

Copper losses to slags obtained from the El Teniente process

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The Smelting and Converting El Teniente Process for copper concentrates as well as Slag Cleaning Furnace Technologies to treat slags coming out from the El Teniente Furnaces are widely applied today in Chile and around the world.

Several industrial applications of this process have shown their capability to treat copper concentrates in a wide range of chemical and mineralogical compositions. Main operational parameters determining performance of the process are: oxygen enriched air flow rate, degree of oxygen enrichment, moisture content of the solid materials processed, molten material levels inside the vessel, frequency of molten materials tapping, bath temperature and copper losses in slags.

In this work, the copper losses in the slags from El Teniente pyrometallurgical process are predicted by calculation from thermodynamic data and compared with those determined by microscopic examination and slag industrial data.

Results obtained show that the main part of copper losses in the slag from El Teniente Furnace are mechanically entrapped or floated unsettled droplets of the coexisting matte phase. by the contrary the very low copper losses in the slag from slag cleaning furnace are limited by the physico-chemical form.

Introduction

Current El Teniente pyrometallurgical process for copper concentrate was commissioned at Caletones Smelter during the period 1988–1991, following an intensive R&D program that led to several improvements to the original process developed during the seventies. Several industrial applications of the process, in Chile and abroad, have shown their capability to treat copper concentrates in a wide range of chemical and mineralogical compositions. Main operational parameters that determine the performance of the process are oxygen enriched air flow rate, degree of oxygen enrichment, moisture content of the solid materials processed, molten material levels inside the vessel, frequency of molten materials tapping, bath temperature and copper losses in slags.

The copper losses in the slags from El Teniente pyrometallurgical process predicted by calculation from thermodynamic data has been compared with those determined by microscopic examination of the slag samples from El Teniente pyrometallurgical processes and some slag industrial data.

El Teniente pyrometallurgical process

Simplified flowsheet of the current pyrometallurgical process at Caletones Smelter with production capacity of 383 000 tons of copper annually, is presented in Figure 1. Basically, the current process involves four main stages to transform copper sulphide concentrate into blister copper, as follows:

- Wet concentrate drying down to 0.2 wt.% moisture
- Smelting bone dried concentrate and partial converting to white metal

- White metal converting to blister copper
- Slag cleaning directed to recover copper from the slag produced during the smelting and partial converting steps.

In the particular application of the process at Caletones Smelter, wet concentrate with about 8 wt.% moisture is received from Colón and Andina Concentrator Plants and then conveyed to storage bins. Then concentrate is split into two parallel lines to be conveyed to two direct-fired Fluidized Bed Dryers. After being dried, concentrate with 0.2 wt.% moisture is separated from the gaseous products in bag-filters, the gases being ducted to dedicated stacks and exhausted to the atmosphere, while the bone dried concentrate is pneumatically conveyed to storage bins located adjacent to the Teniente Converters Nos. 1 and 2.

The El Teniente converter process involves the smelting and partial converting of bone dried copper concentrate in a thermally autogeneous operation. This operation mode takes into account an improvement to the El Teniente converter original process. The bone dried concentrate is directly injecting to the molten bath, with a mixture of oxygen-enriched air up to 34 vol.% O₂ through specially designed tuyeres. Siliceous flux and reverts are fed into the reactor through a garr-gun feeder. The products of smelting and oxidizing of copper concentrate with flux are two separate molten phases, the high grade matte or 'white metal' with the degree of oxidation being controlled so as to yield white metal with about 75 wt.% Cu and a slag that contains 7–10 wt.% Cu and 12–16 % Fe₃O₄. These molten phases are intermittently tapped in a countercurrent flow pattern, white metal at 1220°C and slag at 1240°C, through especially designed water cooled tapholes located at each side of the endplates. White metal is poured into ladles and

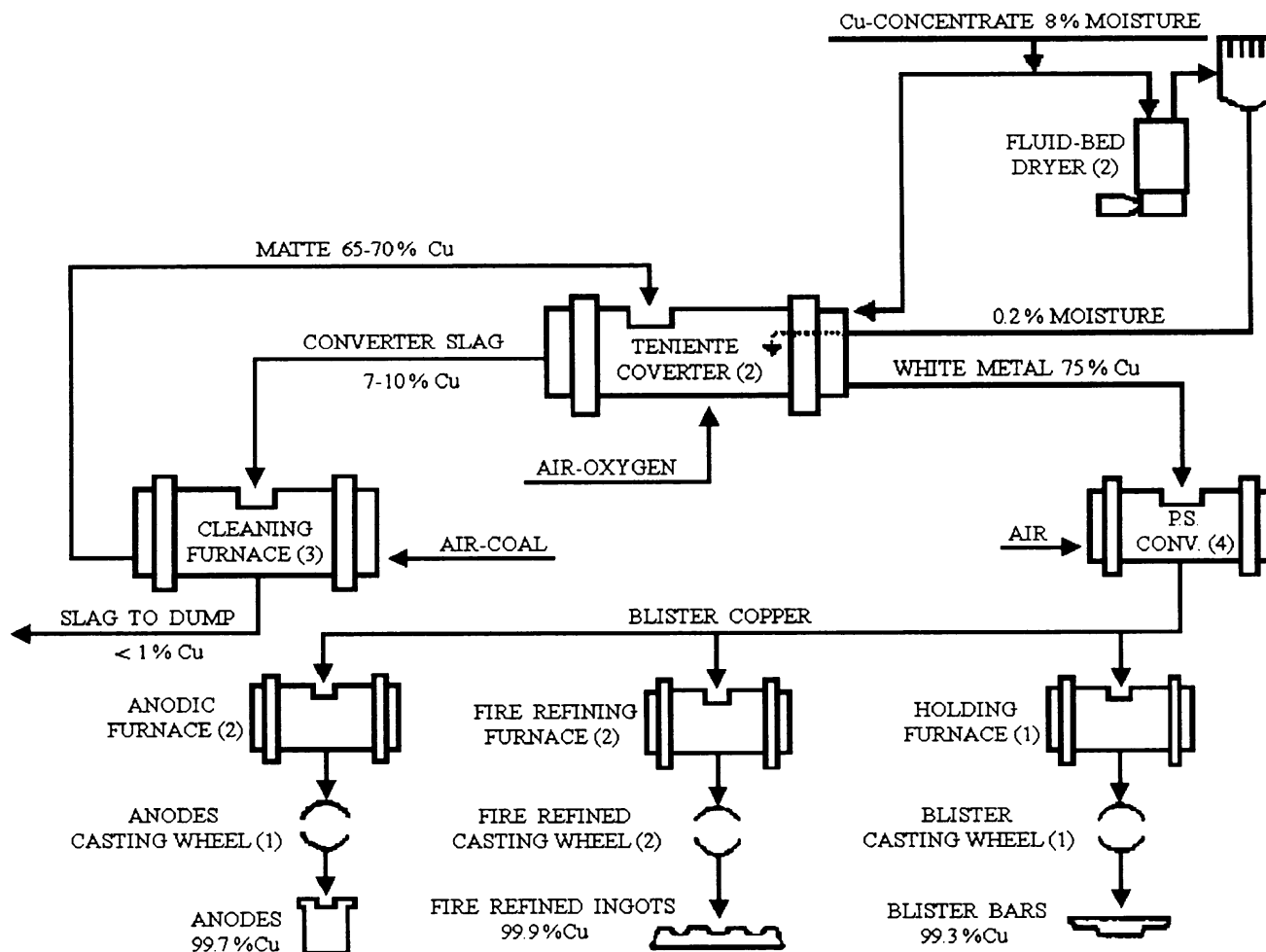


Figure 1. Simplified flow-sheet of the current El Teniente pyrometallurgical process at Caletones smelter

transferred to the Peirce-Smith Converters, where final blowing to blister copper takes place. Normally three Peirce-Smith Converters are operating while another unit remains on stand-by or under maintenance. Slag produced is transferred by ladles or directly by launder, to the El Teniente slag cleaning furnaces for decoppering.

The El Teniente slag cleaning furnace process is based on an intensive reduction of magnetite and copper content in molten slag produced at the El Teniente converter, by injection of a solid, liquid or gaseous reductant directly in to the molten slag through specially designed tuyeres followed by sedimentation stage. The reduction of magnetite decreases the slag viscosity and enhances the settling of copper enriched phase. The molten products obtained after the settling stage are, a discard slag with a copper content less than 1 wt.% Cu, and a high grade copper matte with 60–70 wt.% Cu. The decoppered slag is poured into ladles, and then transported to dump by pot-carriers. The high-grade copper matte is tapped into ladles and then recycled to the Peirce-Smith converters.

Sulphur dioxide and other gases produced inside the El Teniente reactors, continuously exhausted through the off-gas mouths, are cooled, dedusted and used for sulphuric acid production.

Thermodynamic considerations

The thermodynamic study of the copper losses in the slags from El Teniente Process may be discussed on the basis of

the Cu-Fe-S-O-SiO₂ system, in which the metals, sulphur and silica represent the major components of the condensed phases and oxygen is the major component of the gaseous phase. From the available thermodynamic data and phase relations the predominance area diagram was calculated for the system Cu-Fe-S-O-SiO₂ at 1250°C equally, as was described in the author's previous paper¹ and the results were plotted in Figure 2.

The equilibrium between matte, slag and gas phase in El Teniente converter and El Teniente slag cleaning furnace can be represented in Figure 2 by the dotted and the dashed lines. The dotted line corresponds to the condition of coexistence of white metal containing about 75 wt.% of copper, slag nearly saturated with magnetite and silica with high copper oxide activity 10⁻²–10⁻³ and gas phase with partial pressure of oxygen about 10⁻² Pa and partial pressure of sulphur dioxide in the order of between 10⁴–10⁵ Pa in El Teniente converter. This means that intensive smelting and partial converting of bone dried copper concentrates in El Teniente converter produces highly oxidized slag with high magnetite and copper oxide contents. The dashed lines in Figure 2 corresponds to the condition of co-existence of matte with about 60 wt.% of copper, slag nearly saturated with silica and iron with low copper oxide activity 10⁻³–10⁻⁴ and gas phase with low partial pressure of oxygen about 10⁻⁵ Pa and low partial pressure of sulfur dioxide in the order between 10–10⁻¹ Pa in El Teniente slag cleaning furnace. This means that the decoppering process, based on

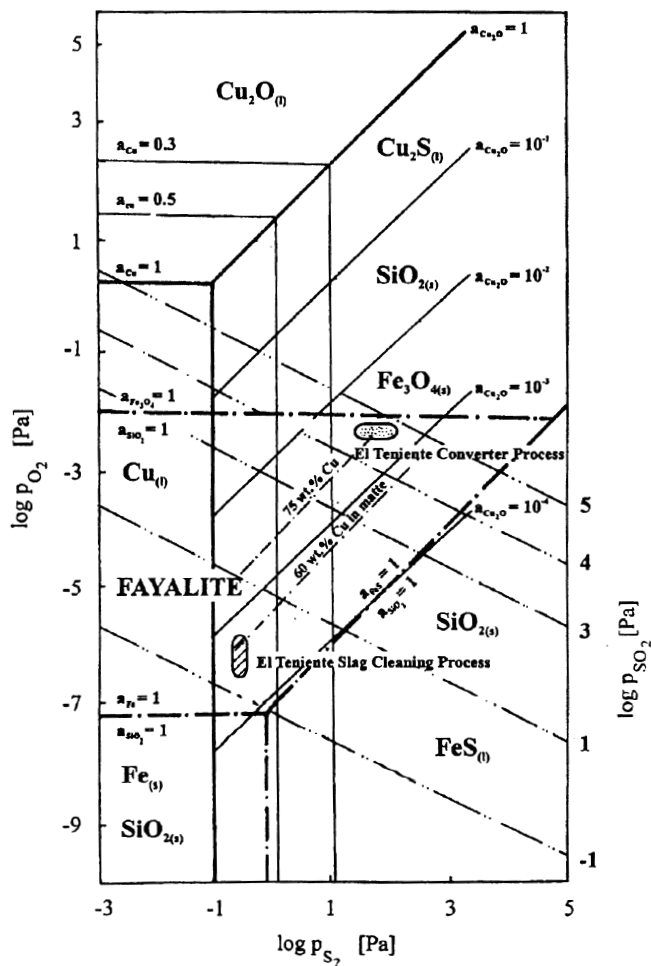


Figure 2. System Cu-Fe-S-O-SiO₂ at 1250°C

the slag reduction by injection of a solid, liquid or gaseous reductant directly into the molten slag with following settling stage, produce slag with low magnetite and copper oxide contents.

Copper losses in slags

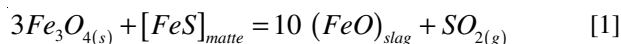
The pyrometallurgical extraction of copper from copper sulphide concentrate consists of two essential steps that are chemical reactions followed by phase separation. The copper content in sulphide copper concentrates is limiting by impurities. The main impurities are iron sulphide minerals. Part of iron sulphide minerals is selectively oxidized and fluxed as fayalite (2FeO.SiO₂) and second part is oxidized and fluxed as magnetite (Fe₃O₄) which increases the viscosity of the slag and decreasing the matte-slag separation. The correlation between the silica, magnetite and copper content in a sequence of 100 samples taken at the end of the first period of matte converting is illustrated in Figure 3. From the above it may be concluded, that the magnetite content in the slag will have great influence on the total copper content in discharged slags (%Cu_T) from the El Teniente slag cleaning furnace.

Despite the contradictory opinions regarding the forms of copper losses in the slag that have appeared recently³⁻¹⁷, the two forms considered here are mechanical and physico-chemical losses.

Mechanical copper losses in slags

The mechanical copper losses in slags (%Cu_{mech}) can be

considered as particles of mechanically entrapped or floating unsettled droplets of the coexisting matte phase, their sizes varying from several millimeters to a few microns. Poggi and co-workers⁴ suggested that matte-phase droplets are floated into the slag by SO₂ bubbles that originate in the melt according to the reaction:



By evolving SO₂ gas bubbles the droplets of matte phase are floated to the slag surface. After coagulation of very fine droplets on the slag surface the large particles sink through the surface and settle down to the bottom. The settling rate of the matte particles mechanically entrapped or floated in the slag may be theoretically calculated by Stokes' law:

$$v = \frac{2}{9} \frac{g(\rho_1 - \rho_2) \cdot r_D^2}{\mu_2} \quad [2]$$

where v is the rate of settling (cm.s⁻¹), ρ_1 is the density of matte (g.cm⁻³), ρ_2 is the density of slag (g.cm⁻³), μ_2 is the viscosity of the slag (P), and r_D is the diameter of the particle (cm).

Assuming that the variation of the densities of slag and matte on composition is negligibly low and the matte particle diameter is constant, the main factor to influence the rate of matte settling will be the slag viscosity. The significant effect for viscosity of fayalite slag has magnetite content. According to Figure 2 the homogeneous liquid matte-slag region is limited by the lines corresponding to solid iron and solid magnetite separation. Between these lines in the fayalite slags the ferrous and ferric content depends on partial pressure of oxygen in gaseous phase. The higher oxygen potential in the gas phase the higher is the magnetite content in the slag as is documented in Figure 4.

Higgins and Jones¹⁸ showed that the viscosity of the slag is rapidly increased when magnetite saturation is reached and the solid magnetite crystals are separated in homogeneous fayalite melt. To verify this claim the magnetite content in the slag after decoppering with pyrite, under constant settling conditions, were analysed and summarized in Figure 5. From Figure 5 it is evident that the copper content in the slag is altered rapidly when magnetic

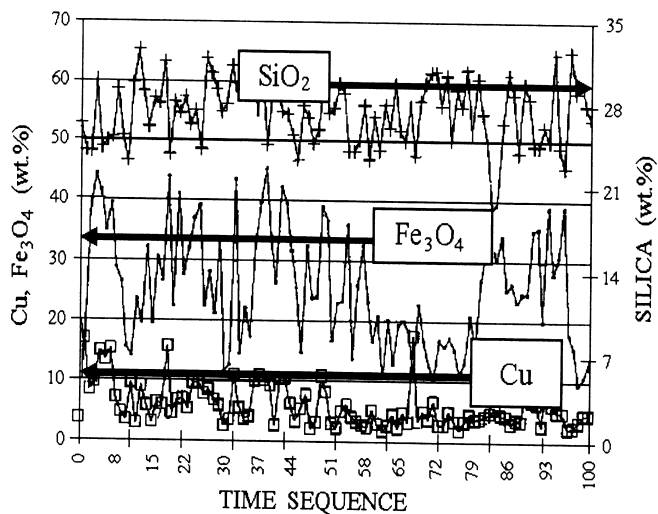


Figure 3. The correlation between the silica, magnetite and copper content in a sequence of 100 samples taken at the end of the first period of matte converting

saturation is reached. Microscopic analysis showed that the higher copper contents in slags at higher magnetite contents after washing with pyrite concentrate are due to the fact that the mechanically entrained copper and matte particles did not settle down¹⁹.

Physico-chemical copper losses in slags

The physico-chemical losses in slags (%Cu_{sol}) are caused by solubility of copper in the sulphide and oxide forms so the following common equation is valid:

$$\%Cu_{sol} = \%Cu_{Cu_2O} + \%Cu_{Cu_2S} \quad [3]$$

A function of the physico-chemical copper losses in silica-saturated slags of temperature and matte grade was calculated based on thermodynamic investigations of the Cu-Fe-S-O-SiO₂ system^{1,6,22} and can be described by the following equations:

$$\%Cu_{sol} = A \cdot \sqrt{\frac{N_{Cu_2S}}{1 - N_{Cu_2S}}} + B \cdot \sqrt{N_{Cu_2S}} \quad [4]$$

$$\log A = -5000/T + 2.101 \quad [5]$$

$$\log B = -22500/T + 14.707 \quad [6]$$

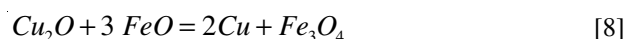
where *A* and *B* are constants depending on temperature, *T* is temperature (K), and *N*_{Cu₂S} is the mole fraction of Cu₂S in matte coexisting with slag.

The first term in Equation [4] represent copper losses in slags arising from Cu₂O solubility, which at constant temperature and silica saturation is only a function of matte grade and FeO activity in slag. The dissolved cuprous oxide in molten slag may react with ferric oxide producing delphosite²³ by following chemical reaction:



According to Rosenqvist²⁴ cuprous oxide may react with

ferrous oxide by chemical reaction:



This means that the separated copper would be found in solid slag together with magnetite crystal as copper prills¹⁷.

The second term represents copper losses in slags owing to Cu₂S dissolution, which, under the conditions given, depends only on matte grade.

Discussion

The total physico-chemical copper losses in slags calculated from Equations [4] [5] [6] at 1250°C are plotted in Figure 6 as a function of the matte grade, together with results obtained by the other investigators⁵⁻¹⁷ and industrial data from El Teniente processes. The measured and calculated data from different investigators summarized in Figure 6 are significantly scattered, mainly at low matte grade where sulphidic copper is the predominant dissolved form, which depends on matte grade, slag composition and partial pressures of sulphur and oxygen in gas atmosphere. If matte grade rises to near 80 wt.% Cu and the oxidic copper is the predominantly dissolved form because the partial pressure of oxygen is high and slag is almost saturated by magnetite, all the solubility curves for total solubility of copper are similar and rise sharply. This is in a good agreement with thermodynamic calculations, illustrated in Figure 2.

It is clear from Figures 2 and 6 that if the copper content in the matte is around 75 wt.% and slag is nearly saturated with magnetite and silica corresponding to smelting and partial converting conditions in the El Teniente converter, the mechanically entrapped matte particles form the predominant copper losses in the slag. From the flotation tests of the finely ground samples of slags from the El Teniente converter slag²¹, was suggested that 87.70–90.70% of the copper in the slag is presented in the form of mechanical losses, whereas the remaining 9.30–12.30% represent the physico-chemical copper losses in the slag. The physico-chemical copper losses are approximately 70% in the form of dissolved Cu₂S and 30% in the form of dissolved as Cu₂O. The microscopic examination of polished samples of the slags from the El Teniente

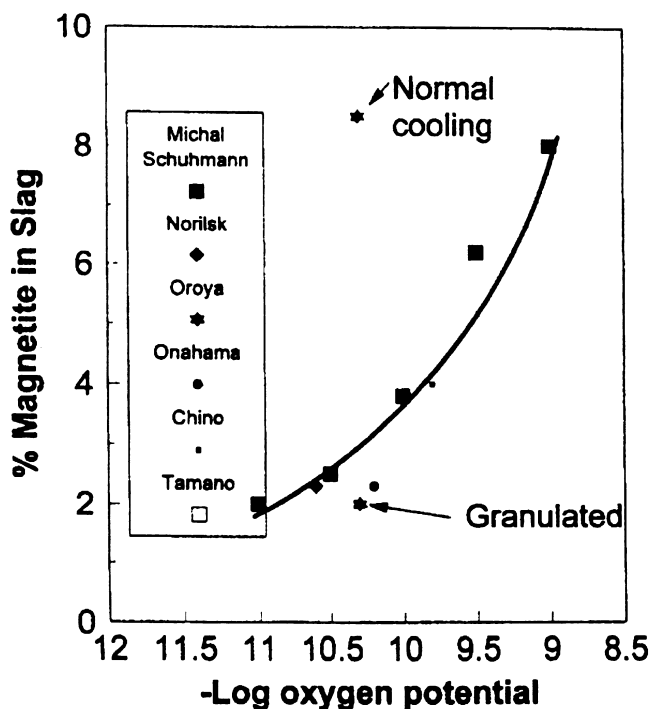


Figure 4. Relationship between the magnetic content in slag and oxygen pressure at 1250°C

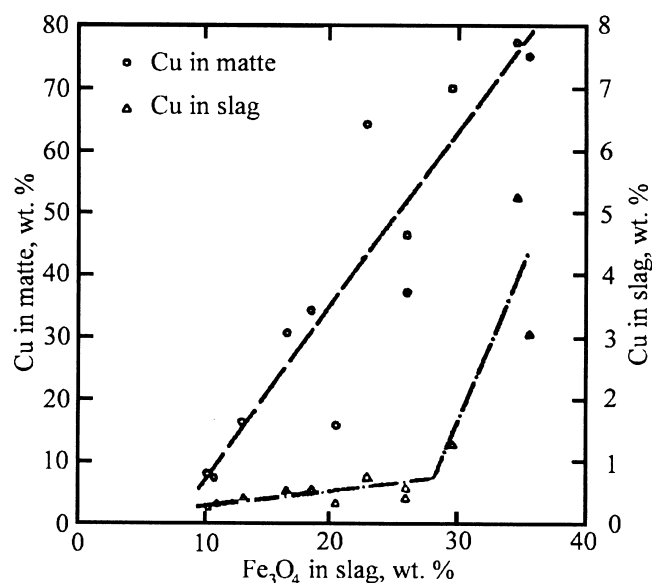


Figure 5. Copper content in slag and matte versus magnetic content in slag at 1250°C

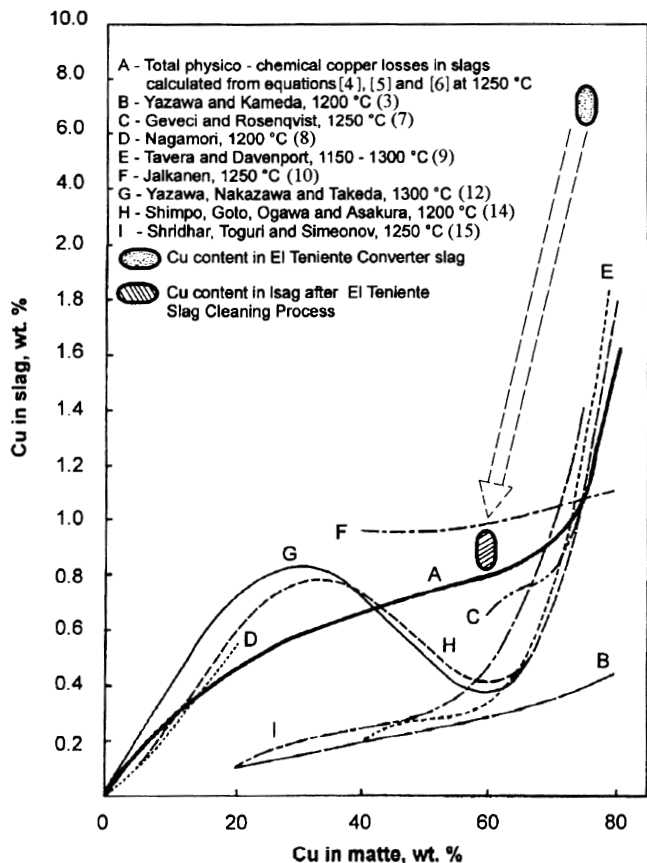


Figure 6. Solubility of copper in silica saturated slags versus copper content in matte

converter showed (Figure 7) that the primary octahedral and secondary dendritic crystals of magnetite and needle-shaped crystals of fayalite are present in the slag and the copper losses in the slag are mainly as mechanically entrained matte particles their sizes varying from several millimeters to a few microns. Some metallic copper prills associated with magnetite crystals were also found. Dissolved cuprous sulphide precipitated during the slag solidification in the form of beta chalcocite (Cu_2S) forming finely dispersed particles mainly in the spinel slag matrix.

During the decoppering of slag by reduction in the El Teniente slag cleaning furnace, reduction of magnetite took place, which improved the condition of matte-phase separation, as is documented in Figure 8. Because the settling time was not sufficient the copper content in the slag after reduction and matte settling is slightly higher as predicted from theoretical calculation by Equations [4], [5] and [6] in Figure 6. If the reduction conditions in the El Teniente slag cleaning furnace is high, the liquid system becomes saturated by iron and silica, and the settling time is sufficient for matte phase separation the copper content 0.79 wt.% in discarded slag is mainly in the form of physico-chemical losses which represents the minimum copper content in the slag after reduction process²¹. This is in a good agreement with the microscopic examination of polished samples²¹ of decoppered slag from the El Teniente slag cleaning furnace (Figure 9). The copper content in the slag was mainly in the form of very fine particles of beta chalcocite (Cu_2S) precipitated during the slag solidification in a glass spinel matrix with large needle-shape crystals of fayalite. Some metallic iron particles were also found. Only

a few droplets with very small particle diameters of mechanically entrapped unsettled matte particles was detected. From these results it could be concluded, that copper losses in the slag saturated by iron and silica from the El Teniente slag cleaning furnace are present mainly as physico-chemical copper losses which could be predicted from Equations [4], [5] and [6] and hence represent the minimum copper content in a discard slag after reduction process.

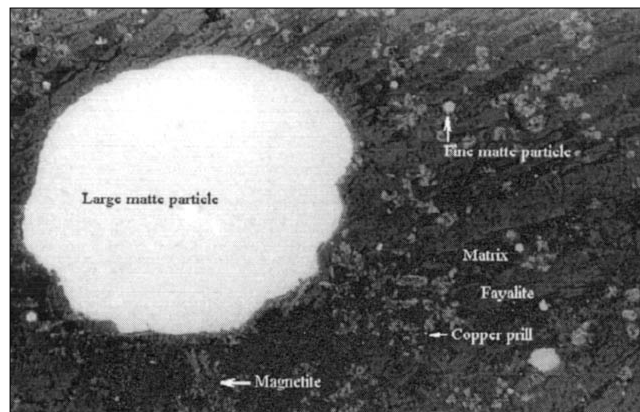


Figure 7. Microstructure of El Teniente converter slag. Magnification $\times 300$

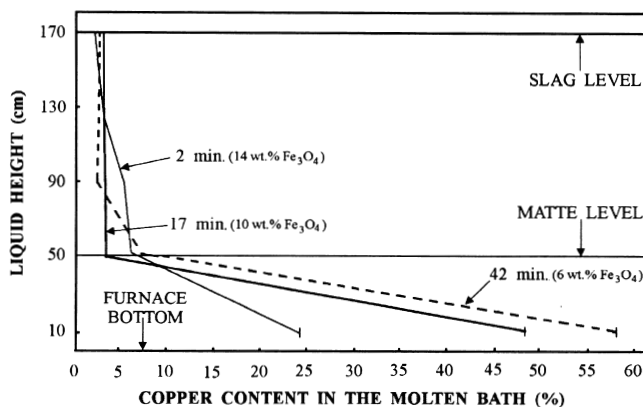


Figure 8. Vertical and longitudinal dynamic composition of copper in the El Teniente slag cleaning furnace

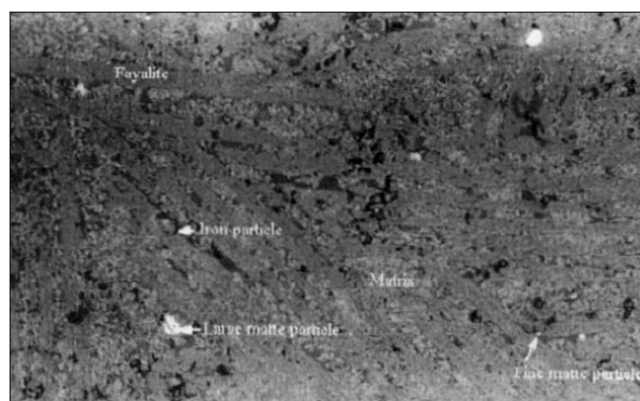


Figure 9. Microstructure of El Teniente slag cleaning furnace slag Magn $\times 750$

Conclusions

The mechanical copper losses in slags are difficult to predict but the effect of slag viscosity is significant. Therefore, there is a reason to believe that good slag composition with low viscosity and well-mixed reactor with good coagulation of fine matte particles will result in the lowest mechanical copper losses in a discard slag. The El Teniente slag cleaning furnace is such as reactor.

During the decoppering of molten slag, produced at the El Teniente converter, by reduction process in the El Teniente slag cleaning furnace the reduction conditions are so high that the reduction of magnetite took place and the liquid system became saturated by iron and silica. The reduction of magnetite decreasing the slag viscosity and improving the condition of matte phase separation which means that a substantial part of copper in discarded slag exists in the form of physico-chemical losses which could be predicted from Equations [4], [5] and [6] and, hence, represent the minimum copper content in a discard slag after reduction process.

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