

Research Article

A Kinetic Comparison between Laboratory and Industrial Scales in the Copper Blowing Process

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Received 9 January 2009; Accepted 29 May 2009

Recommended by Seetharaman Sridhar

An experimental investigation into the oxidation kinetics of molten sulfide has been conducted at laboratory scale to provide information concerning the influence of the gas feed (flow and oxygen pressure) and melt temperature on the desulfurization rate. Data showed that the reaction rate was strongly dependent on the gas flow rate and significantly from oxygen pressure, whereas the influence of temperature was negligible. The variation of the sulfur conversion with the operation time was similar to that found in industrial trials when “white metal” was blown to blister copper in a Peirce-Smith converter. A unique equation for both scales could be established. This correlation made it possible to calculate the operation time in the converter at different gas flow rates and oxygen enrichments.

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1. Introduction

About 90% of the world primary copper is extracted from sulphide ores by pyrometallurgical processes. The flow sheet includes the concentration of minerals by flotation, matte smelting, converting to blister copper, and electrolytic refining.

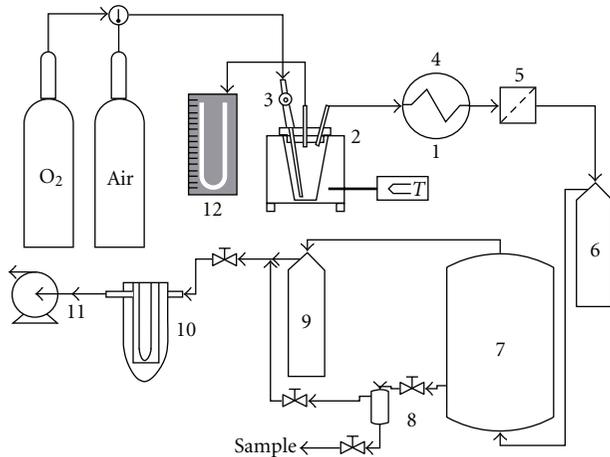
Copper converting proceeds in two stages: the slag-forming stage, during which the iron is oxidized, and the copper-making stage, during which blister copper is obtained. There are different procedures to carry out this process, the Peirce-Smith converter being the most common device. In this reactor, air is continuously bubbled into the batch matte.

Data of matte compositions during the copper-making stage in a Peirce-Smith (PS) converter proved that it behaved as a well-mixed tank for the melt and that the sulfur removal rates sharply dropped when very high conversions were achieved [1]. Two kinetics stages were proposed in order to quantify this change: in the range of sulfur conversion 0.00–0.90, the desulfurization rate and the oxygen efficiency remained constant, while with higher conversions, the oxygen efficiency and the desulfurization rate decreased when conversion increased. These results could be explained

assuming a negligible chemical resistance in the bulk of the liquid, and so, only the gas phase and liquid boundary layer would contribute to the overall resistance, the liquid film becoming resistance controlling during the second kinetic stage.

This empirical model was based on data of operations where essential kinetic parameters such as temperature, oxygen pressure, and gas flow rate scarcely varied throughout the blowing. On the other hand, the control of the trials had to be loose because in the industrial practice nonregular introductions of additional material (“cold charges”) are used to maintain the temperature of the melt. Besides it is not a simple task the sampling in a reactor with 160 t of matte per batch at 1200–1300°C, and it is difficult to provide very accurate compositions of melt and off-gas.

A more fundamental kinetic approach is necessary to consider some possible improvements in the operation in the Peirce-Smith converter, but it is only feasible at a smaller scale than that of the commercial process. Results concerning the desulfurization of copper sulfide at laboratory scale have been previously reported, with different conclusions. This is not surprising at all, given the change in hydrodynamic conditions resulting from the devices where experiments were carried out: capillary tubes [2], top lancing [3, 4], bubbling



1- Temperature control
2- Furnace
3- Air inlet
4- Gas outlet (chiller)
5- Solid filter
6- Safety vessels
7- H₂O₂ tank
8- System of sample extraction
9- Safety vessels
10- Safety vessels
11- Vacuum pump
12- Pressure gauge

FIGURE 1: Set-up for the desulfurization of copper sulfide.

gas through a submerged nozzle [5, 6], or thermobalance [7]. In general, the data were explained by accepting the control of the gas-side resistance, which has been considered consistent with the high oxygen utilization efficiency of the copper converter. Nevertheless, as has been stated before [1], the relationship between desulfurization rate and sulfur conversion during the copper blow in PS was incompatible with controlling resistance in the gas phase.

The aim of this work is to obtain a new kinetic expression for the desulfurization of copper sulfide where the influence of temperature, gas flow rate, and oxygen pressure should be included. A laboratory reactor was employed to establish this expression and to look for a relationship between data at this scale and the results of a commercial converter.

2. Experimental

The oxidation of copper sulfide by oxygen was carried out in a laboratory furnace where the gas was continuously bubbled through a lance into the melt which was contained in a crucible. It was considered that this operation in this bubble reactor may resemble that in the Peirce-Smith converter, where the gas is fed through tuyères. The experimental set-up is shown in Figure 1.

The operations conditions were

- (i) system pressure: 2 bar,
- (ii) molar fraction of oxygen in the in-gas: 0.210 (air) and 0.500,
- (iii) temperature: between 1175 and 1290°C,
- (iv) gas flow rate in feed conditions (20°C, 2 bar): $10^{-3} - 3 \cdot 10^{-3} \text{ m}^3/\text{min}$,
- (v) initial copper sulfide in the crucible: 200 g.

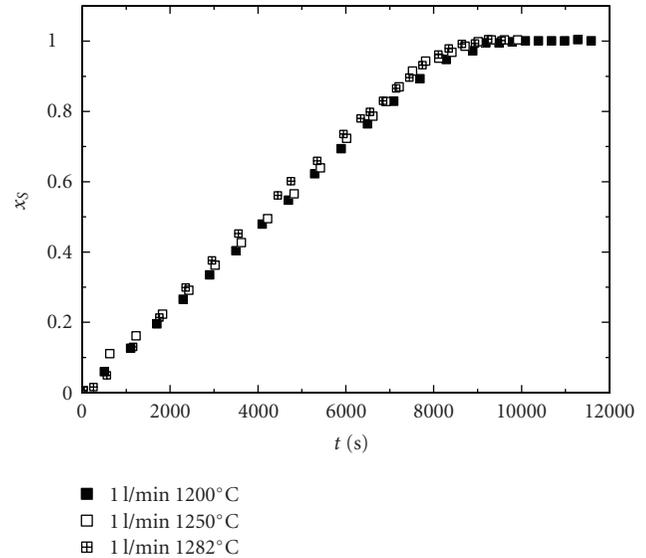


FIGURE 2: Conversion versus time (parameter, temperature).

The sulfur conversion as a function of the operation time was obtained from the concentration of sulphur dioxide in the off-gas. The gas was quenched in a 32 pct of H₂O₂ solution in water, and samples of this liquid were analyzed by titrating it against a 0.08 N NaOH solution.

The temperatures of the melt and temperature, initial flow rate, and initial oxygen pressure for the gas were fixed in each run. The reaction is irreversible; hence, the driving force of composition is the characteristic oxygen pressure in the bubble, P_{ox} . The value of P_{ox} is between initial and final oxygen pressures. The latter depends on the conversion and the flow model. We assumed plug flow for the gas; therefore P_{ox} was the logarithmic mean of those pressures. The experimental kinetic equation has the following pattern:

$$(N_S)_0 \left(\frac{dx_S}{dt} \right) = K \cdot A \cdot P_{\text{ox}}. \quad (1)$$

A is the interfacial area, and K is the overall coefficient for the mass transfer and reaction. The final oxygen pressure was deduced from the converted sulfur. In this way P_{ox} and $[KA]$ could be straightforwardly obtained using experimental measurements and mass balances. The mean gas flow rate for each run was calculated from the initial gas flow rate and the representative gas temperature, the final gas temperature being obtained by a heat balance (appendix). In this case the group $[KA]$ is a more suitable variable than the volumetric coefficient, because it can be calculated avoiding the uncertainties related to the interfacial area.

3. Results

Changes in sulfur conversion as a function of blowing time are shown in Figures 2, 3, and 4.

These results were correlated in order to solve the function $[KA] = f(v_G, P_{\text{ox}}, T)$. A model including temperature, oxygen pressure, and gas flow rate was used for

TABLE 1: Analysis of variance table for the multivariable regression model of KA using the predictor variables of temperature, oxygen pressure, and gas flow rate.

	Degrees of freedom	Sum of squares	Mean squares	F-statistic	P-values
Temperature	1	0.042	0.042	1.55	0.249
Gas Flow rate	1	2.816	2.816	104.30	$1.8 \cdot 10^{-5}$
Pressure	1	0.442	0.442	16.37	$4.7 \cdot 10^{-3}$
Residuals	7	0.187	0.027		

TABLE 2: Analysis of variance table for the multivariable regression model of (dx_S/dt) using the predictor variables of oxygen pressure and gas flow rate.

	Degrees of freedom	Sum of squares	Mean squares	F-statistic	P-values
Gas Flow rate	1	0.306	0.306	50081	0.0028
Pressure	1	0.012	0.012	1964	0.0141
Residuals	1	$6.11 \cdot 10^{-6}$	$6.11 \cdot 10^{-6}$		

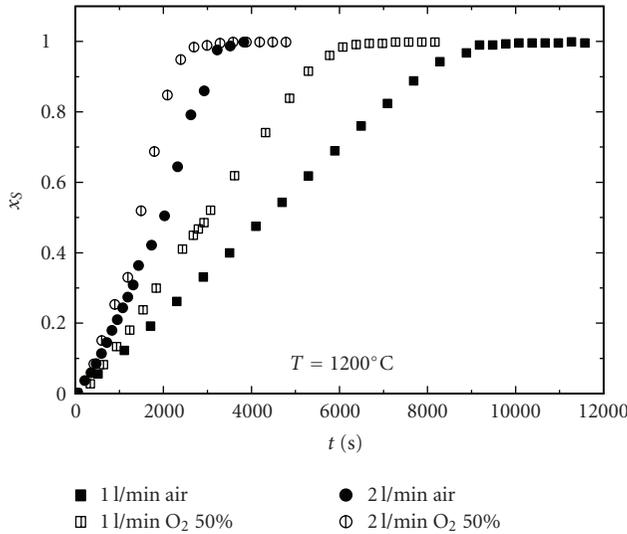


FIGURE 3: Conversion versus time (parameter, oxygen pressure).

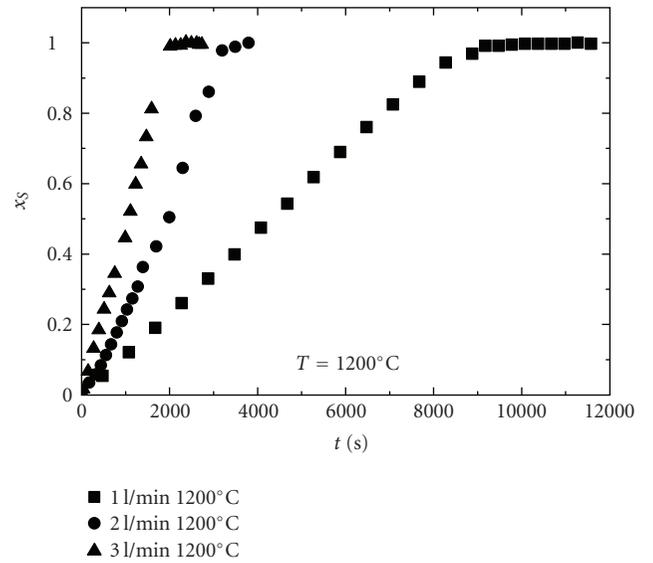


FIGURE 4: Conversion versus time (parameter, gas flow rate).

adjusting experimental values of KA . The dependence from the temperature was introduced through the Arrhenius equation:

$$[KA] = \alpha k_0 e^{-(E/RT)} v_G^m P_{\text{ox}}^n = a e^{(b/T)} v_G^c P_{\text{ox}}^d. \quad (2)$$

A multiple regression analysis of this model was made. The $R^2 = 0.976$ ($P < 1 \cdot 10^{-5}$) shows highly significant relationship between each one of the variables and $[KA]$. This analysis also confirms that the gas flow rate and the oxygen pressure are the primary and secondary predictor variables of $[KA]$ (Table 1). The coefficient b shows a low significance level for the temperature.

The final model was:

$$[KA] = 3122 e^{-(4640/T)} v_G^{1.27} P_{\text{ox}}^{-0.55}. \quad (3)$$

Equation (3) shows the following.

- (i) The temperature is not a determining factor in the sulfur removal. When its influence is quantified by the Arrhenius equation, E/R is low.

- (ii) The oxygen pressure is a significant factor: when it increases, there is an increase in the reaction rate, (x_S/t) being proportional to $P_{\text{ox}}^{0.45}$.
- (iii) The sulfur conversion strongly depends on the gas flow rate: (x_S/t) is proportional to $v_G^{1.27}$. This marked influence is easily understandable: when v_G increases, the interfacial area A must increase a lot. Also the overall coefficient K provided that the melt resistance to mass transfer is important.

These results agree with some features of the kinetics previously obtained in other laboratory reactors. The same negligible influence of the temperature was reported by Alyaser and Brimacombe starting from experiments in a top blowing reactor [3]. A constant slope (x_S/t) was found by Ajersch and Toguri [2], Asaki et al. [5], and Sohn et al. [6], during the desulfurization of mattes or copper sulphide, in the same trend that our results show up to very high conversions.

TABLE 3: Operation time for conversion 0.9 in Pierce-Smith converter at different gas flow rates and oxygen pressures. Melt temperature, 1180°C. Pressure is 2 bar. $(N_S)_0$ is 988.17 kmol. Numbers in heavy types belong to the correlation of actual operations in a Peirce-Smith converter.

In-gas, y_{ox}	$(v_G)_0$ (Nm ³ /s)	v_G (m ³ /s)	(dx_S/dt) , s ⁻¹	Oper. time, min
0.21	5.500	12.917	$8.5 \cdot 10^{-5}$	177
0.21	5.736	13.448	$8.8 \cdot 10^{-5}$	170
0.21	6.200	14.512	$9.5 \cdot 10^{-5}$	158
0.21	6.400	15.650	$10.2 \cdot 10^{-5}$	147
0.25	5.500	13.909	$11.2 \cdot 10^{-5}$	134
0.30	5.500	14.143	$13.9 \cdot 10^{-5}$	108

4. Discussion

Sulfur conversion and blowing time for the PS converter and the laboratory bubbling reactor can be correlated by linear functions. Nevertheless, while an equation is enough to quantify the whole range of conversion in the laboratory data, two equations were necessary to define the behavior of the commercial reactor (one for each side of the critical conversion, 0.90). So, the essential analogy which is being sought between both reactors has to be restricted to one of the kinetic stages of blowing in the PS converter, where sulfur is removed from the melt at constant molar flow within the conversion range 0.0–0.9, the slope (x_S/t) being about 10^{-4} s⁻¹. This value is similar to those found in the laboratory reactor when air is used as gas phase.

This similarity was unexpected, taking into consideration the size and operation of both reactors and their effects on the hydrodynamic conditions. The bubbling in the laboratory reactor can be considered homogeneous, in spite of the fact that the gas velocity in some operations was on the limits of this regime. On the other hand, the Eötvös number was lower than 40 and the Morton number much lower than 0.001; therefore it is unlike the coalescence or the break-up, and independent spherical or spheroidal bubbles may be assumed. The picture of the gas phase in the converter is very different: a stream of huge bubbles is surrounded by a lot of small ones [8].

To foresee the behavior of the commercial converter at different gas flow rates or oxygen pressures, a relationship for the PS converter in the pattern of (3) is necessary. Of course, (3) cannot be used directly, because K or A are variables related to the reactor size and, as a consequence, $[KA]$ is much bigger in the converter than in the laboratory reactor. However, it is possible to develop a unique equation for both scales, referring the variables v_G and $[KA]$ (or dx_S/dt , more suitable to calculate operation times) to the initial amounts of sulfides (copper sulfide or white metal) in each one. Hence, the sought function is

$$\frac{[KA]}{(N_S)_0} = \left(\frac{1}{P_{\text{ox}}}\right) \cdot \left(\frac{dx_S}{dt}\right) = f\left\{\left[\frac{v_G}{(N_S)_0}\right], P_{\text{ox}}\right\}. \quad (4)$$

An expression for (dx_S/dt) starting from correlated laboratory data and converter data was tried by multiple regression analysis (Table 2; $R^2 = 1$; $P = .004$), in the same way that the model developed for $[KA]$ (bubble reactor; (3)). The following overall correlation is applicable to both

reactors if the operation is carried out at 1180°C, which is the melt temperature in our PS converter when $x_S < 0.9$:

$$\left(\frac{dx_S}{dt}\right) \cdot \left[\frac{P_{\text{ox}}^{2/3}}{(P_{\text{ox}})_0}\right] = 9.326 \left[\frac{v_G}{(N_S)_0}\right]^{1.06}. \quad (5)$$

Equation (5) makes it possible to predict the operation time if different gas flow rates or oxygen enrichments are used and the reaction temperature in the converter is maintained by the addition of cold charges. Results of this forecasting are tabulated in Table 3.

As it has been previously reported, the overall volumetric coefficient for the desulfurization in a PS converter is much lower when $x_S > 0.9$ than for $x_S < 0.9$. So, greater shortenings of the operation time are possible at the end of the copper blow. The key factor is the gas flow rate, given that the oxygen pressure is not influent in that kinetic stage, that is, when $x_S > 0.9$ [1]. Anyway, data of the bubbling reactor can only be correlated with those of the first kinetic stage in a PS converter. Therefore the first reactor does not provide useful information for improving the operation of the second one at the end of the copper blow.

5. Conclusions

It has been found that the rate of desulfurization of copper sulfide in a laboratory bubbling reactor was strongly dependent on the gas flow rate. The dependence of the initial oxygen pressure was also significant. On the contrary, the influence of the melt temperature was weak, and it may be neglected in estimations where a great accuracy is not necessary.

Data of the bubbling reactor and the Peirce-Smith converter were correlated by a relationship between the variables dx_S/dt and v_G where the initial sulfide contents in the reactors are included. This correlation is valid for a PS operating below $x_S = 0.90$ and was applied to forecast the behavior of the converter during the copper blow if it works at different conditions from those usually used in industrial practice. The shortening of the operation time to achieve a conversion 0.90 by increasing the gas flow rate or the oxygen pressure was quantified for a constant temperature of the melt. Of course, the possible improvements in the operation have to be limited by the control of the bath temperature taking shorter times to add the “cold charges.”

Appendix

Calculation of the Mean Oxygen Pressure and Flow Rate of the Gas

(i) Starting variables: $(N_S)_0$, T_0 , $(P_{ox})_0$, $(v_G)_0$; $(F_{ox})_0 = (P_{ox})_0((v_G)_0/RT_0)$

(ii) From experimentation: (dx_s/dt) ;

$$(x_{ox})_f = \frac{(N_S)_0}{(F_{ox})_0} \left(\frac{dx_s}{dt} \right),$$

$$P_{ox} = \frac{(P_{ox})_0 - (P_{ox})_f}{\ln[(P_{ox})_0/(P_{ox})_f]};$$

$$(P_{ox})_f = (P_{ox})_0 [1 - (x_{ox})_f],$$

$$v_G = (v_G)_0 \left(\frac{T_{mean}}{T} \right),$$

$$T_f = T_0 + \frac{(N_S)_0(\Delta H_R)}{((F_{ox})_0 C_G)} \left(\frac{dx_s}{dt} \right);$$

$$T_{mean} = \frac{T_f - T_0}{\ln(T_f/T_0)}.$$

(A.1)

Nomenclature

A,B,C,D:	Mathematical model coefficients(2)
A:	Interfacial area (m ²)
C:	Molar heat capacity (J · mol ⁻¹ · K ⁻¹)
E:	Activation energy (J mol ⁻¹) (Arrhenius equation)
F:	Molar flow (mol·s ⁻¹)
K:	Overall kinetic coefficient (m s ⁻¹)
k ₀ :	Pre-exponential factor (Arrhenius equation)
(N _S) ₀ :	Initial number of sulphur mol (mol)
P _{ox} :	Oxygen pressure (atm)
R:	Universal gas constant (J mol ⁻¹ K ⁻¹) (Arrhenius equation)
t:	Time (minute, second)
T:	Temperature (K)
v _G :	Gas flow rate (m ³ s ⁻¹)
x:	Conversion (-)
ΔH _R :	Reaction enthalpy increment (J · mol ⁻¹)
α:	Constant (2).

Subindex

f:	final
G:	Gas
S:	Sulphur
ox:	Oxygen
0:	Initial.

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