MOLTEN - LAYER REACTOR FOR COPPER SMELTING AND CONVERTING

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ABSTRACT

A novel reactor for smelting or converting is being developed. The reactor makes uses of the intensive reaction layer formed by injecting a concentrate, copper matte or white metal into an oxygen-rich atmosphere, forming a reacting emulsion that flows by gravity along the water – cooled walls of the reactor.

The reactor is flexible an can operate either as a smelting or converting unit. Operating as a smelting unit with copper concentrates of 29.3% Cu and 0.89% arsenic it is possible to obtain a white metal of 78% Cu with less than 0.05% As and a slag with 6% Cu. Operating as a converter with white metal of 62-66% Cu it can produce blister copper with over 98% Cu and slags with less than 8% Cu.

INTRODUCTION

Copper smelting technology is dominated by the Outokumpu flash technology, although with an increasing participation of others new technologies such as the El Teniente and Ausmelt processes. The excisting technology for converting, nonetheless, is almost exclusively done in the old-tech Pierce Smith converters, with their well known shortcomings.

In the flash smelting process as well as in the flash converting, all chemical reactions and heat transfer takes place in the short-lived flame of reacting particles and oxygen emerging from the burner, which last less than 3 sec. In cyclone smelting a similars phenomena takes place, with reactions lasting even less than 2 sec.

In bath smelting the situation is different, since they operate semicontinuosly and all reactions occurs only in the interface gas bubles –molten material like in the El Teniente-bath smelting or in the gas jet immersed in the bath, such as in the Ausmelt process.

In a new concept of reactor for smelting and converting, a different approach has been taken: instead of forming a reacting flame like in flash or cyclone processes or a reacting bath like in Ausmelt or El Teniente reactors, all reaction occurs in a molten layer of material flowing by gravity inside the reactor which allows a reaction time of several minutes of the liquid phase with the gaseous atmosphere, reaching the equilibrium conditions before the metal is separated from the slag. The large reacting surface of the molten layer reacts intensely with the oxygen of the gas phase generating SO_2 and a large amount of heat, which is removed both in the off gases and through the water – cooled walls of the reactor. Due to the low temperature of the reactor wall a solidified layer of blister copper or magnetite it is formed, which protect the wall from erosion and corrosion. In Figure 1 it is shown a schematic representation of the phenomena that takes place along of a reacting molten layer of material.

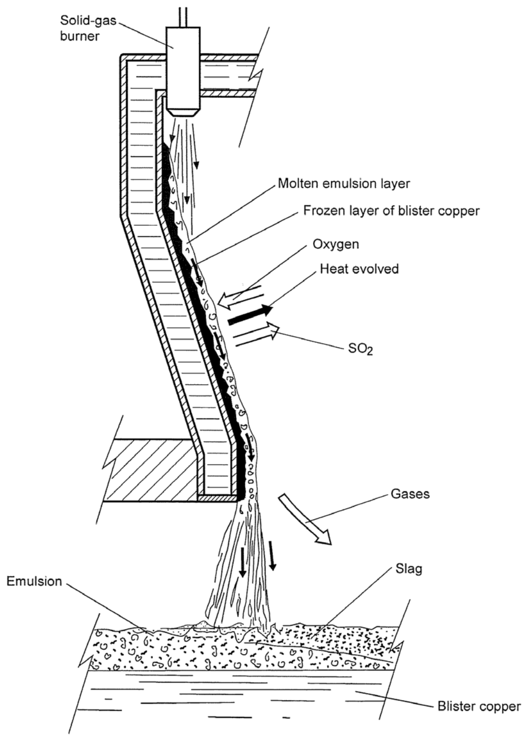

Figure 1: Schematic representation of the pysico-chemical phenomena taking place on a molten – layer reactor wall

The physico – chemistry of the copper matte or copper white metal convertion is fairly well understood, with the secuential oxidation of the iron to wustite and further neutralization to fayalite, followed by the oxidation of copper sulphide to oxide and reduction of it with sulphide to metallic copper:

$$FeS_{(l)} + O_{2(g)} = FeO_{(l)} + SO_{2(g)} \tag{1}$$

$$2FeO_{(l)} + SiO_{2(g)} = 2FeO{\cdot}SiO_{2(l)} \tag{2}$$

$$Cu_2S_{(l)} + 1.5O_{2(g)} = Cu_2O_{(l)} + SO_{2(g)} \tag{3}$$

$$2Cu_2O_{(l)} + Cu_2S_{(l)} = 6Cu_{(l)} + SO_{2(g)} \tag{4}$$

All reactions are exothermic, with a total heat release for a typical white metal of 72% Cu of -83,500 Kcal/ton. For the smelting step, reactions are all well know, and can be found elsewhere while for high-arsenic copper concentrates, for the most common arsenic - bearing mineral (enargite) it decompose to arsenic polysulphides, mainly As_2S_3, according to:

$$Cu_3AsS_{4(s)} \rightarrow 1.5\ Cu_2S_{(l)} + Cu_3AsS_{3(g)} + 0.5S_{2(g)} \tag{5}$$

TECHNOLOGY DEVELOPMENT

To probe the concept, an initial study was done at the University of Concepcion using a small cyclonic-type reactor with a single gas-solid burner. The results were very encouraging [1] and also shows that for this type of reactor, high speed gas-solid injection precludes the formation of a flame from the burner, since clouds of copper and iron sulphides and oxygen (or air) has a propagation velocity of the flame of only 2 to 5 cm/s [2] therefore, reactions takes place on the walls of the reactor rather than in a flame.

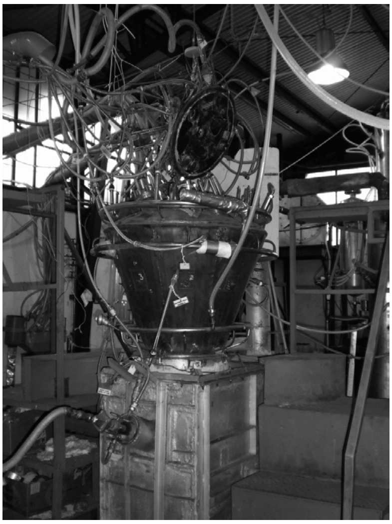

Figure 2: Molten layer convertion reactor mounted over a settler with the cover removed

Figure 3: Molten – layer reactor showing the inner walls covered by a layer solidified blister copper after operation

To develop the technology, a new reactor was designed and operated at pilot scale. The reactor has 45 cm diameter and 75 cm height with three burners installed on the top for copper matte, white metal or copper concentrate. Three central NG burners permit to iniciate the operation and to add additional heat, if required.

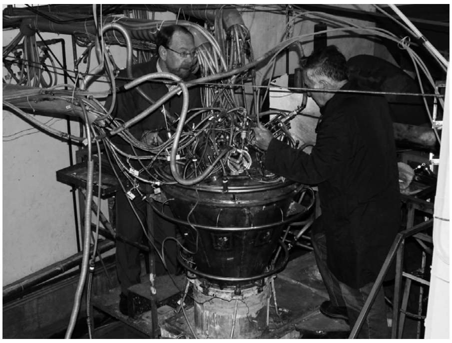

Figure 4: Molten - layer reactor being prepared for a test

The molten emulsion of material and gases discharge to a 55 lt settler where the slag, metal and gases are separated. The feed rate to the reactor was 25 to 30 kg/hr (600-750 kg /day) with a maximum capacity near 1200 kg/day. In Figures 2 to 4 it is shown the pilot installation at the University of Concepción.

EXPERIMENTAL RESULTS

The unit was operated both as a converter to blister copper using low grade white metal and also as a smelter unit using an high-arsenic copper concentrate.

Operation as a Copper Converter

Two white metal materials where tested. Its chemical composition is shown in Table 1.

Table 1: Chemical composition of white metal used (wt-%)

White metal	CuT	Cuox	Cus	FeT	Fe3O4	ST	Insol.
CT2-1	62.10	2.30	59.77	7.28	3.04	15.80	1.25
CT2-2	66.90	0.31	66.59	7.52	2.35	18.04	2.41

The feed was a blend of white metal, lime, silica sand and fluorite, according to a previous laboratory study that determinate the optimal composition of the olivine-type of slag required. Conditions of the test performed are given in Table 2.

Table 2: Experimental conditions of white metal convertion to blister copper

Test N°	White metal	Feed rate (kg/h)	Oxygen (N lt/min)	Average reactor temp. (°C) (±20°C)	Flux (wt-%) (*)		
					CaO	CaF_2	SiO_2
16	CT2-1	23.3	55	1550	2.2	3.1	8.7
17	CT2-1	28.3	45	1540	0	5.0	0
18	CT2-1	29.6	48	1570	0	5.0	0
19	CT2-1	29.8	52	1560	5.0	0	0
20	CT2-1	27.9	52	1570	5.8	5.0	0
23	CT2-2	27.6	66	1550	4.0	5.0	6.9
26	CT2-2	27.7	70	1540	4.0	5.0	6.9
30	CT2-2	27.7	70	1560	4.0	5.0	6.9
31	CT2-2	26.8	67	1560	4.0	5.0	6.9
32	CT2-2	26.7	70	1550	4.0	5.0	6.9
33	CT2-2	28.8	70	1585	4.0	5.0	6.9
34	CT2-2	28.4	70	1585	4.0	5.0	6.9
35	CT2-2	31.8	69	1600	4.0	5.0	6.9

(*) wt-% respect to the total feed

Results of the 13 test are shown in Table 3, and indicate that it is possible to obtain blister copper with 98-98.5% Cu and less than 0.8% S in the converting unit, with slags with less than 8% Cu.

Table 3: Results of reactor operating as a converting unit

Test	Blister copper (wt-%)			Slag (wt-%)			
N°	Cu	$Fe_{(ppm)}$	S	Cu	Fe	CaO	SiO_2
16	98.4	-	0.92	10.4	22.3	7.67	15.1
17	98.9	124	0.10	14.9	18.7	11.0	31.6
18	97.4	1217	0.66	11.7	18.6	10.0	28.0
19	98.0	591	0.54	11.2	18.0	14.5	28.7
20	98.2	166	0.79	10.1	18.1	17.0	28.7
23	94.4	4200	1.30	11.9	22.3	12.1	32.9
26	89.6	1050	0.70	15.8	21.2	11.8	28.9
30	98.3	26	0.90	13.4	22.3	7.7	27.4
31	98.4	31	0.88	12.1	24.6	12.1	32.3
32	97.9	19	1.12	4.3	25.5	14.8	34.4
33	98.8	100	0.54	5.9	21.2	12.6	30.7
34	98.7	104	0.82	7.4	23.4	12.9	28.0
35	98.6	110	0.83	5.6	23.9	11.6	30.0

These results are also shown in Figures 5 to 7 as a function of the reactor operation temperature. Although the span of temperature is rather narrow ($\Delta T \sim 60°C$) its influence appears to be significant, particularly on the copper content of the slag, where viscosity is critical. Nevertheless, the operational temperature of the reactor is only a nominal value, since it does not indicate the actual temperature of the reacting layer, which have a large radial gradient of temperature from the solidified layer of solid blister copper up to the external reacting surface exposed to the oxygen, which approaches to the measured temperature.

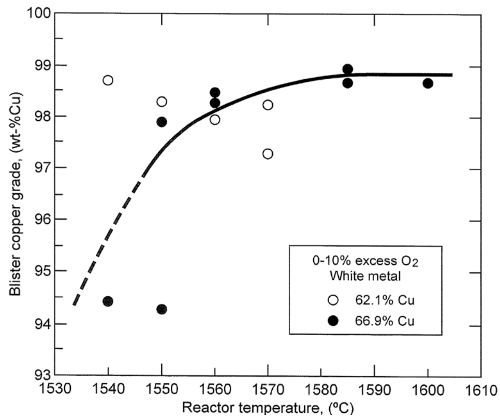

Figure 5: Blister copper grade as a function of the converter reactor temperature

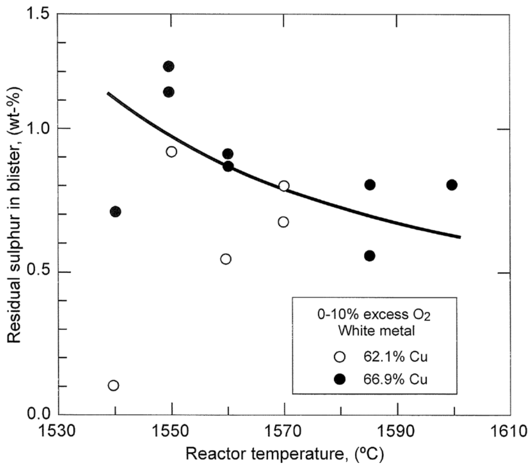

Figure 6: Residual sulphur in the blister copper as a function of the temperature of the converter reactor

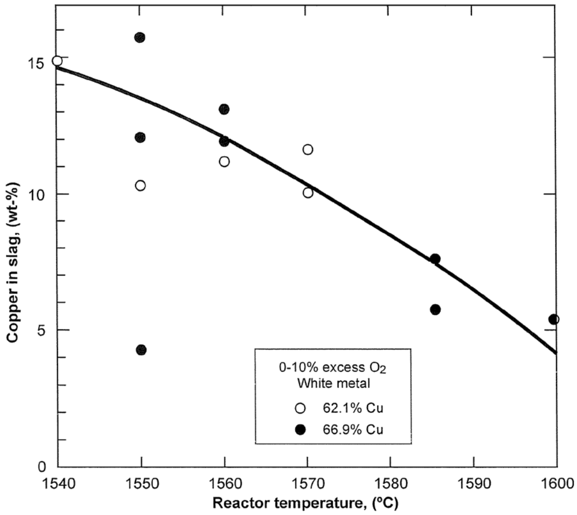

Figure 7: Total copper in slags a function of the temperature of the converter reactor

Operation as a Smelting Reactor

The reactor was also operated as a smelting unit using standard copper concentrate from Chuquicamata´s CODELCO Norte Division. The chemical composition of the concentrate used is given in Table 4.

Table 4: Chemical composition of Chuquicamata copper concentrate tested

Element (wt-%)							
Cu_T	As	S	Fe	Sb	Zn	Bi	Insol.
29.3	0.89	33.1	23.9	0.05	0.5	0.01	10.5

The arsenic was mainly in the form of enargite Cu_3AsS_4. The feed was a blend of 89.2 wt-% copper concentrate, 6.7 wt-% CaO, and 4.1wt-% silica. The feed rate was 19.9 kg/h and the oxygen flow rate 70.7 Nlt/min. The average operation temperature of the reactor was 1600°C, (±20°C). The white metal and slag obtained is shown in Table 5.

Table 5: Chemical composition of the white metal and slag obtained

	Element (wt-%)					
	Cu	As	S	Fe	Zn	Insol.
White metal	77.88	0.05	19.41	0.85	0.003	-
Slag	6.08	0.00	0.62	35.07	-	20.8

As it can be observed, the removal of arsenic was 97.2%, with a high grade white metal produced and a relatively low copper content in the slag.

FUTURE DEVELOPMENT

A larger reactor is being built to demonstrate the technology [3, 4], with a capacity of 5 TPD. The reactor (shown in Figures 8 and 9) will be mounted on a large El Teniente pilot reactor at Chuquicamata smelter, which will operate as a settler.

Figure 8: 5TPD demonstration molten - layer pilot reactor
to be operated at Chuquicamata smelter

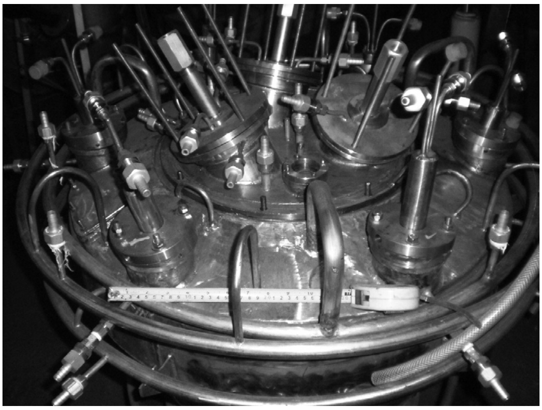

Figure 9: 5 TPD demonstration reactor to be installed in 2009 at Chuquicamata´s
smelter showing the six peripherical copper matte or white metal burners

CONCLUSIONS

The new type of reactor of molten – layer has demonstrated to operate efficiently both as a copper converter to produce blister copper from white metal equivalent to blister produced in conventional P-S converters and also as a smelting unit to process high-arsenic concentrates generating a good quality white metal with a high removal of the arsenic.

REFERENCES

Wilkomirsky, I. & Parra, R. (2003). *Direct Production of White Metal and Blister Copper by Cyclonic Smelting.* Copper´ 2003, Vol. IV, Book No. 2, pp. 47-60. [1]

González, O., Richards & Rivera, J. de D. (2006). *Measurement of Flame Speed in Copper Concentrate Clouds*. J. Chil. Chem. Soc., 51, No. 2, pp. 869-874. [2]

Wilkomirsky, I., Parra, R., Parada, F. & Balladares, E. (2008). *A Continuos Converter Reactor to produce Blister Copper from Matte or White Metal*. Chilean patent application No. 3349-2008. [3]

Wilkomirsky, I., Parra, R., Parada, F. & Balladares, E. (2008). *A Smelter Reactor to Treat Copper Concentrates with High Arsenic Content*. Chilean patent application No. 3350-2008. [4]