SLAG REDUCTION KINETICS OF COPPER SLAGS FROM PRIMARY COPPER PRODUCTION

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Keywords: Copper Slags, Reduction, Slag cleaning

Abstract

In the classical pyrometallurgical route for copper production from sulphide concentrates, the treatment of slags aims to recover copper through the coalescence of copper metal and copper sulphide particles. To assist with this settling process, a reductant is added to the slag to reduce the spinel precipitated phases (magnetite) in order to diminish the viscosity of the slag. While the impact on viscosity is typically the majority of reports in the literature, there is also the potential to reduce Cu_2O and Cu_2S dissolved in the slag. This can result in improved settling and increased recovery of copper.

An experimental study on the reduction kinetic of industrial slags was done to evaluate the intrinsic rate of reduction of those types of copper slags by methane. The results are compared with the available literature on the rate of reduction for these types of reactions, showing that copper reduction is one the order of magnitude higher than the reduction of FeO, which is the key step of the smelting reduction processes developed in the '80s.

Introduction

The recovery of Cu is a key parameter that impacts on the performance, and therefore, on the business of a smelter. Independent of the technologies used for the smelting and converting steps, all smelters treat their slags so that they are discarded with less than 1% Cu. The recovery process, called slag cleaning, is typically based on the coalescence and settling of copper and copper sulfides particles dispersed in the slag. This is achieved by decreasing its viscosity by increasing the bath temperature and reducing the iron spinel solid phases (commonly known as "magnetite") that increase the apparent viscosity of the slag. The process is usually called a reduction process because of the use of reductant as fuel for temperature control and magnetite reduction. Typically, the reduction does not extend to the reduction of copper, and soluble copper (mainly as oxide) is lost in the slag at concentrations at or above 0.5%.

An alternative to slag cleaning as discussed above is the slow cooling/flotation process where there is some settling of copper and copper sulphide particles followed by the slow cooling of the slag in beds or ladles. The slow cooling promotes precipitation of the particles from solution and the slag can then be milled to recover the copper through flotation. The use of slag

cleaning combined with slow cooling and flotation as an alternative to treat copper slags is more costly but leaves Cu in tailings typically about or below 0.4% - a level not possible from slag cleaning alone. Nevertheless, a detailed evaluation must be done considering the energy cost related to grinding, the use of water, and the availability of tailing dumps. At the same time, the retreatment of the Cu concentrate produced in the mill will displace fresh concentrate, which ultimately results in a reduction of the throughput.

The standard pyrometallurgical process for slag treatment, either in electric or tilting furnaces, could be improved by increasing the recovery of a major fraction of the dissolved Cu in the slag. Despite the evidence that most of the copper lost in discard slag is in the form of dissolved copper [1, 2], reduction of the slag to elemental copper has seen limited research, although there are reasons to suggest that this process could lead to practical recovery of copper from slags.

The work presented here is intended to give proof of principle that is possible to reduce the Cu content of the primary Cu slag with extended reduction. This experimental study used methane as the reductant and the evaluation was done by characterization of the reduced slag and on line gas analysis from the reduction experimental process to determine the rate of reduction of a mix of flash smelting and converter slags (Peirce Smith).

Physicochemical Background

Thermodynamic considerations
The Cu dissolved in the slag is as Cu^+ corresponding to Cu_2O and Cu_2S. The concentration of Cu_2O is significantly more than that of Cu_2S and therefore, the discussion centres around Cu_2O. The reduction will proceed by a competition between the dissolved Cu_2O and the iron oxides in the slag: solid spinel phases (represented by Fe_3O_4, magnetite), Fe_2O_3 and FeO; the last two ones as part of the liquid slag.

The reduction of magnetite is thermodynamically more favourable than for Cu_2O. There are three stages of the reduction, each overlapping slightly with the others. In the first stage, solid Fe_3O_4 and dissolved Fe_2O_3 are reduced to FeO dissolved in the slag. As the Fe_3O_4 becomes exhausted, the reduction of Cu_2O takes over in the second phase. As the concentration of dissolved copper species drops, FeO in the slag will be reduced to iron in the third phase (with still ongoing Cu_2O reduction). The equilibrium that represents this last condition is be written by the following reaction.

$$(Cu_2O)_{slag} + (\underline{Fe})_{Cu} = 2(Cu) + (FeO)_{slag} \tag{1}$$

The expression that quantifies the limit at which the reduction of Cu_2O is overtaken by the reduction of FeO is the following:

$$\frac{\Delta G^o_{(1)}(T)}{RT} < \ln\left(a_{Fe}\right) + \ln\left(a_{Cu_2O}\right) - \ln\left(a_{FeO}\right) - 2\ln\left(a_{Cu}\right) \tag{1}$$

From this relation, the diagram in Figure 1 is obtained with aCu = 1 (the metallic Cu reduced will form a new phase) and by using the Factsage® software and databases for the initial

conditions of a mixture of 80 wt% flash smelting slag and 20% converter slag according to the compositions shown in Table 1. The FeO activity in the slag varies with temperature only slightly (0.42 to 0.44). This diagram can be interpreted by starting at a(Cu_2O) close to 1 (where the activity of Fe in Cu is 1×10^{-4}) and moving up the line to the left as the Cu_2O is reduced from the slag. For example, for an activity of 0.01 Cu_2O in the slag, the equilibrium Fe in the Cu would be less than 1% (aFe in Cu = 0.01). This indicates that while the precipitated copper will have some iron contained in it, if the reduction is done with good control it may be possible to avoid significant precipitation of iron in copper, and certainly avoid iron solid particles in the slag. The phase diagram in Figure 2 shows that there is about 10% Fe than can be dissolved in copper before and iron rich copper alloy precipitation.
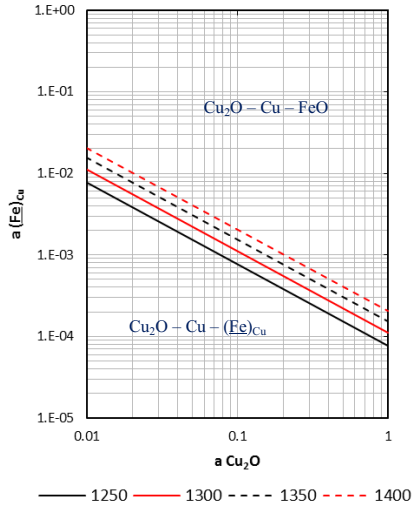

Figure 1. Stability diagram for the reduction of FeO to Fe dissolved in Cu from 1250ºC to 1400 ºC for a composition of 80% of flash smelting slag and 20% of converter slags.
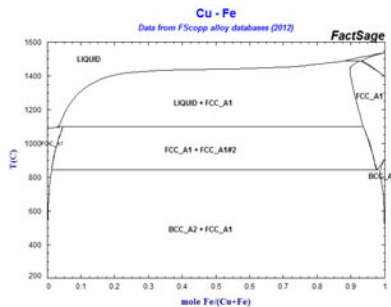

Figure 2. Cu - Fe phase diagram from Factsage® database.

Reduction mechanism

The reduction of oxides from melts has been widely studied in the field of iron production. Figure 3a [3] is a good summary of the measured rate of reduction of FeO with different reductants in different types of slags. In most of the cases, it was shown that the reduction follows a first order reduction with FeO content in the slag. The equivalent information for the reduction of Cu_2O from slags is scarce. A good summary was done in a Masters thesis from the Helsinki University of Technology [4] where a simulation of the co-reduction of Cu^+ and Fe^{+3} is developed from the literature review for slags with 1.5 wt% of Cu_2O and 11% wt% of Fe_2O_3 (Figure 3b) using graphite as reductant. Unfortunately, this simulation does not mention the size of the solid reductant.
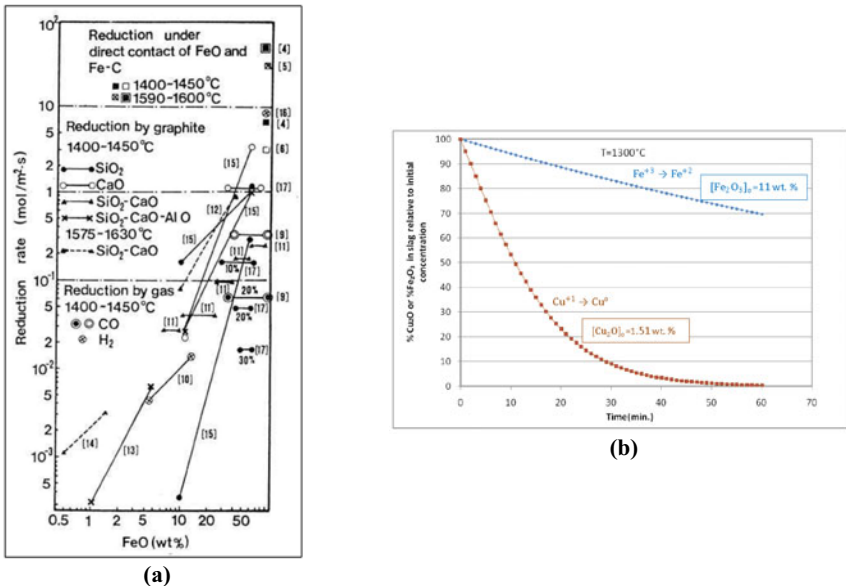

(a)

(b)

Figure 3. Comparative kinetic information for the reduction of FeO and Cu_2O. (a) Rate of reduction of FeO by different reductants, slags and temperature [3]. (b) Simulation of the kinetic of reduction of Cu_2O to Cu and Fe_2O_3 to FeO [4].

A study using graphite as reductant [5] reports that the reduction of Cu_2O to Cu in a fayalite slag is about 1 to 10 moles $Cu_2O \times m^{-2} \times s^{-1}$, that is around 1 ton $\times m^{-2} \times hr^{-1}$. This result is almost one order of magnitude higher than the reduction of FeO in similar conditions. It was shown that the rate of reduction is first order with respect to Cu_2O concentration in the bath with a constant of 4×10^{-3} s^{-1}. The same study shows that for CO as reductant and similar slag characteristics the reaction is first order with CO partial pressure with rates of 0.5 moles $O_2 \times m^{-2} \times s^{-1}$. In both cases the rate of reduction is at least one order of magnitude higher than the one for FeO. Those studies were done with slags at high Cu content (more than 10 wt% of Cu at the beginning), so they represent only a reference to compare with the study reported here where the content of Cu is below 2%.

Experimental Study

Characterization of the slags

The slag used from this study was taken from the Chagres Smelter, north of Santiago, Chile. The analysis reported does not considered the sulphides trapped in the slag. The blend used for the experiments was 80% flash smelting slag and 20% converter slag.

Table 1: Characterization of slags.

Constituent	Flash	Converter	Flash normalized	CPS normalized
Fe_3O_4		13.57%		13.42%
Fe_2O_3	8.39%		8.32%	
FeO	49.77%	52.97%	49.38%	51.74%
Cu_2O	1.31%	3.31%	1.30%	2.94%
SiO_2	29.61%	30.90%	29.38%	30.56%
Al_2O_3	6.40%	0.35%	6.35%	0.35%
CaO	1.90%	0.30%	1.89%	0.30%
MgO	1.10%	0.20%	1.09%	0.20%
Na_2O	2.20%	0.30%	2.18%	0.30%
ZnO	0.10%	0.20%	0.10%	0.20%
	100.78	101.11	100.00%	100.00%

Methane reduction set up

The set-up for the reduction is shown in Figure 4. The on line IR gas analyzer allows for tracking of the $CO_{(g)}$ and $CO_{2(g)}$ content in the gas during reduction. The experimental conditions of the inlet gas were such that the reducing gas flow was always far in excess to ensure that there was no control by mass transfer in the gas phase. For each mole of C that reacts (and forms $CO_{(g)}$ or $CO_{2(g)}$) two moles of $H_{2(g)}$ are produced, which in turn will reduce the reactive oxides from the slag. The calculation of the $H_2O_{(g)}$ formation allows an online determination of the total amount of oxygen released from the bath ($CO + CO_2$ is analysed), and this corresponds to the reduction of Cu_2O and Fe_2O_3 or Fe_3O_4.

The experimental set-up was complemented by a sound recording sytem to follow the breaking of bubbles on the surface, which gives a count of the number of bubbles over a certain time. The gas flow injected into the system and the off gas composition, allowed for a mass balance to estimate the outflow from the reactor. Knowing, for a period of time, the number of bubbles breaking on the surface and assuming uniform size and shape, the area of bubbles can be calculated, and so on the associated total area, which is assumed for the calculations as the reactive area. Although this approach assumes thatthe bubble shape and size are uniform during ascent, it allows an estimation of the order of magnitude of interfacial area, (the coalescence of two bubbles of the same size will result in a loss of 1/3 of the area of the initial two bubbles). An example of the signal and its treatment is shown in Figure 5.
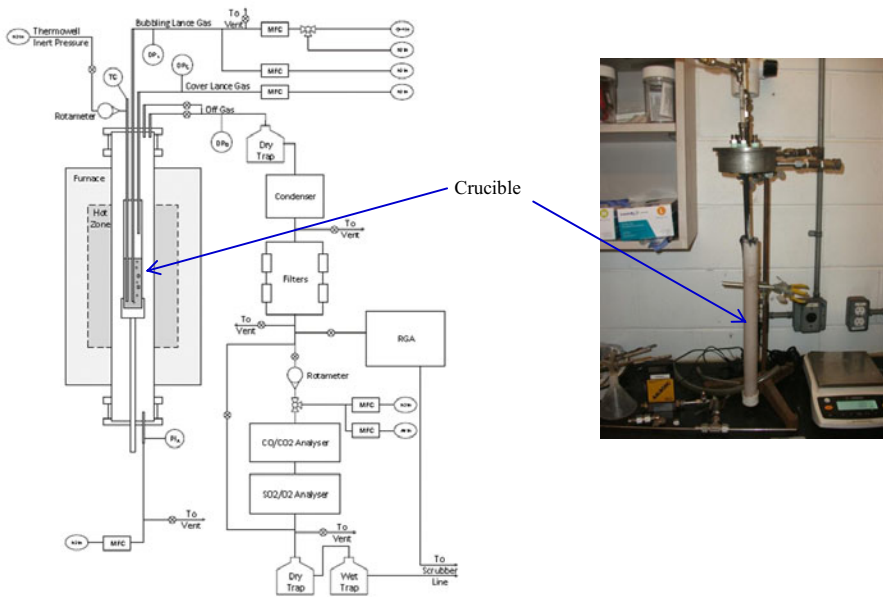
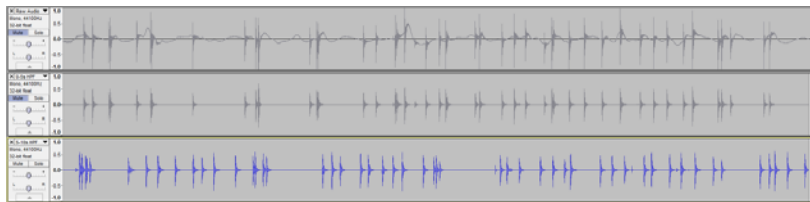Figure 4. Set-up for reduction study.

Figure 5. Audio signal of the bubbling produced during the $CH_{4(g)}$ reduction allowing the quantification of number of bubbles. Each pulse in the blue line represents a bubble.

Results

Methane reduction

The dynamic mass balance allows for a measurement of the oxygen released from the bath and thus provides for a calculation of the slag composition. In a first part, a parallel reduction process was considered producing FeO from the reduction of precipitated and dissolved Fe^{+3} compounds (solid Fe_3O_4 and dissolved Fe_2O_3) and Cu from Cu_2O. Once those reactions were modelled, some experiments were extended to push the reduction to reduce FeO to Fe. Figure 5 illustrates this type of calculation for experience Nº3 (Table 2).
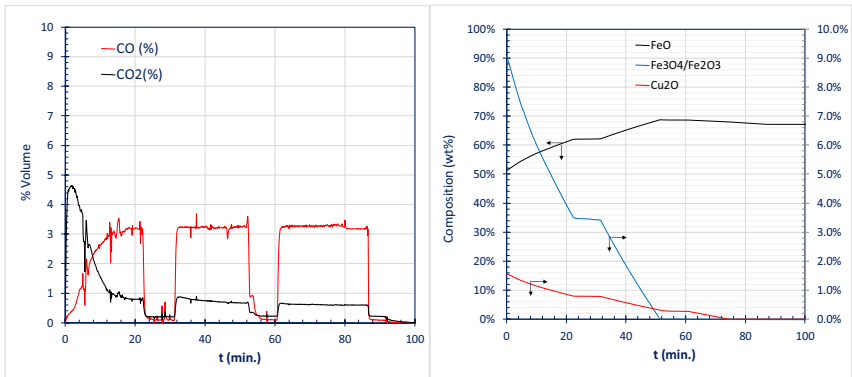
Figure 5. Gas composition of out gases and slag composition estimated from the mass balance using this composition (Test 3 in Table 2).

Table 2: Results for rate of reduction.

Test	Slag	$CH_{4(g)}$ (ml/min)	$N_{2(g)}$ (ml/min)*	dnO/dt (mol/min)	Bubbles area in 1 min. (mm²)	Specific rate of reduction (mol O×m⁻²×s⁻¹)
1	FSF - CPS	120	80	2.00×10^{-2}	9386	3.55×10^{-2}
2	FSF - CPS	220	80	1.50×10^{-2}	11818	2.12×10^{-2}
3	FSF – CPS + CaO	120	80	1.50×10^{-2}	9386	2.66×10^{-2}
4	FSF - CPS	60	60	9.00×10^{-3}	6724	2.23×10^{-2}
5	FSF - CPS	60	60	7.00×10^{-3}	6724	1.74×10^{-2}
6	FSF - CPS	60	60	7.00×10^{-3}	6724	1.74×10^{-2}

(*): $N_{2(g)}$ has used to ensure a neutral atmosphere during the eating and melting of the slag. The lance has also a design where the $CH_4(g)$ was injected shrouded by $N_{2(g)}$.

Microstructural characterization of solidified phases after reduction.

The reduced slags were analysed using electron microprobe to establish the microstructural characteristics of the oxides phases in the slag and also the metal produced. It can be concluded that the reduction of the slag effectively permits a virtually complete reduction of Cu_2O. Likewise, it can be seen that as the Cu_2O becomes exhausted, the metal is enriched with Fe at a non-negligible level. The following figures show those results.
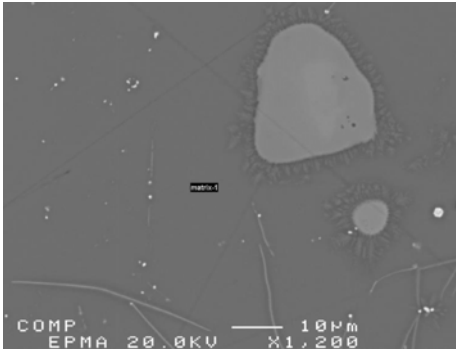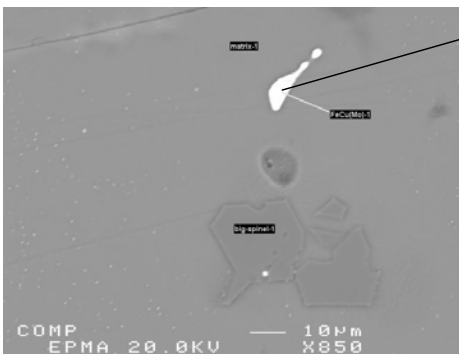
Na₂O	0.135	0.187	0.193
MgO	0.206	0.148	0.211
K₂O	0.367	0.375	0.390
Cu₂O	0.183	0.213	0.200
SiO₂	37.66	37.60	37.58
Al₂O₃	17.49	17.35	17.59
CaO	0.225	0.241	0.249
FeO	43.61	43.90	44.01
Total	100.08	100.20	100.60

Figure 6. Matrix composition for test Nº 5 (Table 2).
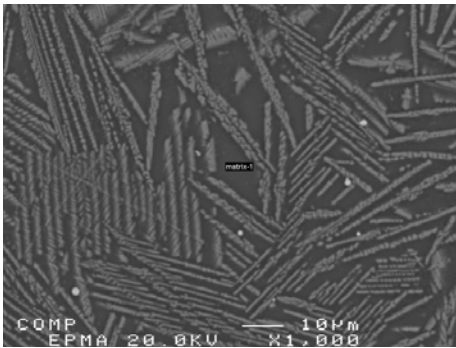
Na₂O	1.427
MgO	0.175
K₂O	1.354
Cu₂O	0.081
SiO₂	52.28
Al₂O₃	20.59
CaO	3.087
FeO	20.06
Total	99.63

Figure 7. Matrix composition for test Nº 3 (Table 2).

	S	Cu	Fe	Total
	0.015	8.330	91.04	99.53
	0.000	8.860	89.90	99.66
	0.034	8.980	89.80	100.37

Na₂O	1.002	1.002	0.977
MgO	0.881	0.873	0.931
K₂O	1.236	1.210	1.260
Cu₂O	0.079	0.110	0.123
SiO₂	37.04	37.15	37.16
Al₂O₃	18.69	18.74	18.93
CaO	1.610	1.605	1.628
FeO	38.87	38.79	38.54
Total	100.21	100.37	100.35

Figure 8. Matrix and metal composition for extended reduction, test Nº 2 (Table 2).

Conclusion

The reduction rates measured in this study were in the order of 0.02 mol $O{\times}m^{-2}{\times}s^{-1}$, higher than those reported for FeO. This result is aligned with the comparative data for reduction rates between Cu_2O and FeO reported in the literature. As for gaseous reduction of FeO (H_2 and CO), the rate of reduction of Cu_2O with CH_4 is comparatively low compared to the one obtained with graphite: 0.02 v/s 1 to 10 mol $O{\times}m^{-2}{\times}s^{-1}$.

In the case of slag with higher content of Cu_2O, the rate of reduction with CO appears to be far superior to that obtained with CH_4 (0.5 v/s 0.02 mol $O{\times}m^{-2}{\times}s^{-1}$), however it is also reported that the rate of reduction is 1st order with Cu_2O concentration in the slag, (possible control by mass transfer in the slag), which explains very well that having slag with as low contents of Cu as used in this study the rate must be lower.

The process conceptualized from this experimental study should consider that the use of the reductant in a first stage is determined by a co-reduction of Cu_2O and Fe_2O_3 / Fe_3O_4. The reduction can be extended to achieve a complete reduction of Cu_2O, leaving a slag with Cu_2O as low of 0.15 wt%.

In the perspective of a complete reduction, beyond the Cu_2O limit, one can conclude that there is no intrinsic physical chemistry limitation to produce pig iron and copper. In this case the remaining oxides of the slag could be fluxes in a similar way that the operation of a blast furnace does, obtaining a co-product available to be used as component of Portland cement. It should be noted that the operating temperature must be controlled at a higher level that guarantees to be in 100% liquid area of the Fe-Cu phase diagram, to prevent the formation of metallic Fe solid accretions.

References

1. The Physical Chemistry of Copper Smelting Slags and Copper losses at Paipote Smelter. Part. II: Sampling and Mineralogical characterization, N. Cardona, P. Coursol, J.C. Vargas and R. Parra. Can. Met. Quart., Vol 50, N°4, December 2011, pp 330 – 340.
2. Nubia Cardona, Aporta al estudio fisicoquímico de las pérdidas de Cobre en escorias de procesos de producción primaria de cobre. Doctorate Thesis, Univesity of Concepción, August 2011.
3. Masanori Tokuda & Saburo Kobayashi, Process Technology Conference Proceedings, ISIJ, 1988, pp 3-11.
4. Fiseha Tesfaye Firdu, Kinetics of Copper Reduction from Molten Slags, Master of Science Engineering Thesis, Helsinki University of Technology, August 2009.
5. "Direct Reduction of Copper-Iron-Silicon Melts", R. Parra, M Allibert & I Wilkomirsky, 4th Internation Conference Copper 99, TMS, Phoenix, Arizona, USA, October 10-13, 1999.