FACTORS DETERMINING THE RATE OF MAGNETITE REDUCTION IN A LIQUID SLAG BY GRAPHITE ELECTRODES

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ABSTRACT

Copper slag cleaning requires reduction of magnetite content. The most common technology of slag cleaning is the slag reduction and copper removal in an electric furnace. Experimental measurements of slag reduction rate in a crucible scale simulating electric furnace showed the strong effect of power density on the immersed surface of graphite electrodes as dominating factor.

The results of CFD modeling, using commercial software COMSOL, allowed for analysis of above phenomena. At the same power input and shallow electrode immersion the high power density results in strong increase of temperature at the electrode surface, accelerating the reduction rate and enhancing mass transfer by convection. At deep electrode immersion the increase of reaction surface does not compensate the effect of temperature and stirring.

INTRODUCTION

The degree of a slag reduction in an electric furnace determines the liberation of copper matte inclusions and co-reduction of cuprous oxide. Thus, the important question is about the rate of magnetite reduction with the carbon of electrodes.

$$Fe_3O_4 + CO = 3\ FeO + CO_2 \tag{1}$$

$$Cu_2O + CO = 2\ Cu + CO_2 \tag{2}$$

$$C + CO_2 = 2\ CO \tag{3}$$

The rates of endothermic reactions of reduction are strongly temperature dependent. The optimal depth of electrodes immersion is one of a key question in process control. The mode of control of slag cleaning processes differs in copper and nickel smelters. The effect of electrode immersion, diameter and distance between them on system resistance and voltage/current configuration were analyzed by [1] and [2]. However, the analysis of operating furnaces on the basis of Atwood and Urghart equations shows large discrepancies and limited possibilities to define the heat liberation.

The effect of power density on the reduction rate was presented in paper [5]. The power density determines the rate of heat liberation and temperature at the electrode/slag interface. The reactions (1-3) are endothermic and strongly temperature dependent. The measured fayalite reduction rate with graphite [4] and coke [3] showed the high activation energy (Ea = 232 kJ/mol). The obtained kinetic equation has a form:

$$k = 8 \cdot 10^5 e^{-\frac{232000}{RT}} \tag{4}$$

The aim of this work was to determine the effect of power density and electrodes immersion on the rate of slag reduction using CFD modeling and direct measurement of the reaction rate.

METHODOLOGY

Rate of Slag Reduction

The rate of magnetite reduction was determined by continuous measurement of CO and CO_2 content in off-gas at controlled flowrate of pure nitrogen as a carrier gas. Slag sample of 400 g from Teniente Converter, containing 16% Fe_3O_4, was melted in MgO crucible inside a close reaction tube, placed in a vertical electric furnace. The experimental setup is presented in Figure 1. When the slag in MgO crucible (O.D. 50 mm, height 120 mm) was melted and the temperature stabilized at 1250°C, two graphite electrodes were immersed at determined depth. The voltage control permitted to stabilize current intensity and power. The depth of electrodes immersion was regulated by micro screw mechanism.

After lapse of required time, the electrodes were pulled out and the crucible taken out of the furnace and cooled in nitrogen stream. The chemical analysis was used to check out the calculated degree of slag reduction on the basis of off-gas analysis.

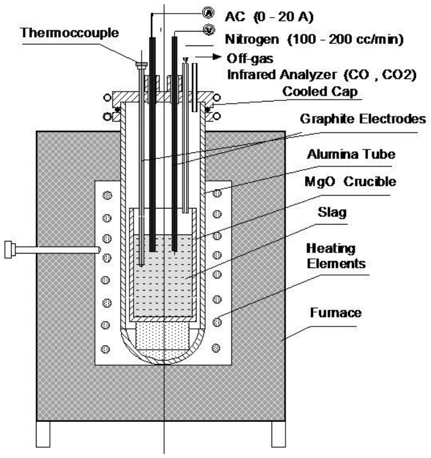

Figure 1: Experimental setup for measurement of rate of slag reduction

Modeling of Slag Reduction

The modeling was carried out using commercial software COMSOL. Simultaneous solving of potential-current, heat transfer by conduction and convection, and Navier-Stokes equations allowed for determination in temperature and slag flow distribution for 3D geometry – the crucible cut in half, as illustrated in Figure 2. The detailed procedure of modeling calculations was presented in a previous work [6].

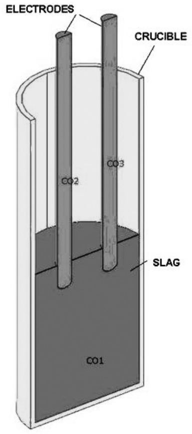

Figure 2: 3D geometry of crucible for modeling

RESULTS AND DISCUSSION

Factors Determining the Rate of Slag Reduction

The example results of slag reduction are shown in Figure 3 as CO and CO_2 content in off-gas and in Figure 4 as the rate of reduction versus time for two stages: immersed electrodes without power and with power input 200 W, for depth of immersion 13 mm.

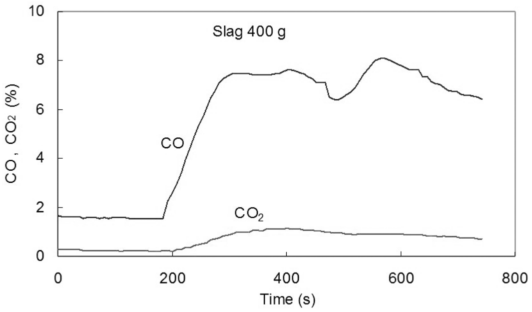

Figure 3: Off-gas analysis versus time

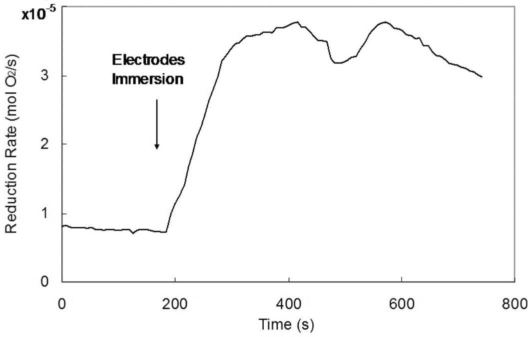

Figure 4: Rate of slag reduction versus time for P=400 W

The power 400 W at electrodes immersion 13 mm corresponds to power density at electrode surface 1.55 MW/m^2. For slag mass 400 g and time 500 s, the unitary energy consumption was 139 kWh/t. The rate of reduction increases five times from 0.7 to 3.5·10^{-5} mol O_2/s.

The results of reduction at constant power input (200 W) for various depths of electrodes immersion are presented in Figure 5 – Figure 7. The change of immersion depth from 8 to 42 mm (Figure 7) did not affect significantly the slag reduction rate, which fluctuates from 1.6 to 2.2 10^{-5} mol O_2/s (Figure 6).

The power input 200 W during 500 s (Figure 7) corresponds to unitary energy consumption 70 kWh/t of slag. The small changes in the reduction rate (Figure 6) does not show the significant effect of the increase of electrode immersion depth. The effect of the increase of the reaction surface with depth of immersion is compensated by the decrease of the current density at electrode/slag interface.

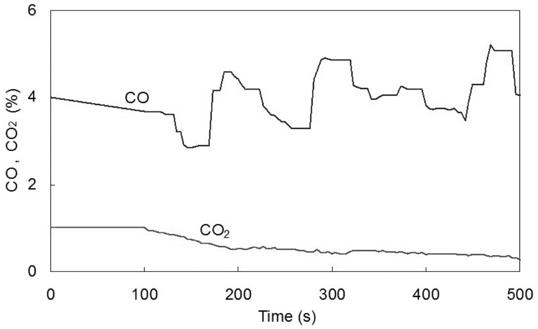

Figure 5: Off-gas analysis versus time

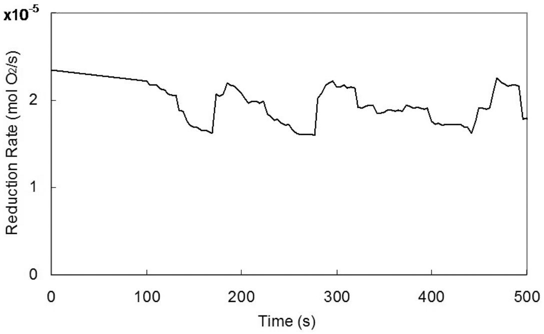

Figure 6: Rate of slag reduction versus time for P=200 W

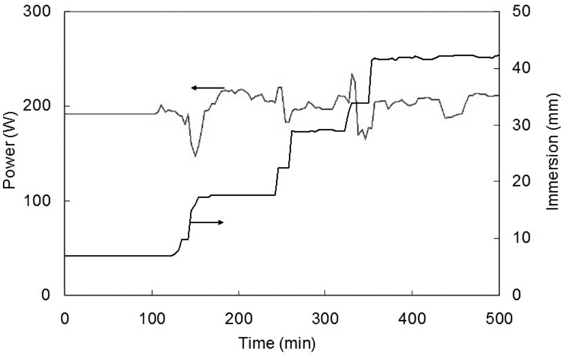

Figure 7: Power input and electrodes immersion versus time

Modeling Results

Temperature of the crucible in 3D view for power input 400 W is shown in Figure 9. The slag temperature between the electrodes increased up to 1450°C at the stable temperature of the furnace chamber 1250°C. According to Equation 4, the rate constant should increase 8 times with the temperature increase from 1250 to 1450°C. The measurements in the Figure 4 show the increase of reduction rate in 5 times. However, the calculated temperature from modeling explains the sharp increase of the reduction rate.

The series of modeling with constant power input and various depth of electrodes immersion (13, 23 and 33 mm) are shown as power distribution in the Figure 9 and temperature distribution in the Figure 10. The temperature distribution at the electrode/slag interface as a function of electrode position presents graph in Figure 11.

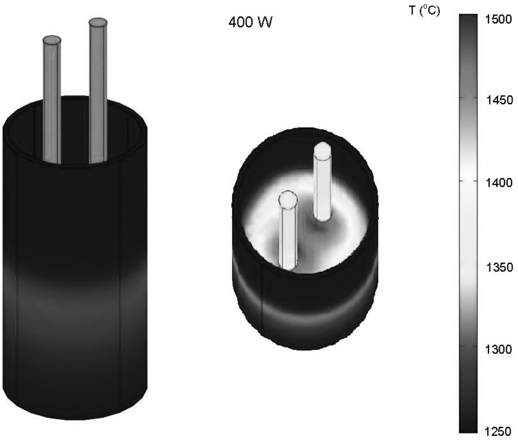

Figure 8: Crucible and slag temperature during reduction. Power input 400 W

The shallow immersion 13 mm results in the highest temperature at the interface (Figure 9 a). With the increasing immersion the temperature profile at the slag/electrode interface is changing. Using Equation 4, for know crucible geometry (I.D.= 44 mm, height of slag 60 mm), the rate of slag reduction was calculated by integrating the rate as a function of temperature along the electrode height.

Calculated reduction rate as a function of power density (power for the surface area of the immersed part of electrode) is shown in Figure 12. Triangles represent the results of rate measurement (Figure 6) as an average value in the range of fluctuation. Taking into consideration all simplifications and steep temperature gradient along the electrode height, the calculated rate for various depth of electrode immersion is close to the measured values.

The above results show clearly the role of electrode immersion. Growing surface area at electrode/slag interface with immersion is compensated by lower energy density and interface temperature slag/electrode for the same power input.

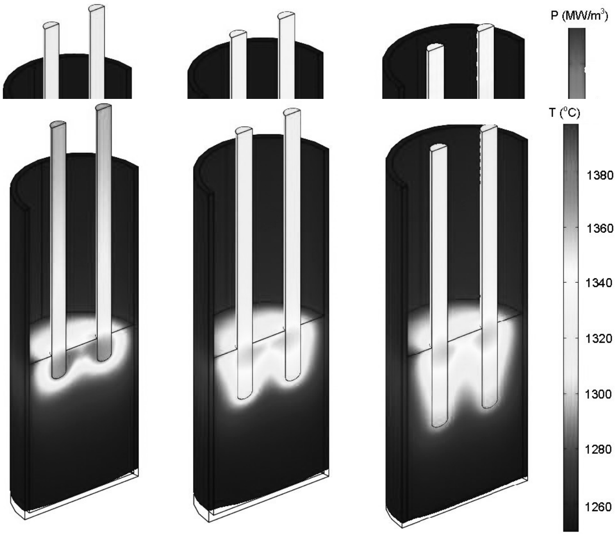

Fig nm

Figure 10: Temperature distribution for electrodes immersion a) 13 mm b) 23 mm c) 33 mm

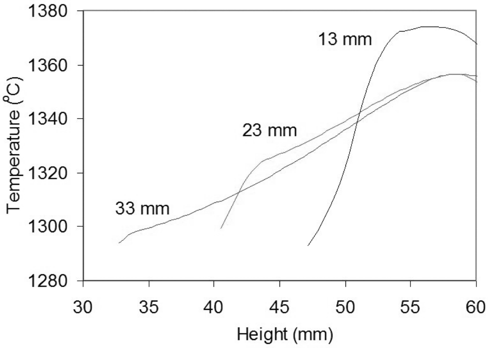

Figure 11: Temperature at slag/electrode interface

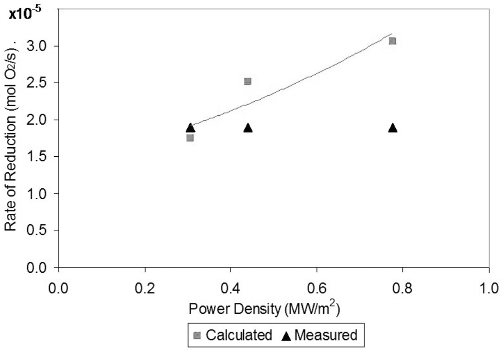

Figure 12: Rate of reduction as a function of power density

The effect of power input on the rate of reduction at the same depth of electrodes immersion is illustrated by results of modeling in Figure 13 for immersion 13 mm. The slag temperature between electrodes increases from 1360 to 1550°C with the increase of power from 200 to 530 W.

In the same manner as before, according to Equation 4 and system geometry the rate of reduction was calculated including previous rate at 1250°C without power input. The calculated results are shown in Figure 14. The reduction rate increases ten times with the increase of temperature from 1250 to 1550°C. The measurements regarding the reduction rate (by using gas analysis) were carried out at similar power input. The calculated reduction rate is also shown in the same Figure 14. The latter are in a good agreement with the experimental data.

The power density is a major factor determining the rate of slag reduction. A large temperature increase between the electrodes results in a big temperature gradient in the slag, generating an intense convectional agitation and enhancing the mass transfer towards the electrodes. Therefore it affects directly the reaction kinetics.

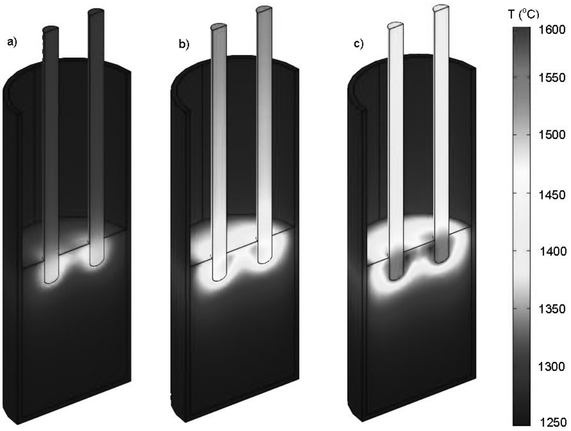

Figure 13: Temperature distribution for power input a) 200 W, b) 400 W c) 550 W

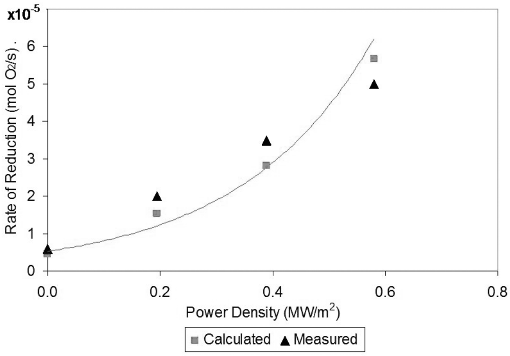

Figure 14: Rate of reduction as a function of power density

CONCLUSIONS

The rate of a fayalite slag reduction with carbon of graphite electrodes depends on the density of power input at the slag/electrode interface. The Joule's heat liberated at the interface covers the required heat of endothermic reduction reactions.

A large temperature gradient along the slag height induces slag convection and mass transfer towards the slag/electrode reaction interface. Slag motion destabilizes the copper matte inclusions, increasing probability of their collisions and coalescence.

The temperature distribution is a complex function of liberated heat and the system geometry, such as electrode diameter, distance between the electrodes, depth of immersion, slag height and crucible diameter. The increase of depth of electrode immersion does not result in significant increase of the reduction rate. The increase of reaction surface is compensated by the decrease of temperature.

Slag reduction and cleaning in an electric furnace demonstrates the similar dependencies. Additionally, the floating coke bed on the slag surface makes the system more complex. The heat generation in the coke layer depends on the coke properties and the depth of electrodes immersion. With increasing immersion the amount of heat generated inside the coke decreases, which results in a rapid decrease in reduction rate of slag by coke. The increasing immersion of electrodes results in the increase of the current intensity/voltage ratio, causing the drop of the power coefficient and energy efficiency of the process.

REFERENCES

Atwood, S. S. (1949). *Electric and Magnetic Fields*. John Wiley & Sons, New York, pp. 88 and 160. [1]

Urquhart, R. C., Remie, M. S. & Rabey, C. C. (1976). Proceeding. International Symposium On Copper Extraction and Refining, Feb. 22-26, Las Vegas, NV, A.K. Biswas and W.G. Davenport, eds., TMS-AIME, Warrendale, PA. [2]

Riveros, G. & Warczok, A., *et al.* (1999). *Optimization of Slag Cleaning Process*. Report Universidad de Chile, Departamento de Ingeniería de Minas, Santiago, Chile. [3]

Warczok, A. & Utigard, T. A. (1998). *Fayalite Slag Reduction by Solid Graphite*. Canadian Metallurgical Quarterly, 1998, Vol. 37 No. 1, pp. 27-40. [4]

Warczok, A., Riveros, G., Diaz, C., Schwarze, H. & Sanchez, G. (2002). F*actors Governing Slag Cleaning in an Electric Furnace*. Canadian Metallurgical Quarterly, Vol. 41, No. 4. [5]

Warczok, A., Riveros, G., Degel, R., Kunze, J. & Oterdoom, H. (2007). *Slag Cleaning in Ccircular and Rectangular Electric Furnaces*. Proceedings of International Conference COPPER2007, ed. Warner T. *et al.,* Toronto, August 2007. [6]