

## Continuos Improvement of the Teniente Slag Cleaning Process

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The El Teniente Division of CODELCO-CHILE has developed an effective slag reduction-cleaning process. This process was designed to recover copper from the slag produced in the El Teniente Converter, which is a highly oxidized slag obtained from the copper concentrate smelting process. The effectiveness and the continuous improvement of this cleaning process have allowed implementing the process in other Chilean smelters. Therefore, the present paper discusses the industrial evaluation of various furnace operational schemes. The results show that the reductant efficiency, the time cycle and the copper recovery could be improved in a safe environmental manner by adopting these new operational schemes.

## I. - INTRODUCTION

The products of the smelting-conversion process performed by the Teniente Converter are a high grade matte containing 73 ~ 75% of Cu and a highly oxidized slag, typically containing 12 ~ 16 % of  $\text{Fe}_3\text{O}_4$  and 4 ~ 10 % of Cu. These slags must be treated in order to recover its copper content. In this way, a dischargable slag with copper levels below 1% and  $\text{Fe}_3\text{O}_4$  contents of around 5% can be obtained.

The Caltones Smelter of El Teniente Division of Codelco-Chile, has developed an efficient slag reduction-cleaning process, performed- in a tilting horizontal furnace and implemented to recover the copper contained in these slags. The continuous improvement in the furnace capabilities, allows operating it in a semi-continuous scheme with highly convenient productivity indexes.

The present work is a technical review of the different efforts performed by the Caltones Smelter in basic and applied research in order to:

- Characterize the slag cleaning mechanism in the Teniente Slag Cleaning Furnace.
- Optimize the process through the application of a semi-continuous operational scheme.

## II. ANTECEDENTS

### 1. - General description of Caltones Smelter<sup>[1]</sup>

The Caltones Smelter is part of the El Teniente Division of Codelco-Chile. Its present smelting capacity is close to 1,250,000 metric tonnes of copper concentrate per year, which is mainly supplied by El Teniente Mine. **Figure 1** shows a schematic diagram of the smelter. The main equipment are two fluidized bed dryers, one reverberatory furnace, two Teniente converters, four Peirce-Smith converters, three Teniente slag cleaning furnaces, two anode furnaces, three refining furnaces for fire refined copper, two oxygen plants, and one acid plant. **Table 1** presents the smelter main production parameters.

The smelting-conversion process is mainly performed in the Teniente Converters. These reactors autogenously process almost 90% of the copper concentrate, being the rest smelted in the reverberatory furnace. This furnace also operates as a slag cleaning facility<sup>†</sup>.

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The shut down of the Reverberatory Furnace has been scheduled for October 2000. From this date on, all the concentrate will be smelted in the Teniente Converter, while the slag will be processed in the Teniente Slag Cleaning Furnace.

The dried concentrate processed in the Teniente Converter is pneumatically injected into a molten bath through specially designed tuyeres. The obtained matte is periodically tapped out through a tapping hole located in one side of the Teniente Converter and then transferred to the Peirce-Smith Converter to be converted into blister copper.

To recover the copper contained in the Teniente Converter slag, the slag is skimmed from the reactor and then processed in the Teniente Slag Cleaning Furnaces and in the reverberatory furnace. The recovered matte is transferred to the Peirce-Smith Converter while the cleaned slag with copper contents lower than 1.0% is delivered to the land field.

The blister copper produced at the Peirce-Smith Converter can be either refined and cast as anodes (99.6% copper grade), or cast as fire refined copper (99.9% Cu). The annual production of anodic and fire refined copper are 200,000 and 120,000 tonnes, respectively.

The off-gases generated in the smelting-conversion process are cooled in an evaporative system and then treated in electrostatic precipitators to recover the contained dust. Actually, about 40% of the sulphur and 50% of the arsenic fed to the smelter is treated in a sulphuric acid plant. A second acid plant, presently under construction, is scheduled to start-up in November 2000. This new plant will increase the sulphur recovery to 93%.

## **2. - Teniente Slag Cleaning Furnace process description**

The Teniente Slag Cleaning Furnace is a tilting furnace. It was developed and implemented in 1991 by Calteones smelter to process in an economic and efficient way the slag generated in the Teniente Converter.

The cleaning process is based on an intensive reduction of the magnetite contained in the slag followed by a sedimentation stage. The reduction of magnetite decreases the slag viscosity and enhances the settling of a copper enriched phase and the separation phase. **Figure 2** shows a schematic diagram of the furnace. A mouth located in the shell of the furnace is used for exhausting the process off-gas and also for loading and unloading the slag. The matte is tapped through a taphole located on one side of the reactor. The furnace is equipped with four tuyeres to inject the reductant/air mix, and an oil burner for supplying the heat required by the process needed in the different stages of the process. A garr-gun located at the opposite side of the matte taphole allows to add flux if required.

## **3. - Batch process description**

In its original conception, the Teniente slag cleaning furnace was designed to operate on a batch process with a treatment capacity of 150 tonnes per cycle in the following steps:

- (i) Slag loading
- (ii) Reduction of metallic oxides contained in the slag.
- (iii) Settling and separation of matte and slag phases.
- (iv) Products unloading

In this operational scheme, the furnace requires to be fully charged with slag before starting the reduction phase. Then, the charging, waiting and unloading time represent around 60% of the whole process cycle (each cycle takes 4 to 5 hours). This fact indicates a real need to modify this operational scheme.

On the other hand, variability of slags generated in the Teniente smelting-conversion process, which is mainly detected by the significant changes in the slag viscosity, made it difficult to perform a standard control of conditions during the slag cleaning reduction process phase.

The above-described fact raised the need to modify the furnace operation from a batch to a semi-continuous strategy, in order to improve the operational indexes and to have a better-controlled process.

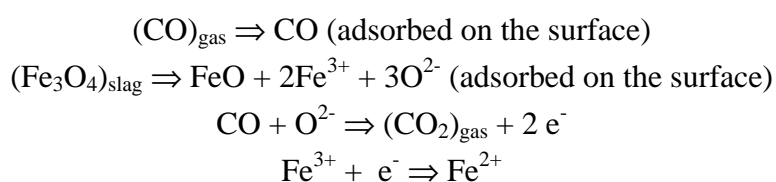
#### 4. Theoretical fundamentals of the slag cleaning process <sup>[2]</sup>

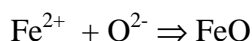
Copper in the Teniente Converter slag is present typically 2/3 as matte and metallic copper inclusions, and 1/3 as dissolved cuprous oxide.

The injection of the reductant/air mix into the liquid slag through tuyeres generates a number of complex phenomena and chemical reactions, as illustrated in **Figure 3**.

As soon as the pulverized coal/air mix enters the bath, the hydrocarbons in the coal start to decompose. Eventually, the ignition of carbon and hydrogen takes place. The combustion of the reductant produces reducing gases containing H<sub>2</sub>, CO, H<sub>2</sub>O, and CO<sub>2</sub>. The gas bubbles rise upward, and carbon monoxide and hydrogen react with magnetite. Some carbon particles are trapped in the slag and finally float. The direct reduction of magnetite by carbon, instantaneously produces a gas film around the carbon particles, and subsequent reduction reactions take place at the gas/liquid slag interface.

Based on the mechanism proposed by Min and Fruehan <sup>[3]</sup> for the reduction of FeO from a liquid slag, magnetite reduction can be described as follows:





The rate of magnetite and copper oxide reduction from the slag depends on temperature, surface area (the dynamic surface area of gas bubbles, carbon particles in the slag and on the slag surface) and the concentration of hydrogen and carbon monoxide in the gas phase. The partial combustion of the pulverized coal produces heat, which increases the temperature of the gas bubbles and the carbon particles, thus increasing the reduction rate. The intensive stirring of the slag, caused by the injection of the coal/air mixture, speeds up reduction rate by increasing the area of contact of the various reactants, as well as by enhancing mixing and, consequently, mass transfer.

### **III. FIRST STEPS IN THE OPTIMIZATION OF THE TENIENTE SLAG CLEANING PROCESS**

In view of the need to optimize the slag cleaning process, the Caletones smelter started a research program on a basic and industrial scale. The first efforts were directed to the optimization of the batch slag cleaning process. Firstly, the kinetics of process sedimentation was characterized to continue with the characterization of reduction kinetics. Conclusions reached at this stage of the research permitted to visualize strategy of the semi-continuous operation of the Teniente slag cleaning furnace.

#### **1. Characterization and kinetics of slag sedimentation in the Teniente slag cleaning furnace<sup>[4]</sup>**

The first researches carried out by the Caletones smelter were developed with the objective of determining the kinetics of sedimentation and separation of white metal and slag in the charging, sedimentation and unloading stages.

Results showed that the settling process of white metal in the furnace, started as soon as the slag was fed into the furnace. In the charging stage, a differential sedimentation phenomenon called “cola de tigre” (tiger tail) was observed. The low charging frequency and the low temperatures of the slags fed into the furnace generated this phenomenon.

At the same time, it was observed that around 50% of the copper content of feeding slag settled in the charging stage. This fact suggested the possibility of tapping the matte settled in this phase before starting the reduction stage. Likewise, measurements of vertical profiles of the liquid composition inside the bath showed the coexistence of the three phases: matte, emulsion and slag. The emulsion-slag phases coexisted at the tuyere area, while in the settling area coexisted the matte phase together with the emulsion and slag phases. The existence of the emulsion interface also explained the increase of copper grade in the reduced slag, during extraction and sampling in the unloading stage.

The above described phenomena permitted to give a new approach to the following stages of the research by considering the possibility of operating on a semi-continuous scheme with white metal being tapped even in the reduction stage.

## **2. Second optimization stage**

The main objectives of this stage of the research were:

- (1) Increase of the Teniente slag cleaning furnace process capacity.
- (2) Decrease the process operational costs.
- (3) Environmental optimization of the process.

The basic researches carried out were conducted to study the following aspects:

- (i) Chemical and mineralogical characterization of the smelting-conversion slag generated in the Teniente Converter.
- (ii) Study of the key factors that influence the reduction kinetics.
- (iii) Effect of the addition of collectors on the slag cleaning.
- (iv) Operational optimization of the cleaning process.

### **(i) Chemical and mineralogical characterization of the Teniente Converter slag**

Slags generated in the Teniente Converter were sampled and then chemically and mineralogically analyzed. **Figure 4** shows a typical microscopic structure of these slags. Primary magnetite, secondary magnetite dendrites and fayalite crystals are present in the slag microstructure. The size of the matte inclusions varies between 1 y 50  $\mu\text{m}$  and they are normally associated with magnetite. Bornite, metallic copper as well as some copper oxide filaments can be also observed.

### **(ii) Main factors in the reduction kinetics**

The slag reduction kinetics shows a strong dependency on the temperature. The activation energy of reduction was measured to be  $230 \pm 30$  kJ/mol. The slag-reductant contact area also plays an important role in the reduction kinetics. The reduction rate increases one order of magnitude, compared with a floating coke layer, when the slag is filtered through a coke layer located on the bath surface. Finally, the intensive slag stirring achieved through the gas injection also improves the reduction rate.

### **(iii) Collectors effect on the slag cleaning process**

Laboratory tests conducted to study the effect of bath collector's addition, such as pulverized matte, on the slag cleaning process did not show conclusive results.

#### **(iv) Industrial scale research**

Industrial scale research was oriented to the global optimization of the slag cleaning process in the Teniente slag cleaning furnace. Main conclusions are presented in **Table 2**. From these conclusions we can point out the optimization reached in the decrease of the slag reduction times from 110 to 40 minutes by adding coke as well as the implementation of the new control techniques applied to the burner. These process improvements allowed an increase of the copper recovery derived from a decrease in the slag copper grade rating from 1.3 ~ 1.1% to 1.0 ~ 0.8% and in the environmental quality of the process.

### **IV. - REDUCTION KINETICS**

Based in the development reached during the first stages of the research, an on line measurement program was scheduled with the objective of determining the reduction kinetics of the slag in the Teniente slag cleaning furnace.

#### **1. - Experimental design**

In order to determine the local chemical compositions of the phases in different points and depths of the molten bath, a metal bar (conditioned with small crucibles made of refractory material and sealed with aluminium or copper) was introduced into the molten bath through perforations made alongside the furnace shell. During each charge, process gases and temperature of all the currents were measured and characterized. A thermographic analysis of the shell was also conducted in parallel.

#### **2. - Results**

The observations performed through this set of measurements allowed to establish the existence of highly reductant areas, in front and over the tuyeres line inside the reactor, and areas where reduction was only superficial, located on the bath surface mainly due to coal remaining from the charging stage. A white metal accumulation was detected under the tuyere line together with a certain amount of primary magnetite due to the low stirring of the area. The separation of the slag and metal phases was more obvious as the reduction of the product advanced. This was reflected in the copper, primary and secondary magnetite contents in each of the phases present in it.

**Figure 5** presents an example of the vertical and longitudinal dynamic chemical composition of (a) magnetite and (b) copper, inside the bath. As soon as the reduction process starts, some matte settling can be observed. No significant vertical dynamic gradients of  $\text{Fe}_3\text{O}_4$  were detected in the liquid slag located in the shell cover, head and hood areas of the furnace.

Notwithstanding, there are longitudinal dynamic gradients of  $\text{Fe}_3\text{O}_4$  in the liquid slag located in the head area and of the more reduced liquid in the head/hood area.

The intensity of the stirring in front of the tuyere line increases as the reduction process advances. This phenomenon contributes to the homogenization of the chemical distribution of the chemical components of each phase. On the other hand, phase's separation is more obvious as the process is in progress. This is reflected in the copper contents and in the primary and second magnetite of each one of the actual phases.

From the achieved results, the dynamic behavior of the reduction and reductant efficiencies corresponding to the average chemical composition of magnetite for different heights in the slag were also calculated. It was observed that the reductant efficiency (kg of coal per ton of reduced magnetite) varied between 30 and 50% at the beginning of the reduction stage, decreasing it to values between 10 to 20% at the end of the stage. The reduction efficiency, defined according to equation 1 by the difference between the initial (i) and final (f) magnetite content,

$$\text{Red}(\%) = \frac{(\text{Fe}_3\text{O}_4)_i - (\text{Fe}_3\text{O}_4)_f}{(\text{Fe}_3\text{O}_4)_i} \times 100, \quad (1)$$

presented maximum values between 50 and 70% during the first 40 to 60 minutes of the reduction process.

**Figure 6** shows a typical example of the thermographies made to the furnace shell at (a) the beginning and (b) the end of the reduction stage. At the beginning of the reduction process, we can clearly see that there is a higher temperature on the molten bath surface at the area next to the furnace mouth. This is produced by the projection of the burner flame over the slag bath, which due to its physical characteristics present a high viscosity at the beginning of the process, acting this liquid as an isolating layer by not permitting the heat to pass through the slag layer. At the end of the reduction stage, a better thermal distribution of the generated heat can be observed. This is due to the decrease of the slag viscosity enhanced by the magnetite reduction.

The above-described observations re-confirm the concept of a semi-continuous operation of the furnace. This operational scheme, possible to be reached by constantly maintaining inside the furnace a slag with less magnetite content, would allow:

- (i) A better distribution and profitability of heat generated by the burner.
- (ii) A better thermal homogeneity in the bath.
- (iii) A longer duration of refractory material

#### IV. INDUSTRIAL SCALE TESTS OF SEMI-CONTINUOUS REDUCTION

Based on conclusions obtained from the characterization of the reduction kinetics of slags, semi-continuous reduction tests were designed. The concept of the tests was to maintain all the time a low viscosity slag inside the bath in order to:

- (i) Increase the magnetite content in levels ranging from 4~7% adding small amounts of fresh Teniente Converter slag (13~18%  $\text{Fe}_3\text{O}_4$ ).
- (ii) Increase stirring inside the bath and improve thermal and reductant distribution.
- (iii) Increase of reductant efficiency.
- (iv) Increase the liquid fluidity and decrease the superficial tension, to improve magnetite-CO buoyancy.

The above mentioned effects can be reached with a partial and timely withdrawal of reduced slag and settled metal, leaving inside the furnace the metal-slag interface, which causes the difference of copper contents detected between sampling in hot and the corresponding land field sampling.

##### 1. Experimental design

Three perforations were made on the upper part of the Teniente slag cleaning furnace in order to carry out sampling of liquid material inside the bath during the reduction stage.

Additions and partial withdrawals of 1 to 2 slag ladles were performed during the reduction stage in order to maintain a constant magnetite content of about 7% inside the bath. Iso-kinetics measurements were conducted in parallel to characterize gases generated during the process.

##### 2. Results

These semi-continuous reduction experiences were performed with partial additions and withdrawals of 1 or 2 slag ladles. **Table N° 3** presents a comparison of main production indicators of batch and semi-continuous slag reduction. Even though, disturbances derived from the interference with the smelting-conversion processes did not allow reaching planned productivity, results obtained under this operational scheme allowed concluding that:

- (i) The productivity of the semi-continuous treatment of the slag is clearly superior to that of the batch process. While the batch process needs to be fully charged before starting the reduction process, the semi-continuous process only requires partial additions and extractions of slag throughout the process.

- (ii) The presence of more fluent slags during the whole reduction process in a semi-continuous process allows a better contact between the reductant and the magnetite. This is reflected in a lower consumption of the reductant.
- (iii) Reduction time for two ladles of slag is close to 15 minutes.
- (iv) The semi-continuous operation strategy practically does not require a sedimentation stage subsequent to the reduction.
- (v) Copper recovery increases in the semi-continuous process. This is mainly because the emulsion phase is kept inside the furnace.
- (vi) There is a big similarity between the “hot” and “cold” copper content of the slags.

**Table 4** presents the results of the isokinetics measurements carried out for the batch and semi-continuous strategy. Particulate emissions decreased from 1300 mg/Nm<sup>3</sup> for the batch case to 350 mg/Nm<sup>3</sup> for the semi-continuous case.

### **3. Redefinition of the operation parameters for the reduction stage**

The results obtained in the semi-continuous reduction tests permitted the redefinition of the operational parameters for the reduction process. The immediate effect was the reduction of the reductant consumption from 7.4 to 3.9 kg per ton of processed slag. This procedure contributed to decrease particulate emissions in more than 70%. In the same way, the reductant injection pressure was reduced in order to increase the reductant residence and diffusion times inside the slag bath. This also permitted to reduce the reductant consumption, and pollution together with an increase of the bath temperature and a decrease of the reduction times.

The implementation of the semi-continuous cycles permitted to reduce in a 50% the reduction cycles.

The reduction efficiency, that in a batch process was very difficult to control, mainly due to the slag heterogeneity, is now a days a totally manageable parameter and it ranges between 75 to 80%. Larger reduction efficiency results in magnetite levels lower than 4% in the final slag. On this reduction level, the co-reduction phenomenon of iron and copper and the formation of carbon-iron compound prevent a thorough distribution of the reductant in the molten bath

## **V. - CONCLUDING REMARKS**

The development achieved by the Teniente slag cleaning process in the last decade has permitted to position this technology in the world copper market with highly competitive indexes. This is the reason behind the successful implementation of the process not only at the Caltones smelter but also in other domestic smelters of Codelco-Chile and abroad.

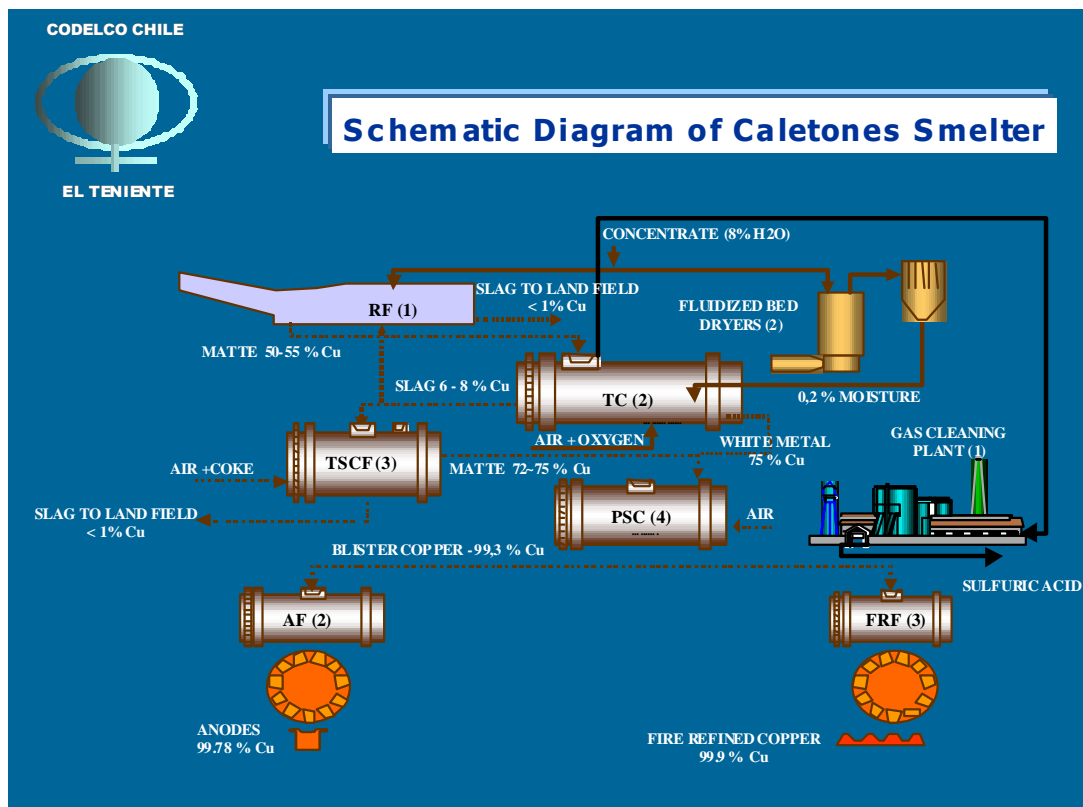
Basic and applied research conducted by the Caletones smelter has allowed the implementation of a series of modifications in the slag cleaning process, thus improving the reactor performance and transforming it into a highly competitive market option compared to similar technologies.

The subsequent step in the development of this technology is the design and implementation of a continuous operational scheme, represented by **Figure 7**. In this scheme, the matte produced in the Teniente Converter will be processed to obtain blister copper through a continuous conversion process performed in the Peirce-Smith converters while slag generated in the Teniente Converter will be continuously fed to be processed in the Teniente slag cleaning furnaces.

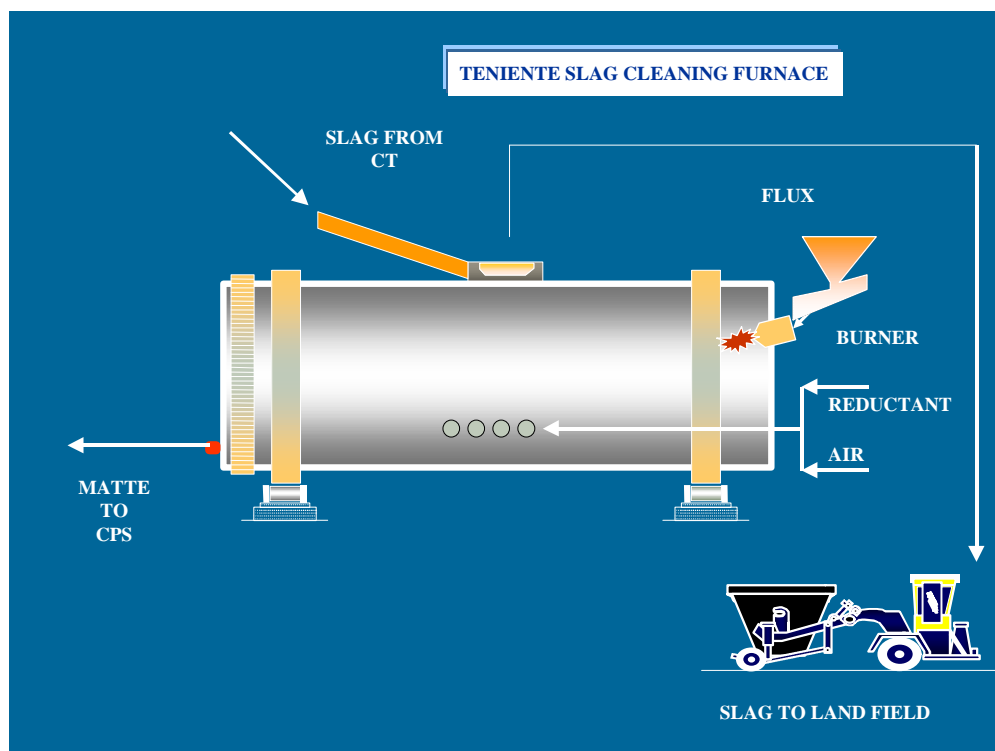
At this stage, new efforts in basic and applied research will be required in order to clarify aspects related to the thermodynamics, kinetics and fluo-dynamics of the slag cleaning continuous process.

## VI. - REFERENCES

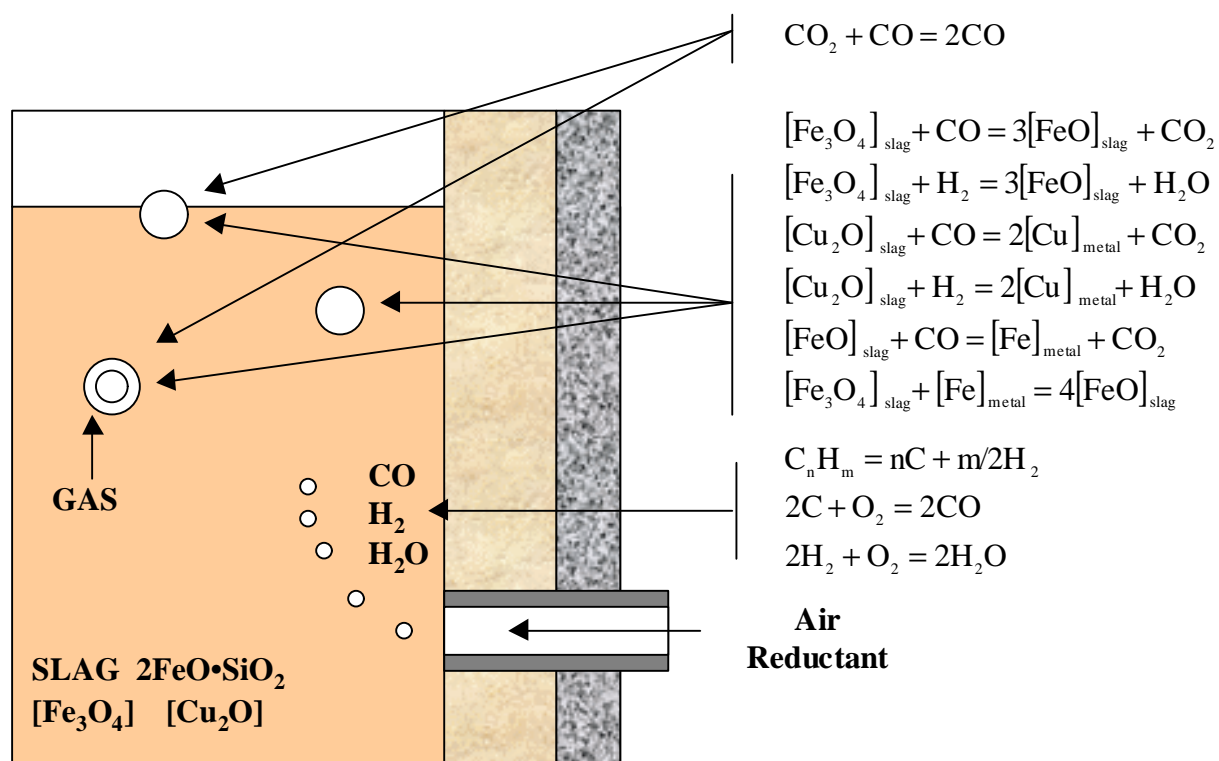
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- [3] D. J. Min and E. J. Fruehan, *Metall. Trans. B*, Vol. 23B, 1992, p. 29-37.
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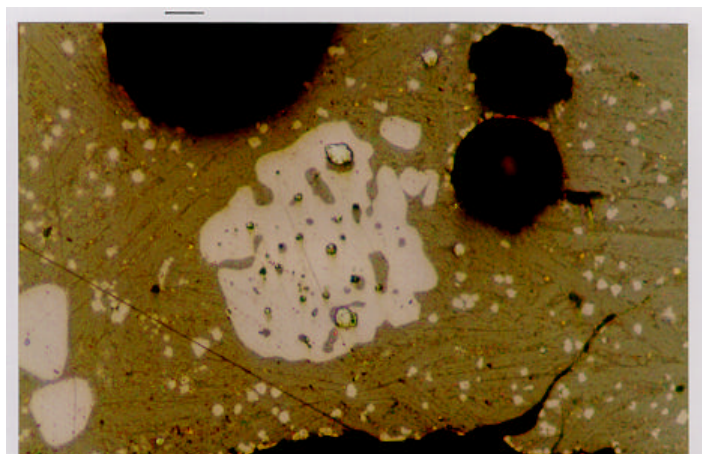
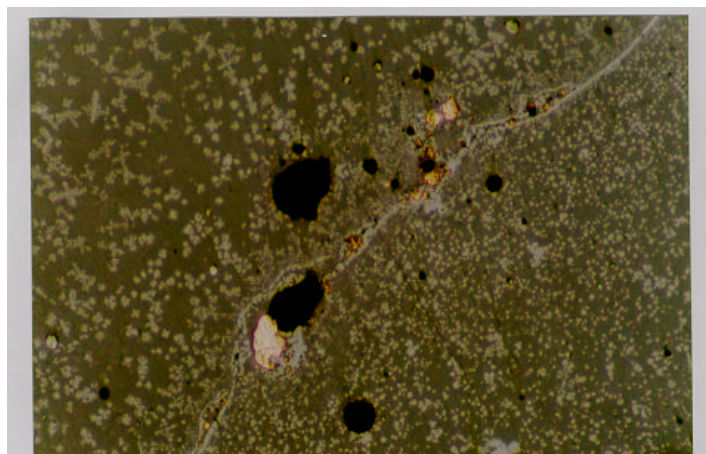
**Figure 1.-** Schematic Diagram of Caletones Smelter ( RF: Reverberatory furnace, TC: Teniente Converter, TSCF: Teniente Slag Cleaning Furnace, PSC: Peirce-Smith Converter, AF: Anode furnace, FRF: Fire refining furnace).



**Figure 2.-** Teniente slag cleaning furnace schematic diagram

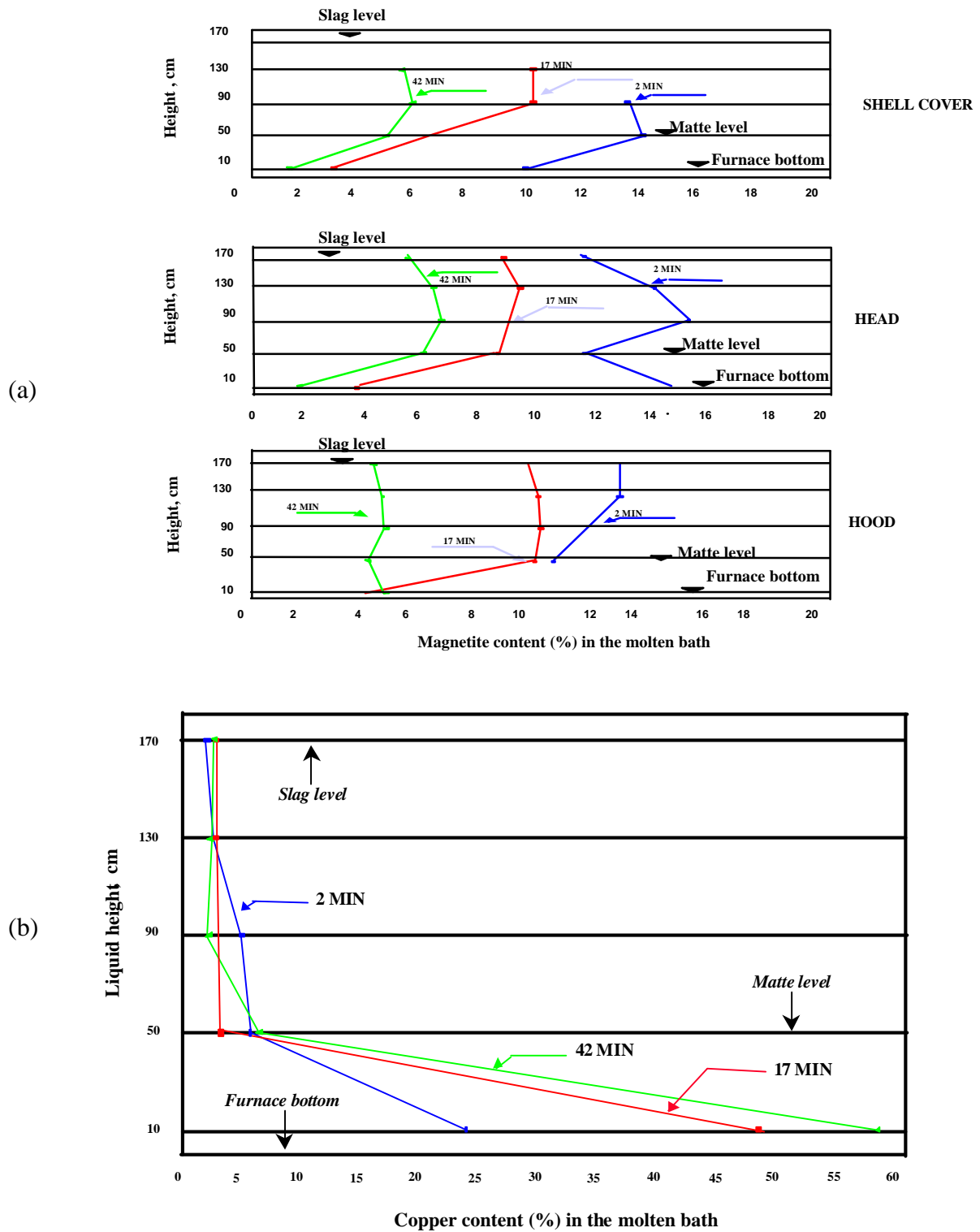


**Figure 3.-** Slag reduction mechanism

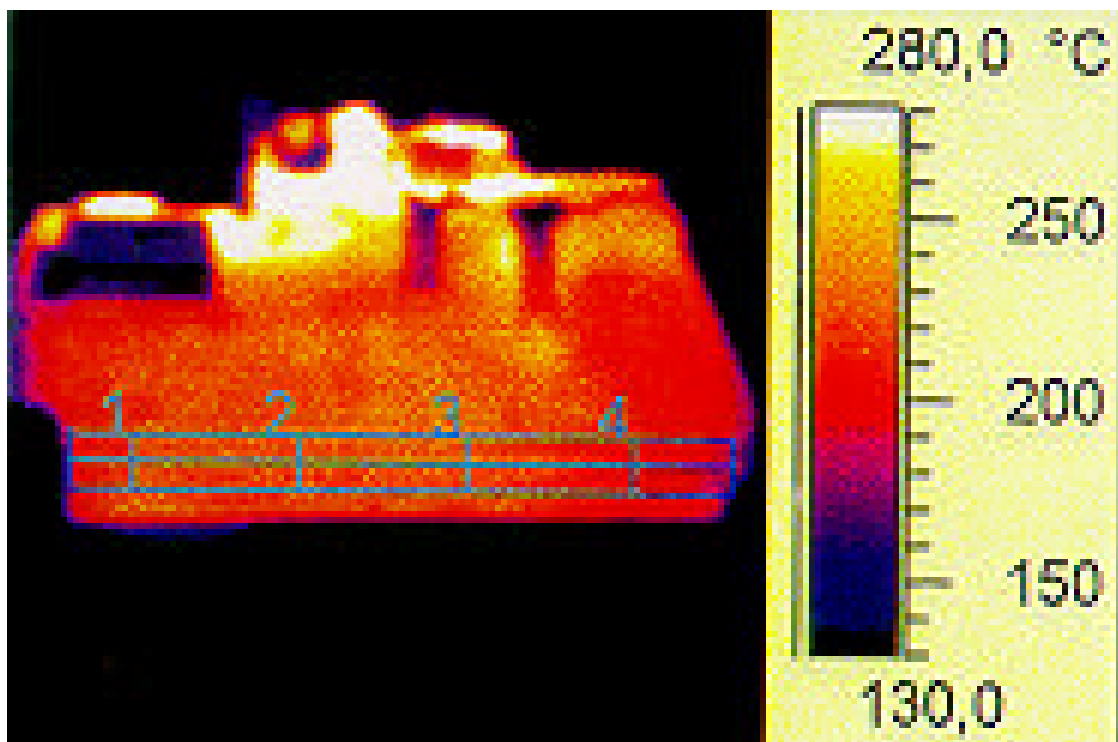


Sample A-23 (a) 1 cm = 42 μm and (b) 1 cm = 21 μm

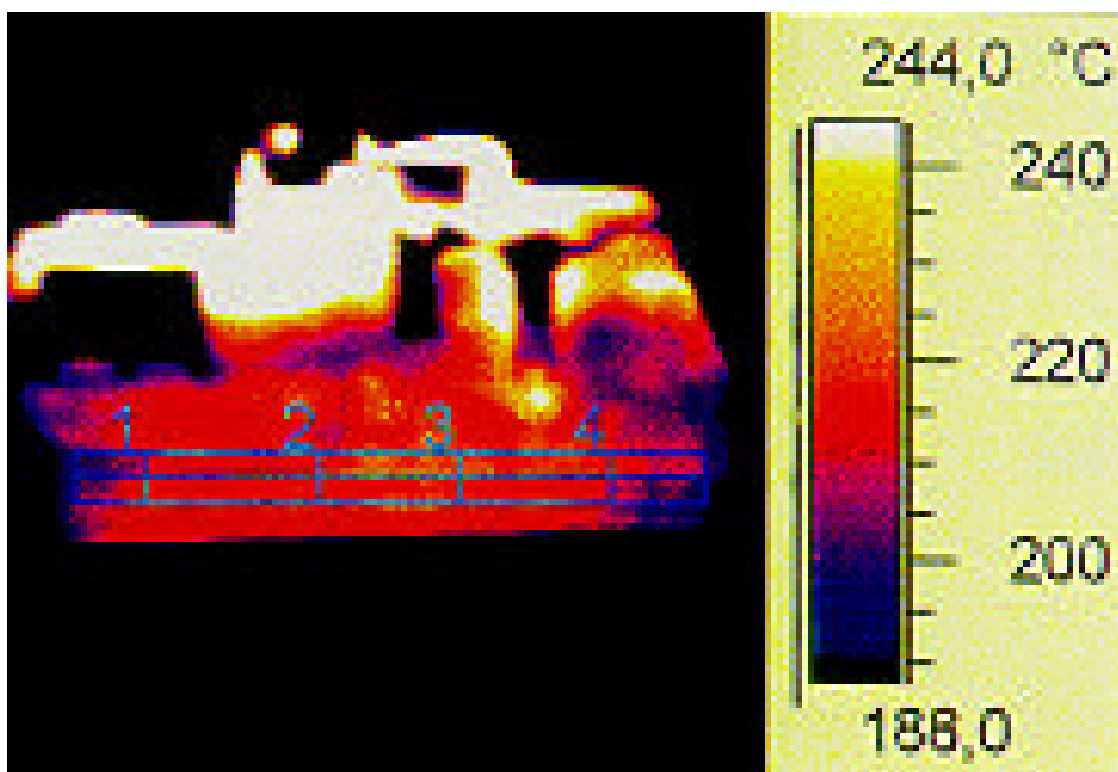
**Figure 4.-** Typical microscopic structure of Teniente Converter slag



**Figure 5.-** Vertical and longitudinal dynamic chemical composition of (a) magnetite and (b) copper in the molten bath.



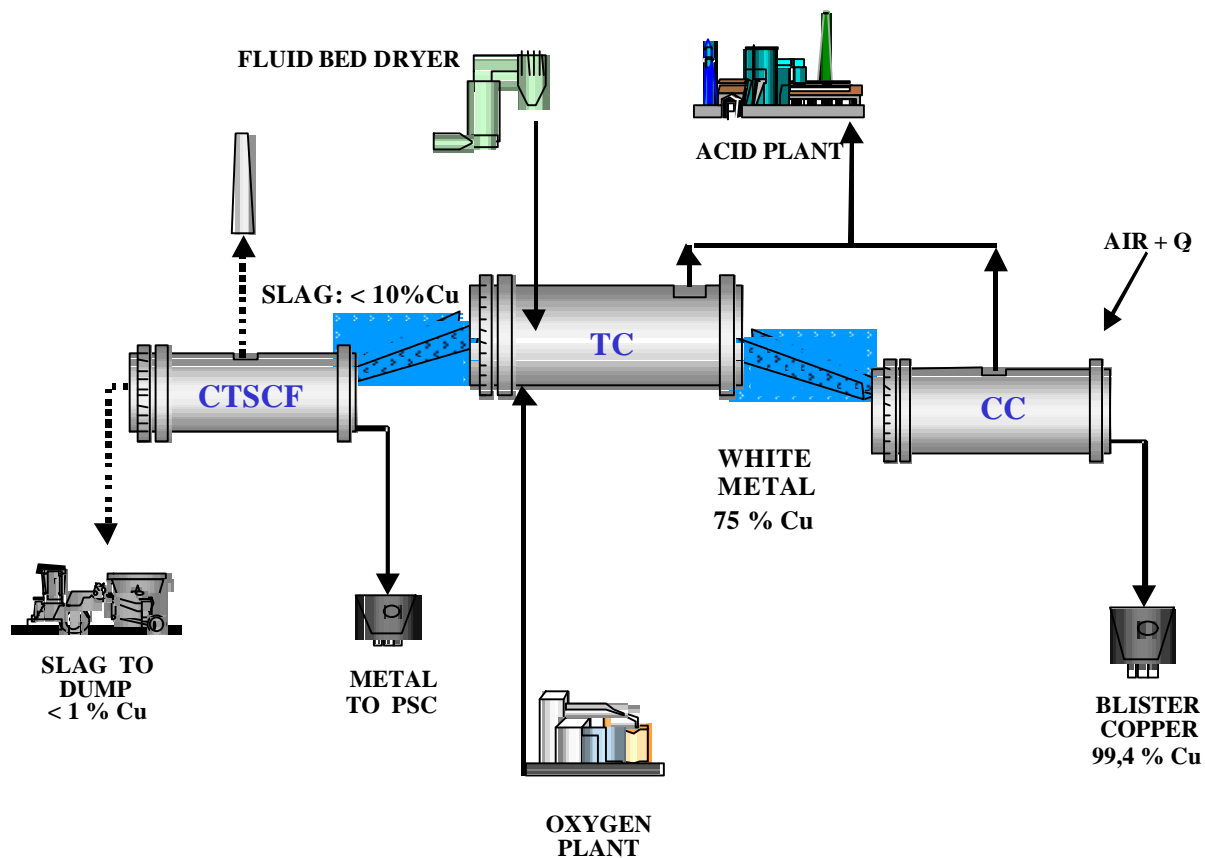
(a)



(b)

**Figure 6.-** Thermographic mapping of the furnace at the (a) beginning and (b) end of the reduction stage.

## FUTURE TENIENTE TECNOLOGY



TC: TENIENTE CONVERTER

CTSCF: CONTINUOS TENIENTE SLAG CLEANING FURNACE

CC: CONTINUOS CONVERTER

**Figure 7.-** Future Teniente Technology

**Table 1. - Main production parameters at the Caletones Smelter.**

<b>Projected operational parameters (base case year 2000)</b>		
➤ Smelting capacity	➤ 1,258,000	ton/year
➤ Copper production	➤ 383,000	ton/year
➤ Sulfuric acid production	➤ 1,200,000	ton/year
➤ Copper recovery	➤ 97.3	%
➤ Sulfur fixation	➤ 94.0	%
➤ Fuel consumption	➤ 33.5	kg/ton of dried concentrate
➤ Energy consumption	➤ 340.0	kWh/ ton of dried concentrate

**Table 2. - Main conclusions reached in the industrial scale experiences developed during the second stage of the slag cleaning process optimization .**

<b>Main Conclusions</b>
➤ The control techniques developed for burner handling permitted to improve the quality of gases generated in the slag cleaning process.
➤ Reduction times decreased from 110 to 40 minutes due to (i) coke addition over the bath (pre-reduction by adding slag to the furnace) and (ii) to the burner control.
➤ A skimming taphole located under the burner mouth permitted matte tapping before slag extraction. This technique reduced the uncontrolled copper losses in the slag.
➤ Preliminary tests with enriched air injections permitted to visualize the possibility of reducing slag in less than 30 minutes.
➤ Re-circulation of white metal conversion slag and fire refined slag has a negative effect in the operation of the Teniente Converter and in the Teniente slag cleaning furnace by increasing the oxidized copper content in the slag to be processed.

**Table N° 3.- Comparison between batch and semi-continuous slag reduction**

Process Indicators	Batch	Semi-continuous		
		Two laddles	One laddle	Two laddles
Date		25 to 30/06/98	13 al 14/08/98	10 al 13/08/98
Productivity, ton slag/day	775	978	917	974
% Cu in slag (hot sample)	0,9	1.01	0.95	0.76
% Cu in slag (cold sample)	1,77	1.20	0.83	0.78
% Fe <sub>3</sub> O <sub>4</sub>	3,2	4.70	4.5	3.65
Coke consumption, kg/ton slag	7.42	3.87	3.87	3.87
Coke cost US\$ cent/ton slag	0,90	0,51	0,51	0,51

**Batch operation (150 ton)**

Stages	Loading	Reduction	Settling	Unloading	Total
Time, min.	63	92	51	77	283

**Semi-continuous operation (1 laddle addition )**

Stages	Loading	Reduction	Settling	Unloading	Total
Time, min	10	10	10	10	40

**Semi-continuous operation (2 laddles addition)**

Stages	Loading	Reduction	Settling	Unloading	Total
Time, min	15	15	10	25	65

**Table 4.- Particulate material emissions**

Process		Semi-continuous Reduction	Batch Reduction
Particulate material emissions	mg/Nm <sup>3</sup>	355	1.263
Time	Min.	37	51
Gas rate	Nm <sup>3</sup> /h	48.486	42.996