as continuous development of the process (Liu et al. 2019; Holappa et al. 2017).

The studies on reaction mechanisms in the flash smelting furnace (FSF) have focused mainly on the reaction shaft, fluid dynamics and oxidation of the sulphide particles. The reaction mechanism and sequences of the chalcopyrite and other sulphide combustion in the reaction shaft were studied on laboratory scale (Jorgensen 1983 and 2001; Jokilaakso et al. 1991; Stefanova et al. 2004 and Perez-Tello et al. 2018) and also industrial scale (Taskinen et al. 2001a; Taskinen et al. 2001b). Jokilaakso et al. also described a mechanistic model for particle fragmentation based on the concept proposed by Kim and Themelis (1986). Some kinetic studies were also carried out (Chaubal et al. 1986; Asaki, 1992). With the development of the commercial fluid dynamics software, several attempts were made to analyse the phenomena and optimize the FS process (Jokilaakso et al. 1995; Ahokainen et al. 1998; Solnordal et al. 2003; White et al. 2015 and Jun et al. 2018) and assisting process control as well as equipment design. The modelling efforts of copper FS has been reviewed by Taskinen et al. (2019).

The reactions for generating and separation of the sulphide matte and iron silicate slag occur mostly below the reaction shaft, on the settler surface. However, only few experimental (Czkowski et al. 2004; Sukhomlinov et al. 2019a and Sukhomlinov et al. 2019b) and simulation (Swinbourne et al. 2011) copper matte-slag system studies have been carried out to study the thermodynamic features, reaction mechanisms and kinetics of the phase separation and the matte settling phenomena (Fagerlund et al. 2000; Henao et al. 2010; Devia et al. 2011 and Hidayat et al. 2016). The settling phenomenon is crucial and affects copper losses in the production. A recent review of the settling phenomena and metal losses in pyrometallurgical operation has been published by Bellemans et al. (2018).

The focus and novelty of this study was in kinetics and mechanisms of the matte-slag reaction as a function of time. The reactions at typical smelting temperature of 1300°C were investigated in both air and argon atmosphere in laboratory scale heat-quench equipment for deriving appropriate rate equations for the matte-slag reactions. This work was contributing to a better understanding of the settling process in the FSF, yielding new experimental data for numerical process modeling purposes.
2. Experimental

2.1 Material

The chalcopyritic copper concentrate powder was provided by Outotec Research Center in Pori, Finland. Its chemical composition and mineralogy are given in Table 1 and Table 2, respectively. Chemical analysis were done by using ICP-OES (Inductively coupled plasma-atomic emission spectroscopy) and ICP-MS (Inductively coupled plasma-mass spectrometry) (Ni, As, Cd, Sb, Pb, Bi); S and C by combustion analysis; Au and Ag with fire assay, and rest with ICP-OES. The mineralogical composition was calculated from the chemical and SEM+EDS (Scanning Electron Microscopy, Energy Dispersive X-ray Spectroscopy) and XRD analyses (X-ray Diffraction).

Table 1. Chemical composition of the sulphide concentrate (mass%)

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Fe</th>
<th>Zn</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>Co</th>
<th>Ni</th>
<th>As</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfide concentrate</td>
<td>27</td>
<td>27.2</td>
<td>0.18</td>
<td>0.27</td>
<td>0.008</td>
<td>3.69</td>
<td>0.014</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>S</td>
<td>29.8</td>
<td>0.29</td>
<td>0.15</td>
<td>0.17</td>
<td>0.78</td>
<td>0.3</td>
<td>&lt;0.005</td>
<td>&lt;0.05</td>
<td>71ppm</td>
<td>2.24ppm</td>
</tr>
</tbody>
</table>

Table 2. Mineral composition of the sulphide concentrate (mass%)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chalcopyrite (CuFeS2)</th>
<th>Pyrite (FeS2)</th>
<th>Quartz (SiO2)</th>
<th>Feldspar (BaAl2Si2O8)</th>
<th>Hematite (Fe2O3)</th>
<th>Dolomite (CaMg(CO3)2)</th>
<th>Buterite</th>
<th>Muscovite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass%</td>
<td>78</td>
<td>4.3</td>
<td>7.9</td>
<td>3.5</td>
<td>1.6</td>
<td>1.4</td>
<td>1.4</td>
<td>1.2</td>
</tr>
</tbody>
</table>

An iron oxide-silica slag was prepared from hematite powder (Alfa Aesar, 99.99 mass% purity Fe2O3, -5 um) and silica powder (Umicore, 99.99 mass% purity SiO2, -40 mesh). The two powders were first mixed with a mass ratio of 65 mass% Fe2O3 and 35 mass% SiO2. After grinding, the powder mixture was heated in a furnace at 1300°C for 8 hours in air to obtain a homogeneous mixture of solid iron oxide and silica grains (shown in Figure 1). Each sample weight in the present experiments was 0.5 g and the crucible 2.7 g. Argon gas (purity ≥ 99.999%) was used in the neutral atmosphere experiments and its flow rate was set to 200 mL/min controlled by a rotameter (Aalborg 052-01-SA, USA).
2.2 Apparatus

The experimental apparatus used is shown in Figure 2. It was comprised of a vertical tube furnace (Lenton LTF 16/450) equipped with four silicon carbide (SiC) heating elements. On top of the furnace, a water cooled metallic flange was fitted to the alumina work tube with holes for gas inlet, thermocouple and for sample suspension Pt-wires. Two tubes were connected to the flange, the alumina work tube with 35 mm I.D. (Friatec AL23, Germany) and a smaller alumina tube for holding the sample crucible (22 mm I.D.) which was inside the work tube. Temperature was controlled by a Eurotherm PID controller. Temperature in the hot-zone of the furnace was constantly monitored using a calibrated S-type Pt/Pt-10Rh thermocouple (Johnson-Matthey Noble Metals, UK). The EMF of the thermocouple was measured and logged using a Keithley 2000 DMM multimeter (Keithley, USA).

A PT100 resistance thermometer (SKS-Group, Finland) was connected to the Keithley 2010 DMM multimeter for cold junction compensation. Temperature data were logged with LabVIEW software. A cone-shaped quartz crucible (Finnish Special Glass, Finland) was used for holding the slag forming material and the sulphide concentrate. Diameter of the quartz crucible was slightly larger than the diameter of the inner tube. Thus, further upward movement of the crucible was limited, placing it precisely at the hot zone when the crucible was lifted from the bottom of the work tube where it was initially placed. Ice-water mixture was used as quenching medium at the lower end of the work tube, for cooling the samples quickly.
2.3 Procedures

During the experiment, the crucible containing the sample was lifted up quickly by a Pt suspension wire. The contact time started once the sample reached the hot zone set to 1300 °C, and after a precise time interval the reactions were stopped by dropping the sample into the quenching vessel.

To study the reactions and the copper loss mechanism in the settling process, the mixture ratio of Fe/SiO₂ is fixed at 1.67 (w/w) based on industrial practice (Yazawa et al. 1953; Schlesinger et al. 2011; Davenport et al. 2015). In that case, the mass ratio of slag to concentrate was calculated to be 1.1 to meet the 1.67 Fe/SiO₂ ratio in the end slag, if the reactions with the crucible are neglected. In the first series, the experiments were conducted in air with the slag/concentrate ratio of 1.1 (w/w). In the second series, the samples with different slag/concentrate ratios of 1.1, 3, and 9 (w/w) were used in argon atmosphere in order to study the phenomena of copper loss. Each experiment was repeated three times and sufficient number of points and areas were analyzed in every sample to ensure the reproducibility and reliability of the results.

2.4 Analyses

The quenched samples were mounted in epoxy resin, polished by standard wet methods and coated with carbon, and then analyzed by scanning electron microscope (LEO 1450, Carl Zeiss Microscope, Germany) equipped with an Oxford Instrument X-Max 50+ INCA (Oxford Instruments, UK), using energy dispersive X-ray spectroscopy.
3. Results and discussion

The experiments in air were carried out to identify the matte and slag forming reactions in environments like the settler of a FSF. Different mass ratios of iron oxide silica mixture to concentrate were used in experiments under argon atmosphere to study the reactions and the copper loss mechanism between matte and slag phases when the oxygen partial pressure is low, typically between $10^{-7}$ and $10^{-8}$ atm on the slag-metal interface as in the industrial Flash smelting furnace reaction shaft.

3.1 Air atmosphere

Figure 3 presents the chemical concentrations in developing matte and slag phases, as a function of contact time in air. The matte grade increased continuously while its iron concentration was reduced. After 300 s, the matte grade reached a level of around 70 mass% Cu, resembling white metal ($\text{Cu}_2\text{S}$). Only small variations could be seen in the other element concentrations in the slag. The copper content of the slag increased slowly and steadily with increasing time (Figure 3b) again up to about 300 s. This obviously indicated copper transfer to the slag phase through oxidation of cuprous sulfide to copper oxide. Micrographs of samples at different reaction times in air are shown in Figure 4.

As can be seen, the chalcopyrite reacted quickly and molten matte phase was observed clearly in the samples after 10 seconds contact time (Figure 4a). A limited fraction of molten slag formed at 20 seconds time (Figure 4b) while solid magnetite and silica were dominant. At 20 s, the iron concentration was at the level of almost 60 mass% in slag phase (Figure 3b) and then decreased with increasing time. Thus, it can be stated that the slag formation process has started. With increase in time molten fayalite slag gradually formed and later separated from the sulphide matte, resulting in a clear silicate-sulphide interface (Figure 4b-d). Copper veins
(Figure 4d) were observed in samples after 300 s, which were associated with the enrichment of the sulphide matte beyond the Cu$_2$S composition, towards copper-rich and sulphur deficient mattes. The copper veins were also probably associated with cracks formed during the quenching process, as reported by Hidayat et al. 2016.

The reactions between copper concentrate and slag in the settler are complex and multiple reactions happen simultaneously. Based on the experimental data in air and considering that the reaction rate may be limited by mass transfer (Guntoro et al. 2018) the kinetics of accumulating different elements in matte phase can be described as follows:

\[ C = f(t) \]  
\[ \frac{dC}{dt} = \frac{df(t)}{dt} = K \]  
\[ K = k' \cdot A \cdot \Delta C_{\text{concentrate}} = k(C_t - C_0) \]

where \( C \) is the mass concentration of an element in matte; \( C_t \) is the mass concentration of the element in matte at time \( t \); \( C_0 \) is the initial mass concentration of the element in matte phase; \( t \) is time; \( K \) is the reaction rate; \( k' \) mass transfer coefficient; \( A \) interfacial contact area for the mass transfer; \( k \) is apparent mass transfer coefficient (which incorporates interfacial area \( A \)).

Figure 4. Micrograph of selected samples treated in air after different reaction times
showing matte (A) fayalite slag, (B) magnetite, (C) silica (D) and a Cu-rich vein (E).

According to the experimental data and equations [1]-[3], the apparent mass transfer coefficient $k$, can be calculated by

$$ k = \frac{dC}{dt} \left( \frac{C_i - C_o}{C_i} \right) \quad (4) $$

From the experimental data of Figure 3(a), the function $C(t)$ was numerically fitted using exponential functions for copper, iron and sulphur in the matte phase. The $R^2$ values for these were all higher than 0.99 indicating excellent fits. Thereafter the apparent mass transfer coefficients were derived using equations [2] to [4] resulting in equations [5] to [7] shown below:

$$ k_{Cu} = f(C) = \exp(8.864 - 0.521C_i + 0.004C_i^2) \quad (5) $$

$$ k_{Fe} = f(C) = \exp(-6.286 - 0.029C_i + 0.003C_i^2) \quad (6) $$

$$ k_{S} = f(C) = \exp(-2.937 - 0.591C_i + 0.02C_i^2) \quad (7) $$

The $k$ values for these three species in the matte phase through equations [5] to [7] were calculated and plotted in Figure 5 as a function of time and as a function of their concentration in Figure 6 including the actual experimental data points. Figure 6(a) is for Cu, 6(b) is for Fe and 6(c) is for sulphur. The apparent mass transfer coefficient of Cu is higher than those of Fe and S and hence Cu is the most active element while S the least. The reactions were practically completed within 300 s.

![Figure 5. Mass transfer coefficients of Cu, Fe and S in matte phase as a function of time.](image-url)
3.2 Argon atmosphere

Usually the oxygen in the settler area in the flash smelting furnace is limited for the oxygen-consuming reactions in the reaction shaft, so the experiments in argon atmosphere were conducted to study the copper loss phenomenon in the settler, different ratios of slag/concentrate were employed to stand for different oxygen pressure in the settler. To fully oxidize all sulfur in the concentrate to gas SO$_2$ (g), the requirement ratio of O/S (mol/mol) is 2.0. In the experiment under argon atmosphere, the source of the free oxygen is from the Fe$_2$O$_3$ in the concentrate and slag, simulated as the following process:

$$\text{Fe}_2\text{O}_3 = 2\text{FeO} + \frac{1}{2}\text{O}_2(g) \quad (8)$$

The free oxygen and sulfur in different slag/concentrate ratios are calculated in table 3 to show the different oxygen pressure in these experiments.

<table>
<thead>
<tr>
<th>Ratio of Slag/concentrate</th>
<th>Sulfur molar amount in each sample (mol)</th>
<th>Free oxygen molar amount (mol)</th>
<th>Ratio of O/S (mol/mol) in each sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>2.2E-03</td>
<td>1.1E-03</td>
<td>0.5</td>
</tr>
</tbody>
</table>
In that case, the source of the oxygen is the “free oxygen” introduced from the Fe$_2$O$_3$ in the slag and concentrate through the

**Slag/concentrate ratio of 1.1**

The minimum reaction time was 5 minutes; the resulting phase compositions as a function of time are shown in Figure 7. With increasing reaction time, copper content in the matte phase increased slowly while the iron and sulfur concentrations decreased. The reactions were practically completed after 20 min, which is in line with the results of Fagerlund and Jalkanen (2000). The final matte grades achieved in these conditions were not as high as those in the experiments conducted in air. The copper concentration in the molten slag did not vary with the increase of the reaction time.

![Figure 7. Chemical assays of matte (a) and slag (b) as a function of time in argon experiments with slag/concentrate ratio of 1.1 (w/w).](image)

As shown in Figure 8 (a), the matte and slag phases were already formed after 5 minutes,
but the fraction of molten iron silicate slag found at that point was small. After 10 minutes of reaction time, molten matte and slag phases were clearly separated as seen in the micrographs (Figure 8 b).

**Slag/concentrate ratio of 3.0**

With this higher slag/concentrate ratio, the element concentrations as a function of time both in matte and slag phases were similar to results with the slag/concentrate ratio of 1.1. The results are shown in Figures 9 and 10. The matte grade stabilized at around 50 % Cu and can be considered to reach a steady state after 10 minutes of reaction time. The copper content in the formed fayalite slag was still very low and did not change with time. As shown in Figure 10 (a), molten matte and slag phases were formed but they were still dispersed with each other after 5 min reaction time. A clear phase boundary between molten matte and slag was observed after 10 minutes (Figure 10 b).

![Figure 9](image_url)

**Figure 9.** Chemical assays of matte (a) and slag (b) as a function of time in argon experiments with slag/concentrate ratio of 3.0 (w/w).

![Figure 10](image_url)

**Figure 10.** Micrographs of the concentrate-silica-iron oxide samples post different reaction times showing matte (A), fayalite slag (B) and silica (C); argon atmosphere, the slag/concentrate ratio of 3.0.

**Slag/concentrate ratio of 9.0**

Figures 11 and 12 present the experimental results with the slag/concentrate ratio of 9. The
matte grade at about 2.5 mins reached quickly to around 60 % which is approximately 10 % lower than final result in the air atmosphere. No matte phase could be detected in the samples after 10 minutes of reaction time so the mass values of these elements were defined as zero (Figure 11 a). The copper content in the slag increased slightly with time (Figure 11 b). From the results in Figure 12 it can be seen that matte was hard to identify while metallic copper droplets were detected dispersed in the slag phase after 5 min lead time. This indicates that the oxidation ability of the slag (silica-iron oxide mixture) was high enough to oxidize all iron rapidly from the sulphide matte and convert the formed white metal into metallic copper.

Figure 11. Chemical assays of matte (a) and slag (b) as a function of time in argon experiments with slag/concentrate ratio of 9.0 (w/w).

Figure 12. Micrographs of samples after different reaction times in argon atmosphere with the slag/concentrate the ratio of 9.0, showing copper (A), fayalite slag (B), silica (C) and magnetite (D).
The results under argon atmosphere with different slag/concentrate ratios clearly indicated that the copper content in the slag phase increased with increasing slag/concentrate mass ratio in the samples (shown in Figure 13). The initial matte grade (before it disappeared) was also the highest with the highest slag/concentrate mass ratio. In the high slag/concentrate ratios, the sulphide matte disappeared and metallic copper globules formed within the slag phase.

3.3 Slag-matte reactions and copper loss mechanism in the flash smelting settler

3.3.1 Matte and slag formation and phase separation in the settler

When the copper concentrates are introduced into the reaction shaft of the furnace, the particles heat up and ignite rapidly releasing the reaction enthalpy to the gas phase (Ahokainen et al. 2006), which makes the flash smelting possible (Fagerlund et al. 2000). During the process, the thermal decomposition of the chalcopyrite happens first and then the decomposed products, mostly iron and sulphur, are oxidized step by step (Jokilaakso et al. 1995).

In the reaction shaft, the reacted and unreacted particles fall down to the settler, where the matte and slag phases start to form and separate. With the addition of silica flux, all these molten and solid particles mix together and further desulfurization and deironization continues as follows (Schlesinger et al. 2011):

\[
3\text{Fe}_2\text{O}_4(\text{s}) + (\text{FeS})_{(\text{matte})} = 10(\text{FeO})_{\text{slag}} + \text{SO}_2(\text{g}) \quad (9)
\]

\[
2\text{Fe}_2\text{O}_3(\text{s}) + (\text{FeS})_{(\text{matte})} = 7(\text{FeO})_{\text{slag}} + \text{SO}_2(\text{g}) \quad (10)
\]

The formed FeO in reactions [8] and [9] can also react with solid silica to produce fayalite slag according to reaction:

\[
2(\text{FeO})_{\text{slag}} + \text{SiO}_2(\text{s}) = (\text{Fe}_2\text{SiO}_4)_{\text{slag}} \quad (11)
\]
3.3.2 Reactions between slag and concentrate
Fine fractions of the sulphide oxidize further than coarse fractions, and cuprous oxide appears through the oxidation processes. The excessive cuprous oxide in the slag phase would react with matte by equations [12]-[14], resulting in the increase of the matte grade and possible formation of metallic copper (Guntoro et al. 2018).

\[
\begin{align*}
(\text{FeS})_{\text{(matte)}}+(\text{Cu}_2\text{O})_{\text{(slag)}} &= (\text{Cu}_2\text{S})_{\text{(matte)}} + (\text{FeO})_{\text{slag}} \quad (12) \\
(\text{FeS})_{\text{(matte)}}+3(\text{Cu}_2\text{O})_{\text{(slag)}} &= 6[\text{Cu}] + (\text{FeO})_{\text{slag}} + \text{SO}_2(g) \quad (13) \\
(\text{Cu}_2\text{S})_{\text{(matte)}}+2(\text{Cu}_2\text{O})_{\text{(slag)}} &= 6[\text{Cu}] + \text{SO}_2(g) \quad (14)
\end{align*}
\]

During industrial processing, some particles may not react completely and they fall to the settler (Kim and Themelis 1986, Jokilaakso et al. 1991). In that case, the decomposition of these particles takes place in the settler area at a low oxygen pressure, equation [15] (Guntoro et al. 2018). It can be explained by that matte phase formed while little fayalite slag was observed with reacting 5 mins in the argon atmosphere (Figure 8a).

\[
5\text{CuFeS}_2 = \text{Cu}_5\text{FeS}_4 + 4\text{Fe}_{1-x}\text{S} + 4x\text{Fe} + \text{S}_2(g)
\]

With increasing slag/concentrate mass ratio, reaction [16] may occur and the fayalite slag forms more easily. The observations of more fayalite slag at 5 mins in argon atmosphere support this (Figure 8a).

\[
2\text{Cu}_5\text{FeS}_4 + 13\text{S}_2(g) + 4\text{Fe}_3\text{O}_4 = 5(\text{Cu}_2\text{S})_{\text{(matte)}} + 10(\text{FeS})_{\text{(matte)}} + 4\text{FeO} + 6\text{SO}_2(g)
\]

With continuous increase of slag/concentrate mass ratio, reaction [17] may occur which explains the existence of copper metal in the slag phase (Figure 12a).

\[
2\text{Fe}_2\text{O}_3+(\text{Cu}_2\text{S})_{\text{(matte)}} = 2[\text{Cu}] + 4\text{FeO} + \text{SO}_2(g)
\]

All these observations indicate that Fe$^{3+}$ (from Fe$_2$O$_3$ or Fe$_3$O$_4$) in the composite slag can oxidize the copper and iron sulphides in a similar way as gaseous oxygen. Figure 14 describes the reaction mechanism in the flash smelting settler based on the experimental observations of this study.
When concentrate is fed to the shaft, chalcopyrite reacts fast while falling to the settler and consumed out most of the oxygen. Subsequently, the matte and slag phase separate, while some reactions continue. However, some unreacted concentrate may drop into the settler. In that case, the chalcopyrite will decompose and react with the slag phase.

### 3.3.2 Copper loss in the matte-slag reactions

In the flash smelting process, majority copper dissolves in the slag phase by two mechanisms, sulfidic mechanical inclusion loss ($\text{Cu}_2\text{S}$) and oxidic dissolution loss ($\text{Cu}_2\text{O}$) (Genevski et al. 2008). When the matte grade reaches 70%, copper in slag phase is predominantly caused by the oxidic dissolution, rather than the sulfidic dissolution (Mackey 1982).

Combining the results of Figure 3b, 7b, 9b and 11b, copper content in the slag is dependent on the oxidation ability of the atmosphere and the slag in contact with the sulphide matte. Micrographs in different experimental conditions at same reaction time were chosen to verify the influence of oxygen potential to the copper loss phenomena, shown in the micrographs of Figure 15. Scattered copper metal droplets were observed in air, dispersing randomly in the slag phase in Figure 15 (a). In the experiments in argon atmosphere, the copper metal droplets could only be observed with the slag/concentrate ratio of 9 (Figure 15 d). No metallic copper or matte was found in the molten slag phase with the slag/concentrate ratio of 1.1 (Figure 15 b), while some matte droplets were formed in slag with the slag/concentrate mass ratio of 3
because of the mechanical inclusion.

Figure 15. Micrographs of copper domains present in slag phase: (a) air atmosphere (t=300 s), (b) argon atmosphere, mix ratio of 1.1, (c) argon atmosphere, mix ratio of 3.0, (d) argon atmosphere mix ratio of 9.0: (A) metallic copper, (B) matte, (C) fayalite slag, (D) silica, (E) magnetite and (F) Cu-rich vein in sulphide matte

Therefore, the results from the experiments reported here suggest that the mechanism of copper losses during flash smelting settling process could be concluded as follows.

(a) In the flash smelting settler, matte droplets enter into the slag phase from the reaction shaft, and may further be oxidized by the slag phase.

(b) If oxygen still exist in the settler area, the oxygen will be dissolved in the slag phase through reaction [18] and then react with the matte droplets through reaction [17], forming metallic copper.

\[ 2(\text{FeO})_{\text{slag}} + \frac{1}{2} \text{O}_2(\text{g}) = (\text{Fe}_2\text{O}_3)_{\text{slag}} \]  

(c) Without oxygen in the atmosphere, the matte droplets can also react with Fe$_2$O$_3$, Fe$_3$O$_4$ or other oxidizing substances similar to reaction [17].

In the industrial process, oxygen amount near the boundary between the matte droplets and slag phase in the settler is usually limited, but after cooling down the slag, the dissolved copper in the slag is mainly as metallic or sulphidic (Wang 1991). It implies the occurrence of these reactions between the matte droplets and Fe$_2$O$_3$, Fe$_3$O$_4$ or other oxidizing substances in the slag phase. The experimental results in this study support this.
4. Conclusions

The matte-slag forming reactions of chalcopyrite concentrate and synthetic solid iron-oxide-silica slag were studied as a function of time at a typical smelting temperature of 1300°C both in air and under an argon atmosphere.

The matte-slag forming reactions between chalcopyrite concentrate and synthetic solid iron-oxide-silica slag at a typical smelting temperature of 1300°C in air atmosphere were completed in few minutes, and the reaction mechanism in the FSF settler was concluded to be mass transfer controlled. The results in argon atmosphere suggest that the separation of matte and slag phases is enhanced by increasing the slag content. However, increasing of slag-to-concentrate ratio ferric oxide completely oxidates sulfur in the matte droplets and metallic copper inclusions form in the slag. Therefore, the copper losses in the slag are caused by the oxidation of cuprous sulfide due to oxygen in air and ferric ions in the slag.

It can further be concluded that the matte and slag forming reactions are so fast that in an industrial FSF settler the limiting step for efficient matte settling through the slag layer is dominated by fluid dynamics (with slag properties like viscosity) and solid particles presence in the slag, such as spinels or magnetite (Bellemans et al. 2018). It seems also evident that the slag/concentrate ratio and thickness of the slag layer are very important factors in controlling chemically dissolved copper in the slag.

In the future, with the rise of the circular economy and recycling requirements, the secondary feed materials behavior and impact on slag properties (viscosity) and slag – matte interaction (such as immiscibility and interfacial energy) bring along a great need for continuous research in material properties of metallurgical slags in general and in ways to improve slag fluidity and settling conditions in all kinds of slag – matte/metal separation cases.

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Disclosure statement

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