

Kinetics of the conversion of copper sulfide to blister copper^(*)

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Abstract The desulfurization of copper sulfide by air and oxygen has been studied in two laboratory reactors where the gas is blown onto the melt surface. Rates of oxidation in a vertical resistance furnace may be explained by the mass transfer control in the gas phase. However, results for a horizontal tube suggest that the chemical resistance is controlling.

Keywords Desulfurization kinetics. Oxidation of copper sulfide. Mass transfer in copper converting.

Cinética de la conversión del sulfuro de cobre a cobre blister

Resumen La desulfuración del sulfuro cuproso con aire y oxígeno se ha estudiado en dos reactores de laboratorio, en los cuales el gas se sopla sobre la superficie del fundido. La velocidad de reacción en un horno de resistencias verticales se puede explicar considerando como controlante la resistencia a la transferencia de materia de la fase gas. Sin embargo, los resultados del horno horizontal indican que la resistencia química es la controlante.

Palabras clave Cinética de desulfuración. Oxidación del sulfuro cuproso. Transferencia de materia en un convertidor de cobre.

1. INTRODUCTION

Pyrometallurgical processes produce the greater part of primary copper. In the conventional procedure, concentrated sulfide ores are treated in blast, reverberatory, electric or flash furnaces to obtain a low to intermediate grade matte which is blown to copper metal in converters.

Copper matte converting is carried out by cycles of matte oxidation in a horizontal bubble reactor, the Peirce-Smith converter. The operation proceeds in two stages. In the first one, the iron in the molten matte is oxidized and forms a slag with silica. Simultaneously sulfur is oxidized to dioxide. The second stage is the copper-making stage: copper sulfide is desulfurized, giving off white metal which is blown to crude metal (blister copper).

Most models to describe the copper pyrometallurgy have been developed assuming that smelters and converters are in thermodynamic equilibrium. This simplification allows compositions to be calculated from a set of mass balances and equilibrium equations. Nevertheless, kinetic-based models are necessary for a better

understanding of copper smelting and converting^[1].

The kinetics of copper converting has undergone some study at laboratory scale, especially for the oxidation of copper sulfide, since it is relatively simple. Moreover, it is the main transformation in the second stage. This reaction was first studied by Ajersch and Toguri in a capillary tube^[2]. Other workers have carried out this reaction by blowing an oxidating gas in a crucible with samples of molten sulfide^[3-6]. Most of the results have been explained considering that the oxidation was controlled by the gas-phase mass transfer^[4-6]. However some of the investigators have suggested that chemical resistance may be controlling as well. Furthermore, calculated mass transfer coefficients when gas control is assumed are very much greater than those proposed by Joshi and Sharma^[7 and 8] for horizontal bubble reactors.

It is likely that these fundamental discrepancies may be explained bearing in mind that the contact between the phases can be different. Our work is focused on the effect of the type of contact, using the oxidation rates of copper sulfide obtained in

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reactors without submerged lance but with a different flow pattern.

2. EXPERIMENTAL

Raw materials were copper sulfide supplied by Aldich and gases (air, oxygen) of commercial purity. Data of the desulfurization rate of copper sulfide were obtained in two equipments which included a reactor, a gas analysis system and a flowmeter for the gas.

One of the devices is similar to that used^[6] (Fig. 1). The reactor consisted of a vertical resistance furnace, with a reaction tube of recrystallized alumina where an alumina crucible was set. Samples of molten copper sulfide were held in the crucible. A lance positioned at the center of the reactor tube introduced the inlet gas.

The second furnace (Fig. 2) is a horizontal ceramic tube with one end isolated by a stream of argon and the other one connected to a vacuum pump. Gas flows on the surface of molten copper sulfide held in an horizontal crucible. Operation conditions for both reactors are given in table I.

Measurements of SO₂ in the off-gas by absorption in hydrogen peroxide solution are directly related to the conversion of copper sulfide, x. Since the interfacial area between molten sulfide

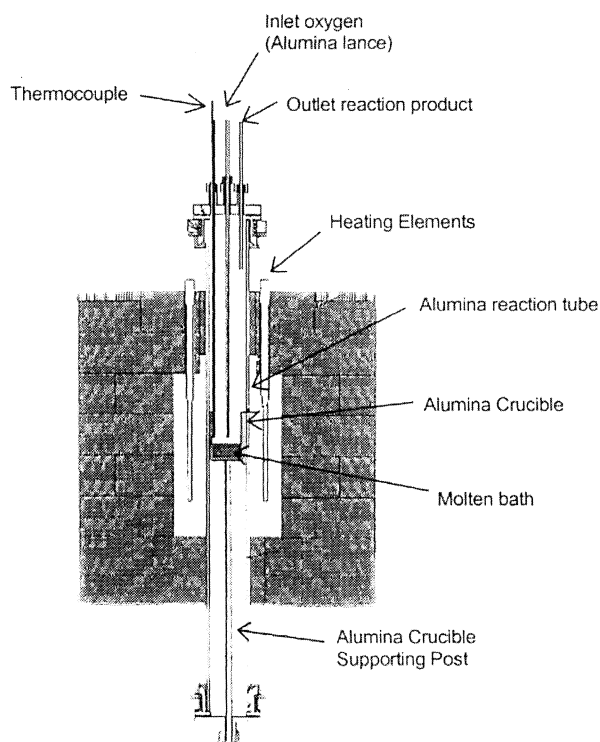


Figure 1. Cross-sectional view of the vertical furnace.

Figura 1. Sección transversal del horno vertical.

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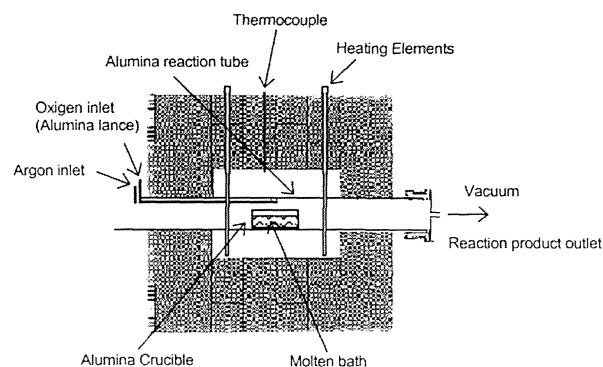


Figure 2. Cross-sectional view of the horizontal furnace.

Figura 2. Sección transversal del horno horizontal.

Table I. Experimental operating conditions

Tabla I. Condiciones experimentales de operación

Variable	Vertical furnace	Horizontal furnace
Temperature, °C	1150, 1200, 1225	1150, 1200, 1250
Pressure, atm.	3	1
Gas	Air	Air, Oxygen
Gas flow, m ³ /min·10 ³	1, 2, 3	1
Samples of sulfide, g	50	1
Interfacial area, m ² ·10 ³	1.452	0.283

and gas is known, values of oxidation rate (u) as a function of time (θ) may be deduced,

$$u, \left(\frac{\text{mol Cu}_2\text{S}}{\text{surface G-L} \cdot \text{time}} \right) = \frac{1}{A} \left(\frac{N_0 - x}{\theta} \right) = \frac{1}{A} \left(\frac{(\text{mol SO}_2)_{\text{off-gas}}}{\theta} \right) \quad (1)$$

This rate is the ratio between the driving force of composition (P) and the overall resistance. Namely, the sum of diffusion resistances in gas and liquid, which are expressed in terms of mass-transfer coefficients k_G and k_L and the chemical resistance, linked to the specific reaction rate k .

$$u = K \cdot P = \frac{P}{\frac{1}{k_G} + H \left[\frac{1}{k_L} + \frac{1}{k C_L^n} \left(\frac{a}{\epsilon_L} \right) \right]} \quad (2)$$

3. RESULTS

The fraction of Cu₂S converted to copper is deduced from the accumulative weight of sulfur in off-gas, shown in figures 3 (vertical furnace) and 4 (horizontal tube).

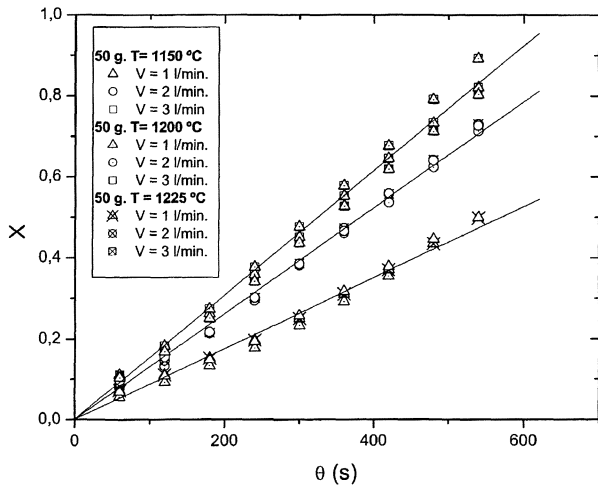


Figure 3. Experimental data for the vertical furnace.

Figura 3. Resultados experimentales del horno vertical.

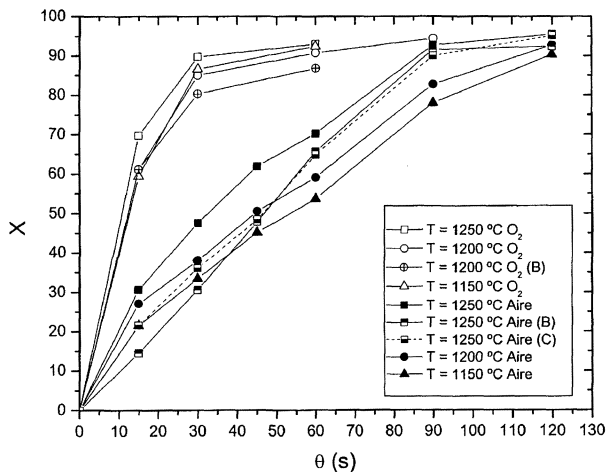


Figure 4. Experimental data for the horizontal furnace.

Figura 4. Resultados experimentales del horno horizontal.

In light of these experimental results several dependences can be established. For the vertical furnace:

- The conversion of the sample is a linear function of time.
- The influence of temperature is negligible.
- There is a strong dependence of the gas flow.

For the horizontal furnace:

- The conversion varies with time, but it is not a linear function.
- There is a small, but non-negligible, influence of temperature.
- There is an increased conversion as the oxygen content in gas increases.

The different shape of the function $x = f(\theta)$ implies different kinetics. In the vertical furnace (x/θ) and oxidation rates are constant for each flow and any temperature. So, the desulfurization rate is mainly dependent on gas flow and a simple relationship for the variation of (x/θ) with the gas flow rate may be proposed, as is shown in figure 5.

Where:

$$\log\left(\frac{x}{\theta}\right) = -0.668 + 0.52 \log v_G \quad (3)$$

This agrees with the hypothesis that mass transfer in gas is controlling. In this case,

$$u \approx k_G \cdot P \rightarrow k_G \propto v_G^{0.52}$$

being K_G the gas-side mass transfer coefficient, in $\text{mol}/(\text{m}^2 \text{ s atm})$. The dependence of the flow rate is smaller than in Alyaser and Brimacombe (they found a power 0.79) or Kikuchi *et al.* (0.66-0.76) [6].

In the horizontal reactor the gas diffusion cannot be controlling, given the non-linear relation between conversion and time. Of course, an overall resistance without negligible individual resistances may be proposed, but it is worth to trying a more simple dependence, with a unique significant coefficient.

In order to consider the importance of the mass transfer in the molten phase, an additional experiment was carried out in the horizontal tube, varying the thickness of the melted sulfide. As it is shown in table II, conversion is inversely proportional to the thickness of molten phase.

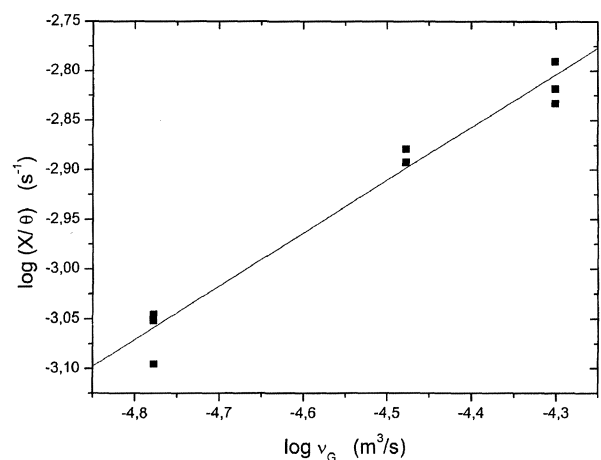


Figure 5. Variation of the Cu_2S conversion as a function of the gas flow.

Figura 5. Variación de la conversión con el flujo.

Table II. Experiences with different hickness of melt

Tabla II. Experiencias a diferentes alturas de fundido

L, mm	1.5	2.15	4.15	6.2	7.7
Conversion	0.940	0.700	0.540	0.390	0.330

This means that the diffusional mass transfer in the phase may be neglected. Consequently, the chemical resistance must be important, even controlling, in the horizontal tube. Therefore, from equation (2):

$$u = \frac{P}{H} k C_L^n \left(\frac{a}{\epsilon_L} \right) \quad (4)$$

Assuming first-order kinetics for the limiting reactant (Cu₂S) and bearing in mind that:

$$C_L \left(\frac{a}{\epsilon_L} \right) = \frac{N}{V_L} \frac{V_L}{A} = \frac{N}{A} = \frac{N_0(1-x)}{A} \quad (5)$$

$$u A = N_0 \left(\frac{\partial x}{\partial \theta} \right) = k \frac{P}{H} N_0(1-x) \quad (6)$$

$$\frac{\partial x}{1-x} = \frac{k}{H} P \partial \theta \quad (7)$$

k and H are constant for isothermic conditions. Hence,

$$-\ln(1-x) = \frac{k}{H} P \theta \quad (8)$$

As can be seen in figure 4, a reasonable fitting of data is achieved when $-\ln(1-x)/P$ is plotted versus θ . The following relationship is obtained:

$$-\frac{\ln(1-x)}{P} = 0.4855e^{-\frac{2907}{T}} \cdot \theta \quad (9)$$

k and H are both dependent of temperature, but the influence on k should be much greater. Neglecting the change in H, activation energy can be calculated. Its low value (24 kJ/mol) is not very different than other reported in literature (Jalkanen, 10.5 kJ/mol; Bryukvin, 16 kJ/mol).

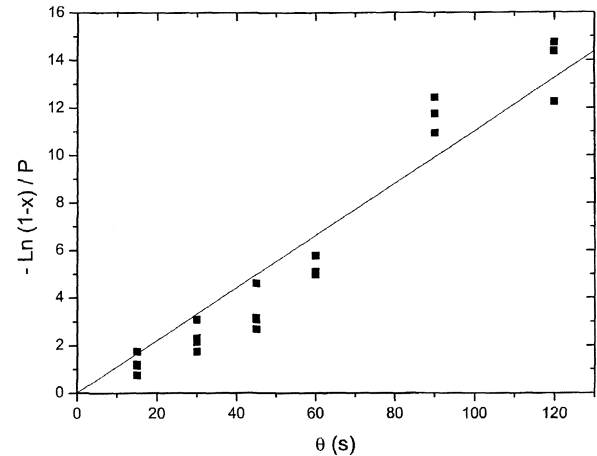


Figure 6. Determination of the reaction rate constant at 1250 °C.

Figura 6. Cálculo del coeficiente cinético a 1250 °C.

4. CONCLUSIONS

Rates of desulfurization of cuprous sulfide by air and oxygen obtained in two different reactors without gas bubbling show different dependences of the gas flow rate and temperature. Reaction rate in a vertical furnace could be correlated by the expression:

$$u, \left(\frac{\text{mol}}{\text{m}^2 \text{s}} \right) = k_G P = 73.75 v_G^{0.52} P \quad (10)$$

which involves the control of oxygen transport in the gas phase. On the contrary, data in a horizontal tube are quantified assuming that chemical resistance is controlling. The estimated activation energy is 24 kJ/mol.

These results show the influence of the type of reactor on heterogeneous kinetics and bring into question the applicability of data between different scales. Although the experimentation in laboratory gives useful information about the basic kinetics, it is doubtful that the direct translation of coefficients obtained in small devices without submerged lance to full scale processes where gas is fed through tuyeres.

SYMBOLS USED

- A: interfacial surface.
- a: effective specific surface.
- C: concentration.
- ϵ_L : enhancement factor.
- H: Henry's constant.

K : overall transport coefficient.
k : reaction rate constant.
 k_G : transport coefficient in the gas phase.
 k_L : transport coefficient in the melt phase.
N: moles of limited reactant.
 N_0 : initial number of mole of limited reactant.
n: order reaction.
P: partial pressure of oxygen.
r : reaction rate based on volume of Cu_2S .
u: reaction rate based on surface area of Cu_2S .
x: fraction of Cu_2S converted.
v: gas flow.
 θ : time.

Subscripts

G : gas.
L : liquid.
0 : initial.

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