RECOVERY OF IRON FROM COPPER FLASH SMELTING SLAGS

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ABSTRACT

Copper slag is produced in large amounts in seven copper smelter plants in Chile, and it is estimated that and around 4 million tons of slag are disposed every year and another 40 to 45 million tons are historically cumulated. Copper slag contains iron in the range of 42 to 45%, which can be recovered and recycled along with the contained copper to obtain an iron-copper alloy and a final slag rich in oxides. Therefore, the present work shows the experimental results of the reduction of a Flash Smelting slag by using coke as reductant up to 150% of the stoichiometric carbon required to reduce copper oxide and magnetite. The characterization and thermodynamic stability of compounds contained in the slag are presented, and the obtained results show the feasibility for recovering an iron rich alloy with iron contents higher then 98%, and copper in the range of 0.6% to 0.8% by using two step process.

Key Words: *Reduction; Copper slag; by-product; copper smelters; iron recovery; zero waste.*

INTRODUCTION

The flash smelting process has been used in copper industry for a number of years and has replaced some conventional copper smelting processes in Chile. The high copper content in the slag in this process, require a further cleaning in an electric furnace. Also, the converter and fire refining slag are recycled to the smelting process to increase the matte grade.

Flash smelting slags are cleaned in an electric arc furnace, where coke is used as reductant and the copper content of the final slag decreases [1, 2]. Also, several practices of recovering metals from slags have been reported [3, 4, 5, 6, 7]. However, copper slags contain other metals with commercial value than copper, such as iron, among others which can be recovered [8]. Thus, the process used to recover metals from slag consisting in reducing the slag at high temperatures with coke as reducing agent can be used to selectively reduce the metallic oxides according to their thermodynamic stability, and metallic phase containing mainly iron and copper is obtained. Therefore, the main objective of this work is to study the feasibility of recovering iron alloy from flash smelter slag and its further refining.

THEORETICAL CONSIDERATIONS

The flash furnace slags are usually fayalitic, and contains metals in the form of silicates and ferrites. Although, copper in the slag is usually ferritic in nature, appearance of metastable copper-iron-sulphide phase is explained by the matte inclusions in the slag. Also, metallic copper has been observed by the microscopic analysis of these slags.

The slag forming oxides, such as silica, alumina and limestone, are stable up to 1600°C approximately, and metallic oxides are expected to be reduced at 1260°C, and therefore separated from the slag forming oxides [9] as shown in Figure 1. At this temperature, considering standard conditions, it is possible the selective reduction of Cu and Fe.

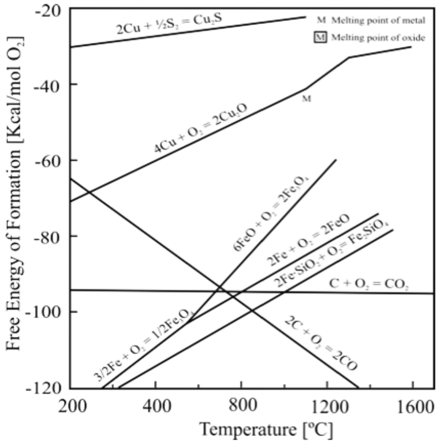


Figure 1: Free energy of formation of copper and iron oxides as function of temperature

In presence of carbon, the copper oxide is reduced to metallic copper and magnetite is reduced to wüstite and then to iron, iron silicate is also decomposed into iron and silica over 1200°C according to the following reactions:

$$Cu_2O_{(l)} + C_{(s)} = 2Cu_{(l)} + CO_{(g)} \tag{1}$$

$$Fe_3O_{4\,(l)} + C_{(s)} = 3FeO_{(l)} + CO_{(g)} \tag{2}$$

$$2FeO{\cdot}SiO_{2\,(l)} + 2C_{(s)} = 2Fe_{(l)} + SiO_{2\,(s)} + 2CO_{(g)} \tag{3}$$

The reduction mechanism of the slag take place in a series of direct and indirect reactions of the oxides with the reducing agent to form a metallic phase and a gaseous CO which also will reduce the metallic oxides, and metal and CO_2 gas will be produced. The presence of carbon fixes the CO/CO_2 ratio in the gas phase at given temperature according to the following reaction

$$CO_{2\,(g)} + C_{(s)} = 2CO_{(g)} \tag{4}$$

The reduction of metallic oxides is controlled by the temperature and the oxygen potential, which is fixed by the CO/CO2 ratio in the system according to reaction (5)

$$2CO_{(g)} + O_{2\,(g)} = 2CO_{2\,(g)} \tag{5}$$

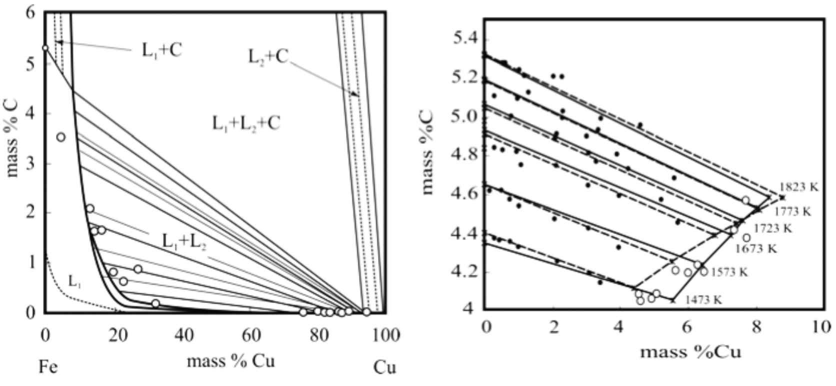
Thus, minor components and oxides such as CaO, MgO and Al_2O_3 contained in small concentration in the slag are not competing with the formation of iron, copper and silica during the reduction processes so that the equilibrium of the Cu-Fe-Si-O-C system can be considered, where the independent variables are temperature and oxygen partial pressure [10]. Therefore, the reactions will proceed in the following order

$$Cu_2O_{(l)} + CO_{(g)} = 2Cu_{(l)} + CO_{2\,(g)} \tag{6}$$

$$Fe_3O_{4\,(l)} + CO_{(g)} = 3FeO_{(l)} + CO_{2\,(g)} \tag{7}$$

$$FeO_{(l)} + CO_{(g)} = Fe(l) + CO_{2\,(g)} \tag{8}$$

At temperatures over 1260°C Cu_2O is reduced at lower CO pressures compared with iron, which required higher CO pressures, in the order of 0.75 P_{CO}/P_T [10], and the iron silicate, where the activity of FeO is approximately 0.4 at 1260°C, will needs even higher reducing conditions as shown in Figure 1.



(a) (b)

Figure 2: Solubility of carbon in the Fe-Cu-C system as function of: (a) copper content at 1723 K and (b) copper content at given temperatures [11]

However, in the presence of carbon in excess and copper, iron forms a Fe-Cu-C alloy. Since, the solubility of carbon in copper is negligible while the melt rich in iron (L_1) dissolves copper and carbon, and its solubility of copper decreases with the increasing of carbon content, as shown in Figure 2 (a). Also, this figure shows the miscibility gap between copper (L_2) and iron (L_1) rich melts. The effect of temperature on the copper solubility of carbon saturated iron melts is shown in Figure 2 (b), and it can be observed that copper concentration increases with temperature up to about 9% at 1823 K.

EXPERIMENTAL

Flash smelter slag was used in this work. After crushing and grinding, the slag was chemical and mineralogical analyzed, and the results are shown in Table 1.

Table 1: The slag chemical and mineralogical characterization

Compound	**Cu_2O**	**Cu_2S**	**FeS**	**FeO**	**Fe_3O_4**	**SiO_2**	**Al_2O_3**	**CaO**	**Other**
Wt%	0.76	2.00	1.17	40.61	12.38	33.00	2.12	0.69	7.27
Element	Cu	Fe	S	Si	Al	Ca	As mg/kg		
Wt %	2.27	41.3	0.83	15.4	1.60	0.49	74		

The experimental work was conducted in a muffle furnace for the slag reduction experiments. High alumina crucibles of 50 mm I.D. cover with a graphite lid and temperature was measured with a Pt-13%Rh thermocouple. A crucible furnace with molybdenum-silicon heating elements was used for the kinetic tests. In a typical run, a cylindrical graphite bar was immersed in the slag under an atmosphere of continuous nitrogen flow, and a steel rod was used for taking samples by submerging it until sufficient slag was adhered for the chemical analysis. In both cases, nitrogen was used to cool down the samples.

RESULTS AND DISCUSSION

The reduction kinetic of copper oxide and magnetite was studied by using graphite rod as reducing agent at 1450°C and a CaO/SiO_2 ratio of 60/40 in the $CaO\text{-}SiO_2\text{-}FeO$ system. The graphite rod was introduced into the melt after 20 minutes of conditioning and samples were taken every 5 minutes during a total time of 50 minutes. The results are shown in Figure 3.

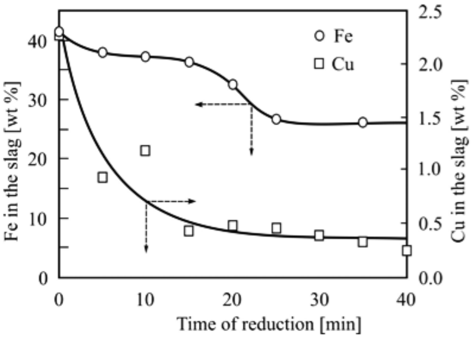


Figure 3: Concentration of copper and iron as function of time

Figure 3 shows the rapid decreasing of copper content in the slag during the first 15 minutes with the graphite rod introduced into the melt, while the iron concentration is maintained almost constant over same period of time, suggesting that a selective reduction according to the thermodynamic stability of both compounds is possible. Also, this figure shows that copper content decreases from 2.3% to 0.5% during the first 15 minutes and to 0.3% in the final slag. The iron oxide reduction start after 15 minutes, when most of the copper oxide has been reduced, and it reaches the lowest value of 27% after 40 minutes of reduction time under these conditions. Therefore, the experimental time for the experimental study was estimated as 50 minutes.

The effect of coke addition referred to the carbon stoichiometric required for reducing magnetite, iron oxide silicate and copper oxide was study under the following conditions; 1450°C, a CaO/SiO_2 ratio of 60/40 in the CaO-SiO_2-FeO system, 50 minutes of time reduction and the slag was cooled off under nitrogen atmosphere. The coke was used in 75%, 100%, 130% and 150% of the required for reducing the Cu y Fe oxides. The results are shown in Table 2, and in this table it can be observed that copper content decreases in the final slag however in the metal phase remain in the range of 6 to 13% suggesting that copper must be also as a separate phase due to the limited mutual solubility between iron and copper under these conditions. Thus, this iron alloy requires a further treatment for decreasing copper to a lower content in the final metal phase.

However, the copper content in the final slag decreases to a minimum value of 0.06% and the iron decreases from 28.53% to 7.11% with the increasing of coke addition suggesting that is possible recover most of the copper content in the slag in the metal phase.

Table 2: Chemical composition of metal and final slag phases as function of coke addition

Carbon addition Wt (%)	**Chemical Composition**					
	Metal		**Final slag**			
	% Cu	% Fe	% Cu	% Fe	% S	%As
75	13.18	82.20	0.24	28.53	0.13	0.03
100	6.6	92.9	0.15	15.94	0.13	0.03
130	7.40	92.2	0.09	9.94	0.17	0.02
150	6.20	93.20	0.06	7.11	0.36	0.02

The final slag and the metallic alloy obtained in the experiment run at 1450°C and 50% in excess over the stoichiometric coke required for reducing copper and iron oxides were analyzed by using a SEM with EDS, and the results are shown in Figure 4. In this figure, several parts of the metal and the slag phases are analyzed, and they are indicated in the crucible placed at the bottom of each picture by a white circle.

In Figure 4 (a), a copper-iron alloy in the lower part of the metallic phase containing 95% of copper is observed, and there are also particles of matte and iron sulfide distributed around the copper alloy. In Figure 4 (b), the central part of the iron alloy containing over 97% of iron is shown, and some particles of matte entrained in the metal phase are also present. The upper part of the metallic phase is shown in Figure 4 (c), and it can be seen a major phase containing mainly iron with minor phases including iron and copper sulfides. The final slag phase contains mainly Si, Ca, Al, O and minor elements commonly present in copper slags as shown in Figure 4 (d). Also, entrained particles of iron-copper alloy are seen in this figure.

The experiments of reduction in two stages; decopperization and a further iron reduction were run under the following conditions: 100% of the coke required to reducing copper oxide and a CaO/SiO_2 ratio of 60/40 were used in the first step which was run during 30 minutes at 1450ºC; the second step was run during 50 minutes using coke addition of

100% and 150% of the carbon required to reduce iron oxide, and the sample was cooled down under a N_2 atmosphere. The results of these experiments are shown in Table 3.

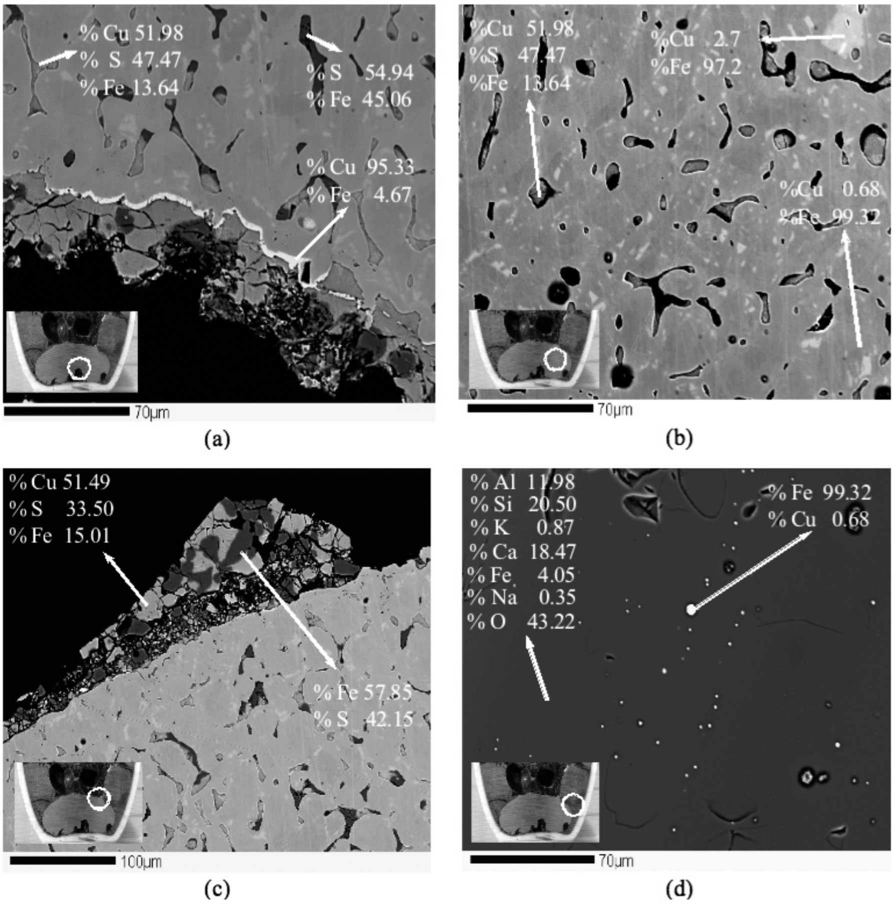


Figure 4: Microstructures of metal and final slag phases: (a) lower part of the metallic alloy; (b) central part of the metallic alloy; (c) upper part of the metallic alloy in contact with the slag phase and (d) final slag phase

Table 3: Composition of the phases obtained during copper and iron selective reduction

Carbon addition Wt%	**1st. step: selective copper reduction**					**2nd. step: reduction to metallic iron**				
	First slag rich in iron			**Metallic phase**		**Final slag**			**Iron alloy**	
	%Cu	%Fe	%S	%Cu	%Fe	%Cu	%Fe	%S	%Cu	%Fe
100	0.32	24.6	0.5	51.0	48.2	0.02	3.8	0.26	1.36	98.0
150	0.20	30.1	0.45	12.2	87.0	0.24	4.2	0.25	0.84	98.9

During the first stage, both iron and copper are reduced and a copper rich metallic alloy is obtained, and on the second stage, a rich iron alloy is obtained. The copper content decreases to 0.24% in the final slag, and to 0.84% in the final metallic alloy. The iron alloy obtained by using 150% of carbon addition was micro-analyzed in order to observe the copper-iron interaction, and the result is shown in Figure 5.

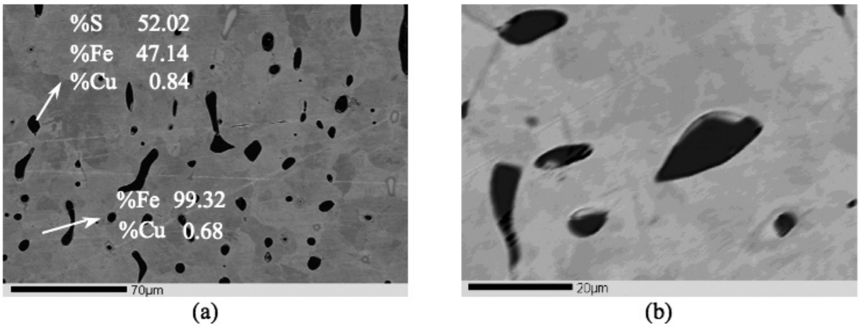


Figure 5: Micrograph of the iron alloy contained 98,9% of iron: (a) 500X and (b) 1600X

In this figure, it can be seen a metallic phase containing 99.32% of iron and 0.68% of copper, which is in agreed with the chemical analysis shown in Table 3, and inclusions of iron sulfides containing 0.84% of copper.

The arsenic distribution was observed during the selective copper reduction, and compared with initial arsenic content in the Flash Smelting copper slag. The results are shown in Table 4.

Table 4: Arsenic distribution during first step of reduction compared with its initial content

Phases	As (ppm)	As distribution (%)
Flash Smelting Slag	74	100
Copper-iron alloy	621	38
First slag: iron rich	22	32
Gas	-	30

The arsenic contained in the Flash Smelting slag is equally distributed among the metal, slag and gas phase however its higher content is in the copper rich metal phase, which is in agreed with high affinity between copper and arsenic.

FINAL REMARKS

The copper content in Flash Smelting slag is selectively reduced with carbon at 1450°C, and its content deceases rapidly in the slag to values in the order of 0.5% while iron content remain almost constant. Thus, iron reduction starts when copper content in the slag is stabilized.

The coke addition is effective for decreasing the copper content in the slag reaching a value of 0.06% of copper in the final slag. However, copper content in the metal phase decreases to 13.18% with 75% of the stoichiometric required carbon addition, and to 6.20% by adding 150% of the stoichiometric required carbon, and it is also observed that copper content remain almost constant around a value of 6% with the increasing of coke addition.

Three phases are observed in the metallic part; mainly an iron rich alloy containing 97% of iron and 3% of copper and a second phase containing 95% of copper and 4% of iron, which is precipitated from the iron-copper alloy under copper saturation condition. A third phase occurs with the presence of sulfur which dissolve copper and iron to form a matte.

To decrease copper content in the iron-copper alloy, two steps are required. The first step to reduce the copper content in the slag and to obtain a copper rich alloy, and the second step for reducing the iron oxide to form a metallic iron rich alloy containing 0.84% of copper, which is one of the lowest obtained values. However, the iron recovery decreases due to the amount of iron dissolved in the first metallic copper rich alloy. Therefore, further experiments must be run in order to increase global iron recovery during the process, and also to decrease the final content of copper in the iron alloy for allowing its utilization in the ironmaking industry.

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