

# CONTINUOUS FIRE REFINING OF BLISTER COPPER

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## ABSTRACT

*Based on a novelty concept of blister copper oxidation and reduction in a packed bed type of reactors the new process of continuous fire refining has been developed.*

*Extensive fundamental research on the kinetic of copper oxidation and reduction, combined with mathematical modeling of the process in the packed bed, showed feasibility of a new process.*

*Laboratory scale installation permitted to carry out continuous refining and demonstrate its advantages.*

*Industrial pilot scale installation, designed capacity 5 t/h, has been built in ENAMI-Poipote smelter. The results showed possibilities of continuous processing of 10-12 t/h of blister copper and production of final copper acceptable for anode casting.*

## INTRODUCTION

Development of continuous copper matte converting processes creates a strong demand for continuous copper fire refining. Copper refining requires two stages: oxidation with slagging of impurities and sulphur removal, and copper reduction before anode casting. So, the continuous process needs two reactors or one reactor with separated zones.

The first continuous refining were in developed at Technical University Berlin [1, 2] based on the principle of separated reverbaratory anode furnace with two zones, where oxidation were carried out by air lances and reduction by lances with reducing flame.

The new concept of continuous fire refining is based on the continuous flow of blister copper through two packed bed type reactors. The principle is shown schematically in Figure 1. Blister copper flows into the first reactor filled with ceramic grains, for example grains of a scrap of chromomagnesite bricks. The copper is dispersed and flows down through the porosity of the packed bed. Three or more tuyers-burners inject air with natural gas into a lower part of packed bed. The ratio of natural gas/air is control in this manner that the oxygen content in combustion gases varies from 5 to 15%.

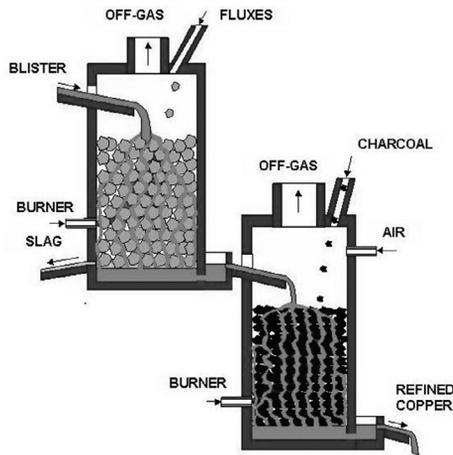
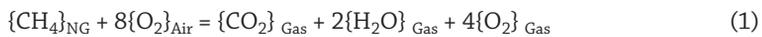


Figure 1: Schematic installation for continuous copper fire refining

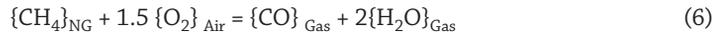
The combustion of natural gas together with the heat of copper oxidation maintain copper temperature at desire level and cover heat losses. The oxygen from combustion gases reacts with copper and dissolved oxygen reacts with sulphur and impurities.



The cuprous oxide and impurities oxides form a refining slag. The motion of blister copper and the increase of its surface area results in very high rate of copper oxidation and

degasification – liberation of sulphur dioxide. Oxidized copper gathers on furnace hearth separating from refining slag. The copper flows out through the siphon and slag is tapped out continuously through the tapping hole in the side wall.

Oxidized copper flows by launder into second reactor filled with packed bed of charcoal. Three or more tuyeres injects the air or natural gas and air into charcoal packed bed. Oxidized copper is reduced by carbon monoxide.



Natural gas and/or charcoal combustion produces heat necessary to cover heat losses and endothermic reactions. The off-gases leaving the charcoal bed of high CO content are post combusted by introduced air. The control of air and natural gas flow allows for precise copper temperature control.

## METHODOLOGY

### Kinetics of Copper Oxidation and Reduction

There are no data in accessible literature on the rate of copper oxidation with combustion gases with low oxygen content. Kinetics of oxidation of pure and blister copper were measured using thermogravimetry. Custom made thermobalance allowed for continuous control and recording of the crucible weight in copper oxidation and reduction tests.

Kinetics of oxidized copper reduction with charcoal was determined as a function of temperature and charcoal grain size using as well thermogravimetry. The liquid copper was oxidized by injection of air through a lance up to the moment of slag formation. The copper sample was taken for chemical assay. Next, charcoal of determined grain size (10% of copper mass) in aluminum foil was dropped onto the liquid copper surface. The reaction tube together with electronic balance inside a plexiglass tube were sealed. Continuous flow of purified nitrogen protected the system against the oxidation.

### Laboratory Scale Simulation of Continuous Fire Refining

The laboratory scale experimental setup for continuous fire refining of capacity 5 kg/h of blister copper is shown in Figure 2. Blister copper was melted in SiN/SiC crucible in upper electric furnace and flew down to SiN/SiC reactor with siphon, slag tapping hole and two tuyeres.

Oxidized copper flew from the middle furnace to lower furnace with SiN/SiC reactor equipped with siphon and two tuyeres. Finally, refined copper flew continuously into receiving crucible outside.

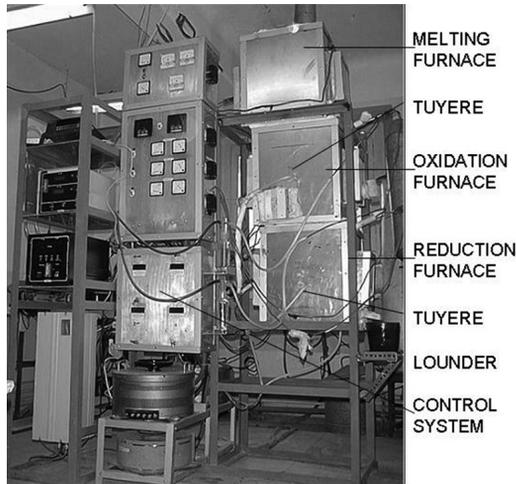


Figure 2: Laboratory installation for continuous fire refining

Copper and slag samples as well as off-gases from oxidation and reduction furnace have been analyzed.

### Industrial-pilot Scale Tests of Continuous Refining

Industrial-pilot scale installation for continuous refining of capacity 5 t/h have been built in ENAMI-Paipote smelter. Schematically the installation is presented in Figure 3.

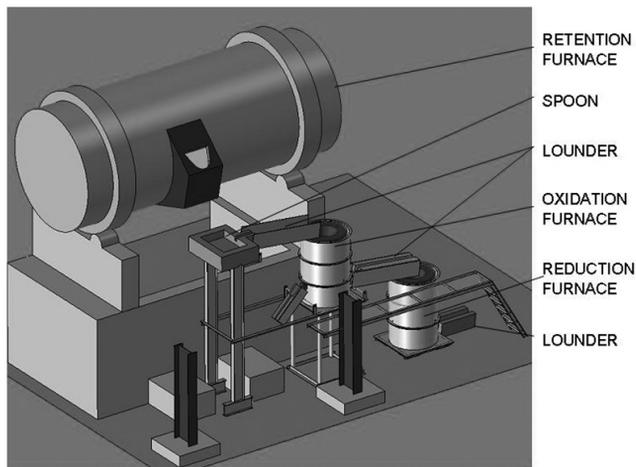


Figure 3: Industrial-pilot installation of continuous fire refining

On the side of a retention furnace (150 t of blister copper) the installation for refining consists of a spoon, oxidation furnace (O.D. 1200 mm, height 1.5 m), reduction furnace (O.D. 1200 mm, height 1.5 m) and connecting lounders.

## RESULTS AND DISCUSSION

### Kinetics of Copper Oxidation and Reduction

Example results of measurements of kinetics of oxidation [3, 4] are presented in Figure 4 and Figure 5. The rate of oxidation is a linear function of oxygen partial pressure pointing out the possibilities of effective copper oxidation by combustion gases.

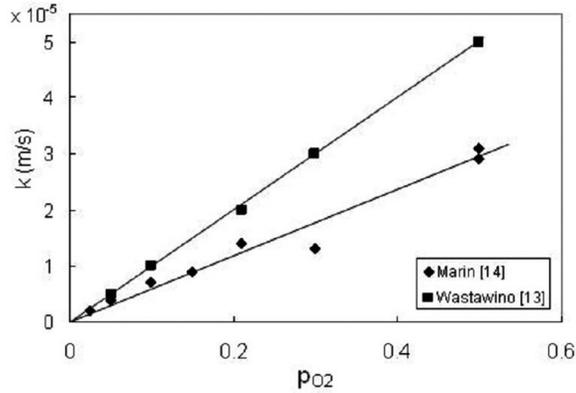


Figure 4: Reaction constant as a function of oxygen content in gas

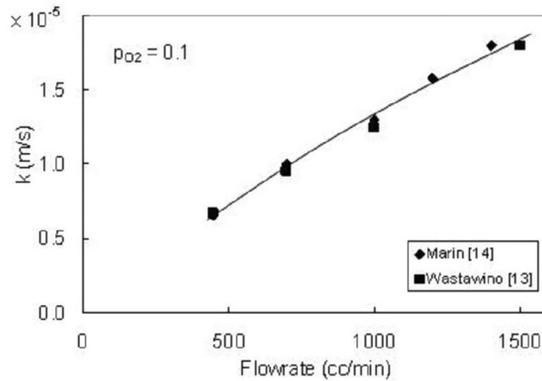


Figure 5: Reaction constant as a function of gas flowrate for 10%  $O_2$  content

The results can be presented in the form of equation, where reaction constant is a function of oxygen partial pressure in oxygen containing gas over a liquid copper surface at 1200°C:

$$k_o = (1.25 \cdot 10^{-6} + 8.41 \cdot 10^{-4} \sqrt{u}) p_{O_2} \quad (10)$$

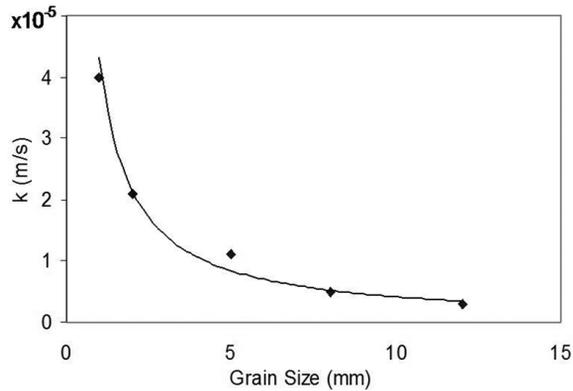


Figure 6: Reaction constant as a function of charcoal grain size

The rate of reduction is a function of charcoal grain size and temperature [5]. The results in Figure 6 can be presented in the form of equation:

$$k_r = \frac{25}{d_c} e^{\frac{160000}{RT}} \quad (11)$$

### Laboratory scale simulation of continuous refining

The example results of continuous copper refining in laboratory scale at blister copper flowrate 5 kg/h in the form of oxygen content in oxidized copper and refined copper is shown in Figure 7. The obtained slag contained approximately 50% Cu, typical for refining process. Oxygen content in reduced copper is about 1500 ppm, satisfying the conditions of anode casting.

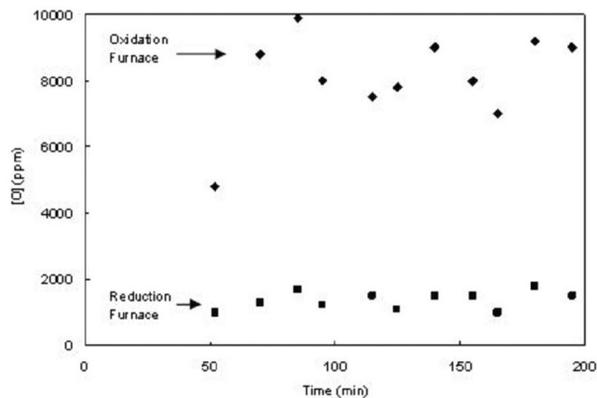


Figure 7: Oxygen content in oxidized and reduced copper versus time

Sulphur content in oxidized and reduced copper is very low (5-10 ppm) in comparison with required 40 ppm. Very efficient copper desulphurization can be related to copper dispersion and increase of surface area enhancing liberation of sulphur dioxide (Figure 8). These properties of copper oxidation in a packed bed are of great importance.

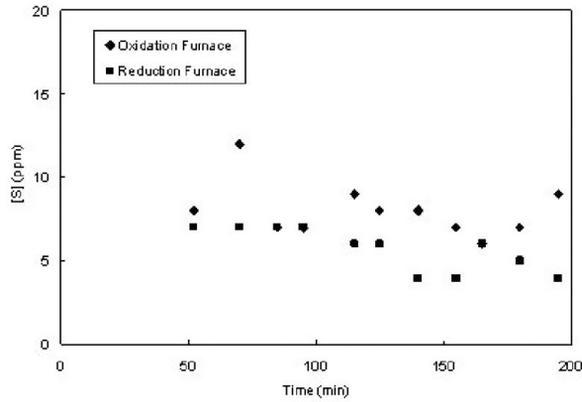


Figure 8: Sulphur content in oxidized and reduced copper versus time

### Industrial-pilot Scale Tests

Photograph in Figure 9 demonstrate the operation of the installation for continuous copper refining in Paipote Smelter. In the front the tapping out and casting of reduced copper from reduction furnace and in the background the post-combustion flame with charcoal charging system can be seen.



Figure 9: Photograph of pilot industrial scale installation during the test

The example results of two tests are presented in Table 1. Test No. 1 shows the copper flowrate  $10^{-12}$  t/h, over two times higher than design capacity (5 t/h). The copper is over-oxidized at the air flowrate  $400 \text{ Nm}^3/\text{h}$  and natural gas flowrate  $10^{-12} \text{ Nm}^3/\text{h}$ . The oxygen content at the beginning is low (748 ppm), later higher due to tendency of forming of a central hole in a charcoal packed bed by a stream of liquid copper. Sulphur content is in acceptable range.

Table 1: Results of industrial tests of continuous fire refining

No.	Blister Flow	Oxidation Furnace				Reduction Furnace				
		Air Blast	Natural Gas	Chem.Assay		Air Blast	Natural Blast	Char coal	Chem.Assay	
				O	S				O	S
		t/h	Nm <sup>3</sup> /h	Nm <sup>3</sup> /h	%	%	Nm <sup>3</sup> /h	Nm <sup>3</sup> /h	kg/h	%
1	12-15	400	10-12	11620	37	150	12-15	65	748	36
				11690	22				3034	23
				12330	12				2609	22
2	5-7	200	14-16	8959	32	150	15-17	45	1778	74
				9176	31				1641	30
				9061	59				1472	62

Test No. 2 with lower copper flowrate shows satisfactory oxygen and sulphur content.

The simple mathematical model of copper oxidation in a packed bed, taking under consideration the reaction constant (Equation 10), system geometry and assumed surface area of ceramic grain being in contact with the liquid copper, allows for calculation of oxygen content and design of the oxidation reactor.

$$[O] = [O]^o + \frac{150\pi D_r^2 H_r \rho_b \beta_b k_o}{d_p F_b} \quad (12)$$

For instance, for required increase of oxygen content from 4000 to 8000 ppm, 10% of oxygen content in combustion gases, ceramic grain size 50 mm, reactor diameter 600 mm, the packed bed height over the tuyeres 1 m is sufficient for oxidation up to 17 t/h of blister copper. The calculated results are close to the tests results (Table 1, No. 1), where 12-15 t/h of blister were oxidized over 11000 ppm of oxygen content.

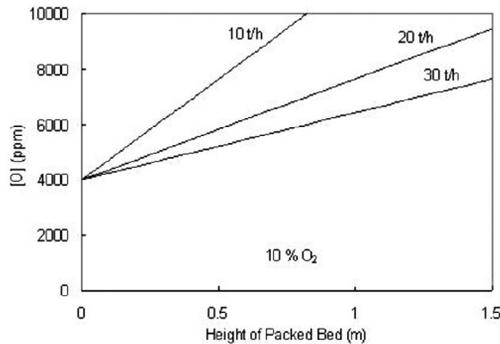


Figure 10: Calculated oxygen content in oxidized copper as a function of packed bed height for various flowrates of blister copper through industrial scale reactor 600 mm in diameter and ceramic grains 50 mm in diameter

In the similar manner the mathematical model of oxidized copper reduction has been developed.

$$[O] = [O]^o e^{-\frac{1.5\pi D_r^2 H_r \rho_b \beta_b k_r}{d_c F_b}} \quad (13)$$

The example calculations are shown in Figure 11. For the same test results, where copper was reduced from 11000 ppm to 1000-3000 ppm at the flowrate 12-15 t/h and bed height 1.0 m, the reasonable agreement can be found.

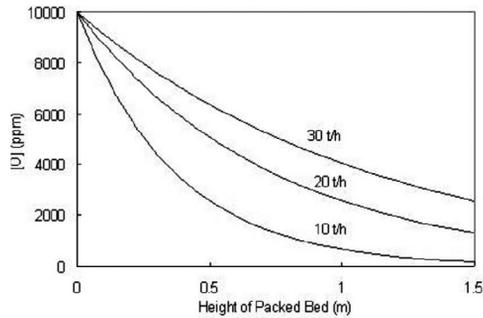


Figure 11: Calculated oxygen content in refined copper as a function of charcoal bed height for various flowrates of copper through industrial scale reactor 600 mm in diameter and charcoal grains 30 mm in diameter

## CONCLUSIONS

The continuous fire refining of copper in a packed bed is a feasible process ensuring the proper copper oxidation, sulphur removal and copper reduction before anode casting.

The dispersion and motion of a liquid copper in a ceramic packed bed increase the gas/liquid reaction surface area resulting in a very high rate of oxidation and copper desulphurization.

Similarly, dispersed copper in a packed bed of charcoal is reduced very fast due to development of reaction surface area.

The installation characterizes simplicity and very low investment cost in comparison to the classical anode furnaces. Thus, two parallel lines, one in operation one in standby, ensure full continuity of smelter operation. Particularly attractive is the operation of continuous fire refining with continuous copper matte converting and twin casting wheels.

## NOMENCLATURE

- $d_c$  = Charcoal grains diameter, m.
- $d_p$  = Ceramic grains diameter, m.
- $F_b$  = Flowrate of blister copper,  $\text{kg s}^{-1}$ .
- $D_r$  = Reactor diameter, m.
- $H_r$  = Height of packed bed (ceramic grains or charcoal), m.
- $k_o$  = Reaction constant of copper oxidation,  $\text{m s}^{-1}$ .
- $k_r$  = Reaction constant of copper reduction,  $\text{m s}^{-1}$ .
- $p_{O_2}$  = Oxygen partial pressure.
- $u$  = Gas velocity,  $\text{m s}^{-1}$ .
- $[O]$  = Oxygen content in copper, %.
- $[O]_o$  = Original oxygen content in copper, %.
- $\beta_b$  = Fraction of surface area contacted with copper.
- $\rho_b$  = Copper density,  $\text{kg m}^{-3}$ .
- $R$  = Universal gas constant,  $\text{kJ mol}^{-1} \text{K}^{-1}$ .
- $T$  = Temperature, K.

## ACKNOWLEDGEMENTS

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## REFERENCES

- Wuth, W., Melcher G., Weigel H.** (Klockner Humbolt Deutz AG) (1977). *Process for Continuously Refining Contaminated Copper in the Molten Phase*. Patent No. ZA7603039, Germany, 1977-04-27. [1]
- Klockner Humbolt Deutz., A. G.** (1978). *Method of Continuous Refining of Impure Copper in the Liquid Phase*. Patent No. GB1525786, Great Britain, 1978-09-20. [2]
- Marin, T.** (2006). *Factors Affecting the Rates of Oxidation and Reduction of Liquid Copper during Fire Refining*. PhD Thesis, Metallurgy and Materials Science, University of Toronto, 2006. [3]
- Wastawino. H.** (2005). *Factors Determining the Rate of Copper Oxidation*. Master Thesis, Universidad de Chile, Departamento Ingenieria de Minas, 2005. [4]
- Puga, H.** (2007). *Kinetic of Copper De-oxidation with Charcoal*. Master Thesis-presented for defence, Universidad de Chile, Departamento Ingenieria de Minas, 2007. [5].