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## COPPER MATTE – SLAG REACTION SEQUENCES AND SEPARATION PROCESSES IN MATTE SMELTING

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#### Abstract

While particle combustion and chalcopyrite oxidation in suspension smelting is well understood, few studies are available regarding the melt-melt reactions and the separation between copper matte and slag in matte smelting. In the present work, experimental investigations in air and argon atmosphere were conducted using a mixture of synthetic slag and chalcopyrite concentrate. The sequential reaction and separation processes occurring in matte smelting are outlined. Possible limiting factors in the overall process are also proposed. The result of the present work forms an important foundation for future work in the kinetic rate formulation of molten phase reactions between copper matte and slag in matte smelting.

Keywords: Melt-melt reactions; Molten phase reactions; Matte; Flash smelting

#### 1. Introduction 1.1 Background

One key target of circular economy is to develop industrial processes toward closed operations where all the material streams are treated inside the process plant and only the finished product(s) exits the process. To achieve such status, it is crucial to gain knowledge of the behavior of elements present in the process, so that their removal can be arranged without emissions and waste streams.

The behavior of these elements can be evaluated using a process model with coupled transport phenomena and reaction kinetics. Besides the information regarding physical phenomena occurring, formulation of such a model would require both kinetic and thermodynamic information of the system. Such data can be acquired through experimental methods and computational calculation.

Thermodynamics of copper matte-slag system have been widely studied and its phase equilibrium has been constructed [1-4]. Some recent studies [2, 5-6] have also included additional components that are often present in industrial smelting, such as CaO, MgO, and  $Al_2O_3$ . Distributions of minor elements (Ag, Au, Pb, Sb, As, Zn, Pd, Pt, and Rh) in copper matte-slag system have also been extensively studied [5, 7-10].

The kinetics of matte smelting can be divided into two major parts: oxidation of chalcopyrite into matte and the subsequent slag formation reactions and

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interactions between the matte and slag. The oxidation of chalcopyrite into matte can be categorized as a series of gas-solid reactions, and its kinetics have been studied on a laboratory scale [11-17], as well as modelled using computational fluid dynamics software [18-21].

Few attempts only have been made to study the melt-melt reactions between matte and slag. Such reactions are critical in determining the final matte grade, as they promote transfer of elements between the two phases. Only Fagerlund and Jalkanen [22] have attempted to elaborate the sequences proceeding in matte-slag reactions and separation processes.

Before proceeding to any kinetic rate equations, a comprehensive understanding regarding the reaction sequences and the physical processes involved in matte-slag system is required. Due to the rapid and aggressive nature of the melt-melt reactions, experimental investigation of such system often possesses challenges. In the present work, a mixture of copper concentrate and synthetic slag was contacted at 1300°C, and quenched after short time intervals. With this technique, the sequences and reaction paths occurring between reacting concentrate, flux, matte, and slag can be evaluated.

#### 1.2 Copper Matte-Slag Interactions in Flash Smelting

In general, copper matte smelting can be described using the following overall reaction



 $CuFeS_{2(s)} + O_{2(g)} \rightarrow (Cu, Fe, S)_{(matte)} + FeO_{(slag)} + SO_{2(g)} \quad (1)$ 

The process utilizes an oxidizing agent, such as air or oxygen gas, to oxidize iron sulfide into iron oxides in the form of slag, leaving behind a matte phase with a high concentration of copper. Silica is used in matte smelting to form molten iron-silicate slag with the iron oxides produced in Reaction 1:

$$FeO_{(slag)} + SiO_{2(s)} \rightarrow FeO - SiO_{2(slag)}$$
 (2)

Reactions 1 and 2 are the basic processes involved in matte smelting of copper sulfide concentrates.

Reaction 1 is initiated in flash smelting process by contacting concentrate particles with oxygen and a silicate flux at temperatures ranging from  $800 - 1300^{\circ}$ C. Fine sulphide particles heat and ignite almost instantaneously, making fast reactions possible. Although the suspension is relatively lean, some particle-particle (or droplets) collisions are also assumed to take place in flight in the reaction shaft [11, 12].

Kim [23] as well as Ahokainen and Jokilaakso [18] have applied the shrinking core concept in their model of chalcopyrite oxidation in gas-solid suspensions. The chemical process sequence can be generally divided into three stages:

(a) Thermal decomposition of chalcopyrite during the heat-up of the particles and the dissociation of the labile sulfur to atmosphere. The actual mechanism and stoichiometry of the decomposition is complicated and not known in full details, but the final products can be assumed as bornite, pyrrhotite, free metallic iron, as well as mono-atomic sulfur gas [23] as shown in reaction:

$$5CuFeS_2 \longrightarrow Cu_5FeS_4 + 4Fe_{(1-x)}S + 4Fe + 2S_{(g)}$$
 (3)

(b) Oxidation of the diffused (mono-atomic) gaseous sulfur from Reaction 3 inside the particles and in the gas phase into sulfur dioxide in a highly exothermic reaction:

$$S_{(g)} + O_{2(g)} \longleftrightarrow SO_{2(g)}$$
 (4)

Due to the exothermic nature of Reaction 4, particle temperature raises at this stage by the combustion products. According to the shrinking core model, Reaction 4 occurs initially in the particle-gas interface. As it progresses, this reaction interface moves inward towards the core of the particle.

(c) Oxidation of decomposed sulfide product from Reaction 3, described in the following reactions:

$$3Fe + 2O_2 \xrightarrow{} Fe_3O_4$$
 (5)

$$3FeS + 5O_2 \longleftrightarrow Fe_3O_4 + 3SO_{2(g)} \tag{6}$$

$$2Cu_5FeS_4 + O_2 \underbrace{\longrightarrow} 5Cu_2S + 2FeS + SO_{2(g)} \tag{7}$$

Reaction 6 occurs on particle surfaces. Molten

sulphide droplets are formed in Reaction 7, with composition of the melt depending on the rates of Reactions 5 - 7 and, thus, the availability of oxygen. Furthermore, the sulfide compounds formed in Reaction 7 can be oxidized further into oxides through reactions:

$$Cu_2S + 1.5O_2 \longrightarrow Cu_2O + SO_{2(g)} \tag{8}$$

$$FeS + 1.5O_2 \longrightarrow FeO + SO_{2(g)}$$
 (9)

As sulfides generally have lower melting temperature than oxides, the particle is observed to have a molten sulfide core, with a solid oxide crust on the outer surface of typically  $Fe_3O_4$  [13]. The  $SO_2$  gas formed within the molten core will result at a later stage in the detachment of the inner molten particle core from the solid oxide crust and fragmentation of molten droplets. Kim [23] as well as Jokilaakso et al. [13] have reported how larger particles will fragment into smaller due to the explosive discharge caused by the pressure exerted by the molten sulfidic core to the outside solid oxide crust of the particles.

The fragmented molten droplets (matte), as well as smaller particles from the oxidation of chalcopyrite will fall downward to settler of the smelting furnace, where the matte-slag reactions and separation processes take place. A study by Juusela [24] has reported that these reactions take place in a reaction layer just beneath the reaction shaft, where the separation of slag and matte is also initiated [25].

Sulfur and iron from Reaction 7 will be preferentially oxidized. Magnetite, asides from the one formed in Reactions 5 and 6 at the earlier stage, will be formed as well from precipitation of some part of the iron oxides that are insoluble in the molten sulfide (matte) phase.

All these solid and molten products will be mixed together in the settler, alongside with the silica flux that has been added. Further desulfurization and deironization reactions will occur, mainly through excess magnetite reduction and fayalite slag formation in the following possible reactions [22]

$$3Fe_3O_{4(s)} + FeS_{(matte)} \longrightarrow 10FeO_{(slag)} + SO_{2(g)}$$
 (10)

Copper sulphide will be oxidized in later stages of the process to metal by gaseous oxygen or ferric oxide

$$CuS_{(l)} + 2O_2(g) \rightleftharpoons 2Cu_{(metal)} + SO_{2(g)}$$
(11)

At some stage, sulphur in matte is also depleted as

$$4FeO_{(1.5)} + S_{(matte)} \longrightarrow 4FeO_{(slag)} + SO_{2(g)}$$
(12)

As the reactions in the settler take place in the forming matte-slag mixture, the pressure of SO<sub>2</sub> must be  $p_{SO2} \ge p(atm)$  for the Reactions 10-12 to proceed [25].

The ability of magnetite to be reduced is affected



by the ferrous sulfide content in the matte; as long as excess ferrous sulfide is present in the matte, Reaction 10 would proceed to eliminate excess magnetite presents in the system [22]. Reaction 12 is of critical importance if the sulfur activity in the forming matte is high [22]. The FeO from Reactions 10 and 12 also reacts with solid silica to produce fayalite slag through Reaction 2. Such reactions to produce fayalite slag could also be represented in the following overall reaction

$$3Fe_3O_{4(s)} + FeS_{(matte)} + 5SiO_2 \longrightarrow 5Fe_2SiO_{4(slag)} + SO_{2(g)}(13)$$

Reactions 10 - 13 will continue to remove iron sulfide from the matte phase, increasing copper content (matte grade) as well as forming more slag in the processing vessel. As the slag is formed, the matte will start to coagulate by surface forces, once its droplet size reaches a high enough value, and settle through the slag layer due to density difference.

During the settling process, there is a possibility that the matte droplets are mechanically entrained in the slag due to several factors, such as gas bubbles [26] and sticking to solids [27]. Another possibility of copper losses is the chemical dissolution of copper [8, 28], in which the sulfidic copper in matte is oxidized to slag as cuprous oxide through Reaction 8.

With the excessive cuprous oxide in the slag from Reaction 8, further interactions between matte and slag are possible in local inhomogeneity, as follows [22]:

$$FeS_{(matte)} + Cu_2O_{(slag)} + 0.5SiO_{2(s)} \overleftrightarrow{Cu_2S_{(matte)}} + 0.5Fe_5SiO_{4(slag)}$$
(14)

$$FeS_{(matte)} + 3Cu_2O_{(slag)} + 0.5SiO_{2(s)} \longrightarrow 6Cu_{(l)}$$

$$+ 0.5Fe_2SiO_{4(slag)} + SO_{2(g)}$$
 (15)

$$Cu_2 S_{(matte)} + 2Cu_2 O_{(slag)} \longleftrightarrow 6Cu_{(l)} + SO_{2(g)} \tag{16}$$

Reactions 14, 15, and 16 are generally raising the matte grade, as well as forming additional metallic copper at copper saturation in white metal. The absence of oxygen in the atmosphere would limit the oxidation reactions so that copper sulphide would not be further oxidized to cuprous oxide through Reaction 8. The only oxidising agent is the slag, and as the oxidation capacity of the slag is exhausted, there would be no more oxidation reactions taking place. Two important factors must be considered, the slag oxygen potential as well as diffusivity of oxygen ions in the slag. The slag oxygen potential is mainly controlled by the Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio [29], whereas its physical properties would affect the diffusivity of oxygen ions in the slag.

## 1.3 Thermodynamics of Copper Matte-Slag Interactions in Flash Smelting

Thermodynamically, the matte-slag reactions in the smelting process are best described through the phase diagram by Yazawa and Kameda [30], shown in Fig. 1.



Figure 1. A constrained phase diagram section of the FeQ<sub>2</sub>-FeS-SiO<sub>2</sub> system at 1200 °C showing how the addition of SiO<sub>2</sub> creates a miscibility gap between oxide melt (slag, 'OXIDE LIQUID') and sulfide melt (matte, 'LIQUID') between FeS concentrations of  $\approx 40$  wt% and 68 wt%; MTDATA calculation using Mtox database vers. 8.2 [31]. The terminal phases in corners of the triangle were stoichiometric FeS, SiO<sub>2</sub>, and FeO with 5.5 wt% Fe<sub>2</sub>O<sub>3</sub>

In relation to the presence of copper in the system, Hidayat et al. [3] have studied the equilibrium of the Cu-Fe-O-Si-S system under atmospheric condition. His study concluded the stabile phases found in equilibrium of the system at 1200 °C, which consists of oxide phases such as tridymite, cuprite, and spinel, as a result of the sulphide phases oxidation in Reactions 8-9. This is illustrated in phase diagram in Fig. 2.



Figure 2. Quasiternary liquidus diagram of the Cu<sub>2</sub>O-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system in equilibrium with air  $P(O_3)$ = 0.2 atm at 1100-1250 °C. Primary phases in the liquidus equilibria are tridymite (SiO<sub>2</sub>), cuprite (Cu<sub>2</sub>O), and spinel ('magnetite', Fe<sub>3</sub>O<sub>4</sub>). Delafossite (CuFeO<sub>2</sub>) stabilizes as a primary phase at lower temperatures; MTDATA software using Mtox database [32]



## 2. Experimental 2.1 Materials

Two primary materials were used in this experiment: a synthetic slag and a chalcopyrite copper concentrate. Fused quartz was used as the crucible material to contain the sample mixture.

#### 2.2 Slag

Slag was synthesized using a mixture of hematite powder (Alfa Aesar, 99.99% purity) and silica powder (Umicore, 99.99% purity). The mixture was prepared using mass ratio of 65%  $Fe_2O_3$  and 35%  $SiO_2$ , then heated at 1300°C in air atmosphere for 8 hours so that it would reach equilibrium. This equilibrium is illustrated in the phase diagram shown in Fig. 3 and 4.



Figure 3. Calculated phase diagram of the system  $Fe_2O_3$ -SiO<sub>2</sub> in total pressure of 0.2 atm  $O_2(g)$ . At 1300°C, both terminal phases are still in the solid state; MTDATA software with Mtox database



**Figure 4**. Calculated phase diagram of the system Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> in total pressure of 0.2 atm O<sub>2</sub>(g). At 1300°C, both terminal phases are still in the solid state; MTDATA software with Mtox database

Fig. 3 is not a true binary phase diagram; it is actually a constrained ternary section along the constant  $P_{O2}$  line of  $p_{(O2)} = 0.2$  atm from the ternary phase diagram shown in Fig 4. This means that while the molar ratio of SiO<sub>2</sub> / (Fe<sub>2</sub>O<sub>3</sub> + SiO<sub>2</sub>) is defined, the overall composition of these phases (SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>) in the whole Fe-Si-O system is not known, because other iron-oxide substances, such as Fe<sub>3</sub>O<sub>4</sub> and trivalent iron oxide (FeO<sub>1.5</sub>), also appeared after the system reached equilibrium.

It was expected that in contact with the sulfide phase (matte) from the concentrate, this solid synthetic slag (iron oxides and silica) would form a liquid fayalite slag phase (Reactions 10 and 2) which is immiscible with matte [30]. The reactions between these two liquid phases were evaluated in the present work.

#### 2.3 Concentrate

The industrial copper concentrate powder was obtained from Outotec Research Centre in Pori, Finland. Chemical analysis of this concentrate is given in Table I, while its mineralogy is given in Table II. Chemical analysis were done by using ICP-OES (Inductively coupled plasma atomic emission spectroscopy) + titration (Cu) or 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. Mineralogical composition was calculated from the chemical and SEM-EDS+WDS (Scanning Electron Microscopy, Energy-dispersive X-ray spectroscopy) and XRD analyses (X-ray Diffraction).

#### 2.4 Feed Mixture

The feed was prepared so that the SiO<sub>2</sub>/Fe ratio of the mixture could represent that ratio of industrial flash smelting furnace [33-34]. In the present work, this ratio was calculated to be 0.6, which was kept constant for all the experiments. According to Yazawa and Kameda [30], a system with such ratio would be over-saturated with silica. This means that in equilibrium, two liquids (matte and slag) and silica solid would be found in the system. This is to ensure matte and slag in the mixtures could effectively be separated during contacting at a high temperature. Nevertheless, the use of quartz crucible means that the system will be over-saturated with silica in equilibrium conditions, as quartz (silica) crucible can also react with the sample.

#### 2.5 Experimental Method

The experimental device used in this work is shown in Figs. 5(A) and 5(B). A vertical tube furnace



Table 1. Chemical Composition of the Concentrate (wt%)																	
Cu	Fe	Zn	Mo	Mn	Со	Ni	As	Sb	Pb	Bi	Na	Mg	Al	K	S	Ag	Au

27 27.2 0.18 0.27 0.008 0.014 <0.005 <0.005 <0.005 <0.005 <0.005 0.15 0.17 0.78 0.29 29.8 71 ppm 2.24 ppm

Mineral composition						
Chalcopyrite	%	78				
Pyrite	%	4.3				
Quartz	%	7.9				
Feldspar	%	3.5				
Muscovite	%	1.2				
Hematite	%	1.6				
Dolomite	%	1.4				

Table 2. Main Minerals of the Concentrate (wt%)



Figure 5. (A) The experimental arrangement used in the present work. The green circle represents the space and isothermal zone where the crucible and sample are located. (B) A close up of the sample and crucible area in the furnace (shown as green circle in Fig.5 (A)). This arrangement makes the whole crucible to be located within the furnace hot zone

in Fig. 5(A) (Lenton LTF 16/450) was equipped with four silicon carbide (SiC) heating elements. An alumina working tube with 35 mm inner diameter (Friedrichsfeld AL23, Germany) was placed inside the furnace. Then, a smaller alumina tube (22 mm inner diameter) for guiding the sample was inserted inside the working tube which, for the sake of simplicity, will be referred to as the inner tube in the present work. Both tubes were connected to a metal head equipped with two small holes, enabling the insertion of thermocouple in protective alumina sheath (Friatec Keramik, Germany) and a Pt suspension wire. The thermocouple tube placement relative to the sample crucible is shown in Fig. 5(B). The furnace heads were also equipped with water cooling system. Temperature of the furnace was controlled using a Eurotherm PID controller. In addition, 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 output voltage of the thermocouple was measured with a Keithley 2000 DMM multimeter (Keithley, USA). A PT100 resistance thermometer (SKS-Group, Finland) was connected to a Keithley 2010 DMM multimeter as a cold junction compensation. Temperature data was logged with a Labview software. The quenching vessel was filled with ice water.

A cone shape quartz crucible (Finnish Special Glass, Finland) was chosen so that materials would accumulate in the bottom of the cone and the contact between materials could be enhanced. The cone crucible dimensions are shown in Fig. 5(B), with its diameter being the same as the inner guidance tube, so that it could not be lifted further upwards after reaching lower end of the inner tube.

Prior to the experiments, temperature profile of the furnace was measured, and the furnace hot zone, where the temperature of the furnace reached the highest stable value, was confirmed to extend 40 mm above the horizontal centre line of the furnace (shown in Fig. 5(B)). As the inner tube position is fixed against the furnace, it was concluded that the whole body of the sample should be in the hot zone whenever the crucible reached the lower end of the inner tube. In the experiments, the crucible with the sample was lifted upward using the Pt suspension wire. The moment when the crucible reached the hotzone was recorded as the zero-time of the reactions. Both air and inert atmospheres were employed in the present work, so that the effect of oxygen in the atmosphere could be evaluated. Vertical crosssections of the quenched samples were taken and



mounted in epoxy resin for analysis, which was done with a LEO 1450 (Carl Zeiss Microscope GmbH, Germany) Scanning Electron Microscope (SEM) equipped with an Oxford Instrument X-Max 50 + INCA energy dispersive X-ray spectroscopy (EDS) analyser (Oxford Instruments plc, UK).

#### 3. Results 3.1 Air Atmosphere Experiments

In equilibrium with air atmosphere, matte (sulphides) is unstable and will be oxidized into cuprite and spinels, as shown by the phase diagram in Fig.2. In order to observe the matte in the system, the experiments were done in short time intervals, as it was expected that due to the aggressive nature of the melt-melt reaction, matte might be oxidized within just a short period of time. Micrographs obtained from experiments conducted under air for 20, 30, 60 and 300 seconds are shown in Figs. 6A-D.

Micrographs in Fig. 6A-D provide the ideas regarding reaction sequences and separation processes prevailing in the matte-slag interactions. In

Fig. 6(A), after just 20 s of contact, matte was already produced through chalcopyrite oxidation at high temperature. Accurate temperature of the samplecrucible system is difficult to estimate. Bornite  $(Cu_5FeS_4)$ , as an intermediate product according to Reaction 3, was not observed, while matte from Reaction 7 was observed. This suggested that after 20 seconds, bornite was already consumed by Reaction 7, so that none was anymore observed in the sample. The observation of magnetite (Fe<sub>3</sub>O<sub>4</sub>) after 20 s indicates the progression of Reactions 5 and 6. Liquid fayalite slag was hardly observed in the sample, suggesting that the slag forming reactions between solid iron oxides and silica (Reaction 8, 9 and 2) progressed rather slowly.

All observations after 20 s suggest that the system is at the last stage of chalcopyrite oxidation, moving thus towards the subsequent slag forming stage. The matte in the sample was also quite randomly distributed, indicating that the coagulation and settling of the matte have not taken place in this stage of the reaction path.





Figure 6. SEM micrographs from contacting synthetic slag and concentrate sample at 1300 °C in air for different time intervals. (A) 20 s (B) 30 s (C) 60 s and (D) 300 s, showing (1) matte (2) magnetite (3) silica (4) fayalite slag (5) Cu-rich vein (6) Cu-rich Cu-Fe oxide (7) Fe-rich Cu-Fe oxide; matte was no longer observed after 300 s (5 minutes), due to the intensive oxidation by the surrounding atmosphere



considerable, indicating initialization and further progress of slag forming reactions. As soon as the fraction of slag has increased, matte began to coagulate and separate from the slag. This is shown as the matte has grown together into larger phase domains, compared to the rather randomly distributed matte droplets after 20 s. Segregated magnetite was also observed in matte, which is thought to precipitate as it is insoluble in solid matte phase. Cu-rich veins associated with the cracks formed during quenching of the sample [3]. This phenomenon is quite well known, as matte is difficult to quench to microcrystalline phase without precipitates [35].

As seen in Fig. 6(D), after 300 seconds (5 minutes), no matte was anymore observed in the sample. All sulfides had been oxidized into their respective oxides. Schlesinger [33] stated that substantial oxidation of  $Cu_2S$  (Reaction 11) would only start when the Fe content in the matte is lower than 1%. Therefore, it could be concluded that iron content in the matte should have been lower than 1% even before 5 minutes, allowing  $Cu_2S$  to be oxidized completely after 5 minutes.

Since in these experiments oxygen was constantly available in the atmosphere, the oxidation of  $Cu_2S$  was taking place continuously to metal and further to oxide until none was left. This is also why no metallic copper was observed, as copper sulfides had been over-oxidized into cuprous oxide. Furthermore, with matte being oxidized quickly into oxides, interactions and reactions between matte and cuprous oxide (Reactions 13 - 15) were also not observed.

## 3.2 Inert Atmosphere Experiments

Some of the micrographs obtained from experiments conducted in the inert atmosphere are shown in Fig. 7A-D.

Comparing Fig. 6(A) and 7(A), it can be seen that magnetite particles were not observed in the matteslag contact in inert atmosphere. This result suggests that while matte formation (Reactions 3 and 7) took place rapidly both in air and in inert atmosphere, magnetite formation (reactions 5 and 6) was severely limited in inert atmosphere due to the shortage of



Figure 7. SEM micrographs from contacting synthetic slag and concentrate sample at 1300 °C under inert atmosphere in different time intervals. (A) 20 s (B) 60 s (C) 300 s and (D) 2400 s, showing (1) matte (2) fayalite slag (3) silica solid (4) a Cu-rich vein; matte was still observed after 2400 s (40 minutes), due to the limited oxygen availability in the system



oxygen. Since, in Fig. 6(A) after just 20 s, magnetite was already observed, this suggested that both reactions [5] and [6] are inherently rapid, as both reactions proceeded with ease under normal air atmosphere. As gaseous oxygen was absent under inert atmosphere, oxygen needed for reactions [5] and [6] was provided by the slag. This involved mass transport of oxygen ions from the bulk slag to the reaction interface, which may potentially limit the magnetite forming reactions, even though it was concluded earlier that these reactions are inherently rapid in air atmosphere.

As shown in Fig. 7(A), fayalite slag was observed in inert atmosphere, while no magnetite was observed in the sample. The absence of magnetite suggested that reactions 5 and 6 did not take place due to the limited oxygen in the system. However, it is also worth noting that hematite was already present in the system in the form of synthetic slag. The slag formed in the inert atmosphere experiments (especially in the shorter time intervals) may be originated from the melting of the synthetic slag, instead of from the deironization of the matte (Reaction 10).

The hematite in the synthetic slag could explain the presence of magnetite in Fig 6(A). The synthetic slag was rapidly molten to form fayalite slag, while reactions between magnetite and matte followed to form additional slag. As "free silica" from the mixture is available readily, these silica solids would be reacted first to form fayalite slag, followed by the silica dissolution from the crucible. In order for the silica crucible to react, mass transport from the crucible to reaction interface must proceed. This mass transport is relatively slower than chemical reactions, leading to unreacted magnetite after short time intervals. While magnetite could react with ferrous sulfide in the matte (Reaction 10) to form FeO, the key substance is still silica. If silica is not available in the reaction interface, the resulting FeO can be oxidized (by air) to form magnetite; only if silica is available in the reaction interface then fayalite slag could be formed.

Similarly to the reactions under air, after liquid slag was formed in inert atmosphere, matte began to coagulate and form droplets. The separation of matte and slag began to proceed as well. The difference between the two cases is that in air atmosphere, matte is unstable, and would be oxidized into cuprous oxide through Reaction 8. This is in agreement with phase diagram in Fig 2, where matte is not found at equilibrium stage. In inert atmosphere, matte is stable, as even after 2400 s (40 minutes) sulfide was still observed in the sample.

# 3.2 Time dependent behavior of Cu, Fe, S in Matte

The time-dependent behavior of these elements in the matte was analyzed using SEM-EDS techniques,

so that the progression of the matte-slag reactions can be visualized and evaluated quantitatively. The obtained EDS results as a function of reaction time are shown in Fig. 8. The fundamentally different reaction environments of air and inert gas atmosphere are clearly observed when considering the matte grade and its sulfur concentration as a function of reaction time.

In air, due to the excessive availability of oxygen, the oxidation reaction would proceed until all the major elements are in their most stable oxidation state. Figure 8(A) shows that the Cu content in matte is increasing due to preferred oxidation of Fe and S from matte (leading to decrease of Fe and S contents in the matte). Iron decreased rapidly in the early stages while sulfur was still stable. Then after 1 minute sulfur content of matte started to decrease as well. This suggested that deironization of matte in the droplets would proceed first through Reaction 5 followed by a further deironization and desulfurization of matte through parallel Reactions 6 and 10. Afterwards, copper sulphide in the matte started to be oxidized to the slag, further decreasing the sulphur content in the matte.

After 150 s, the copper content in the matte was high, close to white metal. It was expected that after this point, the oxidation of Cu would start, as there was not much Fe and S left in the matte phase. The micrograph in Fig. 6(D) revealed that after 300 s (5 minutes) there was no matte in the sample; it had all been oxidized into copper and iron oxides. This finding also indicates that oxygen gas diffusion into reaction interface would not be the rate limiting step, as the oxidation reactions proceeded with ease without any forced draft of air.

Fig 8(B) provided one additional idea regarding slag formation in the inert atmosphere. The slow decrease in iron and sulphide in the matte suggested that the fayalite slag found in the shorter time intervals (below 60 seconds) most likely originated from the synthetic slag, rather than from the deironization reaction (Reactions 10, 2, and 13). The iron and sulphur contents in the matte decreased afterwards, confirming the following deironization and slag forming reactions. Since FeO was not observed in the inert atmosphere samples, it is suggested that the two step slag formations (Reaction 10 followed by Reaction 2) did not take place. Further studies are required to correctly identify the reaction sequences leading to fayalite slag formations in absence of atmospheric oxygen.

Figure 8(B) also shows that in inert atmosphere the assay of the matte was essentially stabilized after 10 minutes, similar to the 15 minutes found by Fagerlund & Jalkanen [22]. This means that after this period, oxidation reactions and separation process between matte-slag under inert atmosphere had ceased.



Figure 8. EDS of matte phases under (A) air atmosphere and (B) inert argon atmosphere, with trendlines. The behavior of Cu, Fe, S in matte as a function of time could be inferred from these results

#### 4. Discussion

The solid and liquid compounds found in the sample are presented in Table 3. Since no gas analyser was installed in the experimental apparatus,  $SO_2$  gases were not able to be captured in the experiment. Based on findings in Table 3 and Fig.8, the results suggest that the following steps and reaction sequences take place in the copper matte smelting:

1. Chalcopyrite in the concentrate is oxidized by the available oxygen in the atmosphere into matte and  $SO_2$  gas through Reactions 3, 4 and 7. Bornite  $(Cu_5FeS_4)$  as an intermediate from oxidation of chalcopyrite (Reaction 3) was not found in the sample, indicating that all stages of chalcopyrite oxidation proceed rapidly so that no intermediate substances are found. In inert atmospheres, chalcopyrite oxidation proceed through the overall reaction with the slag and its three-valent iron oxides:

$$2CuFeS_2 + 4FeO_{(1.5)} \longrightarrow Cu_2S + 2FeS + 4FeO + SO_2 \quad (17)$$

Table 3. Solid and	l liquid	compounds	found	in	the	samples
and some	notes					

Time	Air Atmosphere	Inert Atmosphere
10-20 seconds	Cu <sub>2</sub> S-FeS (matte), Fe <sub>3</sub> O <sub>4</sub> , Fe <sub>2</sub> SiO <sub>4</sub> (slag), SiO <sub>2</sub> notes: matte is still randomly distributed, while not much fayalite slag was observed	$Cu_2S$ -FeS (matte), Fe $_2SiO_4$ (slag), SiO $_2$
30-60 seconds	Cu <sub>2</sub> S-FeS (matte), Fe <sub>3</sub> O <sub>4</sub> , Fe <sub>2</sub> SiO <sub>4</sub> (slag), SiO <sub>2</sub> , notes: matte was isolated from slag, magnetite existed only in small amount, and white metal was observed in some parts of the matte	Cu <sub>2</sub> S-FeS (matte), Fe <sub>2</sub> SiO <sub>4</sub> (slag), SiO <sub>2</sub> notes: droplets of matte were observed
5 minutes	copper-iron oxides, SiO <sub>2</sub> notes: no sulphide compounds were observed	$\begin{array}{c} Cu_2S\text{-}FeS \text{ (matte),}\\ Fe_2SiO_4 \text{ (slag), }SiO_2\\ notes: matte was\\ isolated from slag \end{array}$
10 -20 minutes		$Cu_2S$ -FeS (matte), Fe <sub>2</sub> SiO <sub>4</sub> (slag), SiO <sub>2</sub>
40 - 60 minutes		Cu <sub>2</sub> S-FeS (matte), Fe <sub>2</sub> SiO <sub>4</sub> (slag), SiO <sub>2</sub> notes : SiO <sub>2</sub> resembled the tridymite shape

The oxygen in Reaction 17 in inert atmospheres is released from the oxidizing fayalite slag in the system. Under air atmosphere oxygen partial pressure and gas diffusion would play an important role, while in inert atmosphere, oxygen potential of slag and mass transport in it would be the key factors in this stage. Nevertheless, it was concluded by Figure 6(A) and 7(A) that decomposition and oxidation of copper concentrate's chalcopyrite to form matte takes place rapidly in both air and inert atmospheres.

2. In air atmosphere, the oxidation of chalcopyrite is closely followed by magnetite formation (Reactions 5 and 6) as well as deironization of matte and slag formation. This stage can be seen in Fig 8(A) where iron content in the matte decreased rapidly at 30-60 s, while sulfur content was relatively constant at this period, suggesting the preference of Reaction 5 over Reaction 6. In inert atmosphere, with the absence of air, magnetite formation is limited, as shown by the slow decrease of iron content in matte in Fig. 8(B). It is thought that after the oxidation of chalcopyrite, the slag oxygen pressure in the reaction interface between matte and slag is lowered, therefore limiting further oxidation of iron sulfide in the matte into iron oxides. Further oxidation would rely upon mass transport of oxygen from the bulk slag phase into the reaction



interface, which could potentially limit iron oxide forming reactions.

3. Iron oxides react with silica to form iron silicate slag through further deironization and desulfurization reactions of FeS in the matte (Reactions 10, 2 and 13). Reaction 13 is the overall reaction in this stage, as the resulting slag in the sample had chemical composition close to fayalite (Fe<sub>2</sub>SiO<sub>4</sub>). However, it was also thought that fayalite slag could be formed through oxidation of FeS in matte into FeO by Fe<sub>2</sub>O<sub>4</sub> (Reaction 10), followed by reaction between FeO and SiO<sub>2</sub> to form fayalite slag (reaction [2]). The micrograph (A) in Fig. 6 indicates that this slag forming step proceeds relatively slower than the chalcopyrite oxidation and magnetite, leaving behind unreacted magnetite. This is mostly due to the fact that the slag forming step involves reactions between solid and liquid species (solid magnetite, iron sulfide in matte, silica, iron oxide), therefore making mass transport limitations apparent. Further studies are needed to analyze the slag formation reactions and definitively conclude sequences proceeding in slag formations and limitations of the overall fayalite slag formation reactions.

4. Matte droplets then coagulate together and separate from the slag by density differences. This can be visually observed in Fig. 6(A) and (B) where the previously randomly distributed matte coalescence and form a larger matte phase domain, and in Fig 7(B) where a droplet of matte was formed. During the phase separation process, further deironization and desulfurization of matte also take place. Complete separation of matte and slag is achieved when element content in matte is stabilized. As it can be seen in Fig. 8(B), this is achieved after 10 minutes of matte smelting.

5. In air atmosphere, the copper sulfide (Cu<sub>2</sub>S) in the matte could be oxidized further to cuprous oxide (Cu<sub>2</sub>O), and subsequently react with iron and copper sulfide through Reactions 14 - 16 to produce metallic copper. Since oxidation was not controlled in this experiment, the oxidation proceeded rapidly leaving no metallic copper and matte behind, as in Fig 6(D).

#### 5. Conclusions

As this study was largely based on physical phenomena observations through micrographs of slag-chalcopyrite agglomerates, there are, to some degree, subjective misinterpretations in the result. Confirmations to previous similar studies are also very limited, since the topic has not been studied extensively.

Keeping these things in mind, the results obtained in this work suggested:

1. Fayalite or iron silicate slag formation in matte smelting mostly takes place through reactions between silica, magnetite, and oxidizing iron sulfide. This reaction is relatively slower than the other steps in the matte-slag processes.

2. Gas diffusion did not appear to limit matte-slag reaction rates, as in air atmosphere, most matte-slag reactions happened rapidly, with the matte grade reaching 60-70 wt% after just 2 minutes.

3. Mass transport phenomenon appeared to be the limiting factor in matte-slag reactions. In air atmosphere, mass transport limits the slag forming reactions, while in inert atmosphere, oxygen mass transport limits the magnetite forming reactions.

4. Separation of matte and slag ceased after 10 minutes of contact time at 1300°C. After this time, the final elemental content of the matte could already be concluded.

Summarizing, a flow diagram describing the sequences involved in matte formation and separation by suspension smelting is shown in Fig.9



Figure 9. Sequences of matte smelting using suspension oxidation. In an inert atmosphere, the processes stop at step 4, while in excess air atmosphere it continues until step 6. Step 3 is the rate limiting step in matte smelting under air atmosphere, while step 2 is the rate limiting step in matte smelting under inert atmosphere

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## REDOSLED REAKCIJA IZMEĐU BAKRENCA I ŠLJAKE I PROCESI SEPARACIJE U TOPLJENJU BAKRENCA

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Dok su reakcije sagorevanje čestica i oksidacija halkopirita prilikom topljenja suspenzija dobro proučeni, postoji jako mali broj studija koje se tiču reakcija između tečnih faza i raslojavanja bakrenca i šljake prilikom topljenja bakrenca. U ovom radu izvršena su eksperimentalna istraživanja u vazdušnoj i argonskoj atmosferi korišćenjem mešavine sintetičke šljake i koncentrata halkopirita. Prikazan je redosled reakcija i procesa separacije koji se dešavaju u procesu topljenja. Takođe su dati i mogući ograničavajući faktori u celokupnom procesu. Rezultati ovog rada predstavljaju važnu osnovu za buduće radove u oblasti formulacije kinetike reakcija između tečnog bakrenca i šljake u procesu topljenja bakrenca.

Ključne reči: Reakcije topljenje-topljenje; Reakcije u otopljenoj fazi; Bakrenac; Topljenje u fleš pećima.

