MODELLING OF COPPER CONTENT VARIATION DURING "EL TENIENTE" SLAG CLEANING PROCESS

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ABSTRACT

This work shows a mathematical model to determine changes of copper content in the slag phase, for "El Teniente" slag-cleaning process. Results obtained with this model, can then be integrated to quantify the total copper remaining in the slag at a given time. The effect of surface tension between matte drops and slag in total retention time of slag in the cleaning furnace is also considered, as this is the main parameter influencing the minimum copper content in the final slag to be discharged. Additionally, the effect of magnetite on slag viscosity and hence in matte sedimentation through slag has been considered. Results were validated with actual industrial data from El Teniente processes, concluding that the model developed adequately represents the copper content in the slag.

INTRODUCTION

Due to strong interaction between liquid phases during smelting-converting process, entrapment of matte in slag is always possible. As a consequence, quantification of valuable species existing in these slags is of industrial interest. This problem has been addressed in several works [1, 5, 6, 7, 9, 10, 12, 16], where influence of magnetite and oxygen potential in slag viscosity and hence in matte drops sedimentation rate has been clearly established. As a complement to the studies before described, this work aims to determine the content of copper in the slag by developing a transport model. Thus, the mathematical model allows knowing the copper concentration along the slag and its evolution over time.

Attention has been focused on slag-cleaning Teniente furnace, where slag treatment takes place in two batch mode stages. First stage involves injection of reducing agents (usually natural gas, oil or charcoal) to achieve reduction of magnetite contained in the slag, then diminishing viscosity in this phase and, by this way, increasing sedimentation rate of matte drops contained in the slag. Second stage begins when slag reaches the desired viscosity, so no more reducing agents are fed, and molten system begins to settle on by sedimentation. At the end of the second stage, after a correct sedimentation time, matte and slag phases will be properly separated. Final slag will have residual amount of matte retained as small drops. This slag will still keep a residual content of matte as small drops, unable to settle because of surface tension phenomena.

The model here developed leads partial differential equations then numerical methods for its resolution are required, and the *lines method* has been used. The ordinary differential equations system obtained with the *lines method* is then solved through the *Euler explicit* technique. Profiles of copper concentration in slag are finally integrated using the *trapeze rule*, to obtain finally the total content of copper in slag. Results obtained fit very well when compared with industrial data.

METHODOLOGY

Effect of Magnetite Content On Slag Viscosity

Reduction slag operation stage implies strong agitation into molten bath, due to two reasons: i) injection of reducing agent cause strong agitation into molten phase ii) reducing agent reacts with magnetite producing a strong carbon dioxide bubbling according to the following overall reaction

$$\begin{gathered}\langle C\rangle + [CO_2] \rightarrow 2\,[CO] \\ \{Fe_3O_4\} + [CO] = 3\,(FeO) + [CO_2]\end{gathered} \tag{1}$$

Because of this agitation during the reducing period, it could be assumed any or negligible sedimentation, compared with the transport flow to matte-phase during the sedimentation stage. This is due to the strong mixture created by the agitation in the bath during the first stage. As a result of the first stage, magnetite decreasing is observed. Magnetite content decreasing can be represented by a first order kinetic law with respect to magnetite weight percent $C = \%_{wt}\, Fe_3O_4$ according to references [1] and [16], as follows

$$C = C_o \exp(-kt) \tag{2}$$

Decreasing in magnetite content causes lower slag viscosity. It has been observed an exponential dependency between viscosity and magnetite content [9], i.e.,

$$\eta = \eta_o \exp(\beta C) \tag{3}$$

Combining Equations 3 and 2, relationship between slag reduction time and its viscosity is obtained, i.e., $\eta = \eta_o \exp(\beta C_o \exp(-kt))$. Assuming that the time reduction for the slag is τ_R, then the residual slag viscosity can be determined as follows,

$$\eta = \eta_o \exp(\beta C_o \exp(-k\tau_R)) \tag{4}$$

Where η_S corresponds to the initial viscosity for the sedimentation period. For the industrial practice, viscosity must be the lower as possible, so that, at the beginning of sedimentation, the slag should have the minimum of magnetite concentration as possible.

Drop Entrapping Due to Surface Tension

Slag has a population of matte-droplets due to the interaction between the two molten phases during smelting-converting process. These droplets are immiscible with the slag, but they are submitted to surface tension force $\sigma_{sl/mt}$. Assuming perfectly spherical droplets, surface tension forces can be estimated as $2\pi r_c \sigma_{sl/mt}$. Balancing forces, weight of droplets are equilibrated by the surface tension, which means that a critical droplet radius must exist for starting sedimentation. That is,

$$r_c = \sqrt{\frac{3\sigma_{sl/mt}^{mod}}{2r\,g}} \tag{5}$$

Estimation of this critical size is extremely complex because the surface tension is strongly influenced by temperature and matte and slag phases’ composition. Studies on this subject have been carried out by Ip *et al.* [7], Nakamura *et al.* [11], and Elliot *et al.* [3]. For example, surface tension between matte-droplets and copper slag fayallite, is usually considered in the order of 0.15 [*N/m*] for a matte containing 70% copper. However, this value decreases to 0.10 [*N/m*] for a matte containing 60% copper. This fact is largely due to sulphur content, which is quite well known as surface activator [8]. Then, as sulfur content increases, surface tension decreases. Moreover, in an industrial process, small amounts of impurities may affect properties of drop - slag interface, with a large impact in decreasing the surface tension [4, 7]. For example, assuming equilibrium conditions and considering experimental values already published, ρ= 5100 [kg/m^3], σ ¶ 0.10 [*N/m*], ρ_{sl}= 4010 [kg/m^3] then, the theoretical critical radius given by the expression (5) is ~ 1.73×10^{-3} [m]. This critical radius is higher than those observed in samples from slag furnace treatment for El Teniente process [13]; then, it is possible to find 10 to 200 microns drops size retained. The focus of this paper is addressed exclusively on the gravitational sedimentation phenomena, so only larger size drops than critic radius, $r>r_c$, were considered.

Sedimentation

In the second stage of slag treatment, injection of reducing agent is stopped and sedimentation stage takes place in a batch mode. The initial condition of this stage is given by the copper concentration profile retained in the slag as it remains because bath agitation during the earlier reduction. In addition, the residual magnetite content at the end of the first stage, makes slag holds a residual viscosity η_S, and this is the viscosity considered for the second phase of sedimentation. Moreover from Equation 5, flow sedimentation has been considered for drops sizing $r>r_c$. As drops size is small ($r_{average}$ 200 × 10^{-6} [m]), then terminal sedimentation velocity is $v_\infty = 2\Delta\rho g r^2/(9\eta_S)$Moreover, drops do not freely settle across the slag due to crashes between them (contacts drop-drop or drop-impurities), therefore a model of hindered sedimentation as that developed by Richardson and Zaki [14] has been considered. Then,

$$v(\phi) = \frac{2\Delta\rho g r^2}{9\eta_S}(1-\phi)^a \tag{6}$$

This model of sedimentation rate (6), considers physical and chemical properties of slag and matte $\Delta\rho, \eta_S$ the drop size characteristic r, the gravity g, and matte concentration ϕ. Parameter a is proper to the sedimentation model and it is found by adjusting experimental data.

Transport Model

If the slag thick layers H are divided into n number of the same thickness $\Delta y = H/n$, then the following differential mass balance set in each control volume $A\Delta y$ can be established.

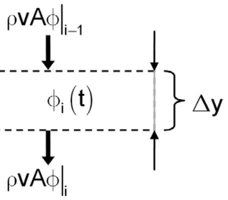

Figure 1: Differential mass balance in control volume

Matte variation within the slag control volume must be equal to the difference between the incoming and out coming flow discharging for sedimentation. Flux of sedimentation is defined as $q = v\phi$. Then, applying the boundary conditions and when thickness $\Delta y \to 0$ and regrouping terms, the equation of matte transport across the slag is obtained.

$$\frac{\partial\phi}{\partial t} + \frac{\partial q}{\partial y} = 0 \tag{7}$$

As a boundary condition for slag surface y = 1.2[m] (see reference [5], not transportation flow has been considered, that is, $q\,|_{y=1.2[m]} = 0$. As initial condition, a known concentration $\phi_i^{(0)}$ for each control volume i=l,....n it has been assumed.

Numerical Solution of Algorithm

Using the *lines method* [15], and the *explicit numerical Euler* method, it is possible to develop a numerical algorithm for the solution of model (7). That is,

$$\phi_i^{(j+1)} = \phi_i^{(j)} - \frac{\Delta t}{\Delta y}\left(\phi_i^{(j)} v_i^{(j)} - \phi_{i-1}^{(j)} v_{i-1}^{(j)}\right) \tag{8}$$

Where $y = 1,....m$ are time steps and $i = 1,....n$ are control volumes. To ensure the stability of the numerical scheme, the *CFL condition* [15] must be fulfilled, and, in this case it should be $|v\Delta t/\Delta y| \leq 1$. This means that the choice of the temporary step is related to the control volume thickness Δy, according to the sedimentation flow rate. For n=4 control volumes, a total time of two hours has been chosen τ=7200 [s] for simulation, with a temporary step Δt=30[s]. The total slag thickness was chosen as H=1.2 [m] (see reference [5], with a thickness for the control volume Δy=0.3 [s]. The density difference is $\Delta\rho$= 1094 [kg/m^3], the slag density is ρ_{sl}= 3906 [kg/m^3]. According to F. Kongoli *et al.* [9], and V. Bazan [2] works, the viscosity of the slag is η= 0.1086 exp(0.0886C) and according to data contained in Figure 4, obtained from reference [5], magnetite content is $C=14.60\%_{wt} \cdot \exp(-0.000353t)$, where t is the time measured in seconds and C is the magnetite concentration in weight percent.

The assessment of the total content of copper slag, requires the integration of (7) with ϕ given by (8) using a numerical method. In this work, the *trapeze rule* was applied to 4 volume control considered. As the thickness of each volume control is constant and equal to 0.3 [m], then the numerical expression of the integration, it simplifies to the following result,

$$\left\{\% \, Cu\big|_{Slag}\right\}^{(j+1)} = 25\sum_{i=1}^{i=4}\left(\phi_i^{(j)} - \frac{\Delta t}{\Delta y}\left(\phi_i^{(j)} v_i^{(j)} - \phi_{i-1}^{(j)} v_{i-1}^{(j)}\right)\right) \tag{9}$$

Where the index $j = 1,....m$ corresponds to the time at which the content of copper slag is required. The total integration time, for a temporary step Δt and after j time intervals, it corresponds to $(j \cdot \Delta t)$. This means that if m the total number of temporary steps, then the final time of integration will be $(m \cdot \Delta t)$. For the application example given in this work, the slag-cleaning Teniente furnace has been considered, which typically operates with 2 hours sedimentation time. That conclude in a total number of temporary steps of m = 240 for a passage $\Delta t = 30$ [s].

RESULTS

When numerical scheme (9) is applied, development of copper content in slag is obtained as follows in Figure 2.

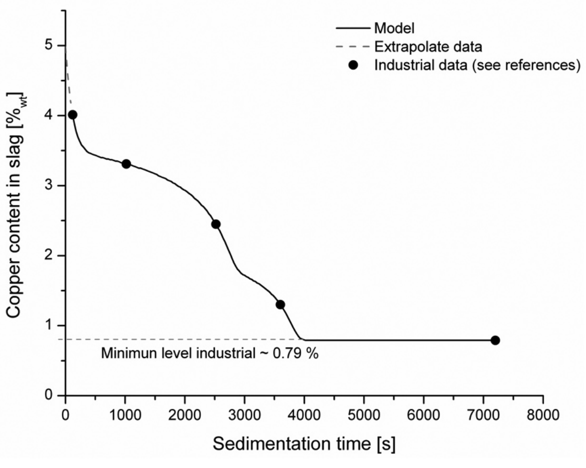

Figure 2: Simulation of copper content in slag

To appreciate the effect of the reduction stage on duration of the sedimentation stage, it is important to analyze magnetite content in slag. To accomplish that, evolution of copper content for several viscosities and hence for different sedimentation time of matte-droplets is determined. This is shown in Figure 3.

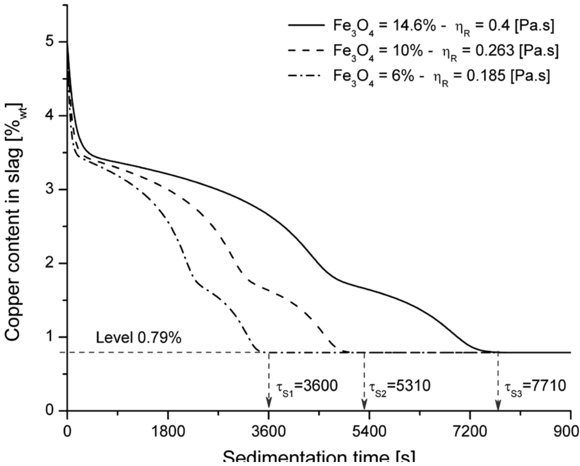

Figure 3: Effect of magnetite content and viscosity on sedimentation time

CONCLUSIONS

Figure 2 shows results for the model simulation (9) compared with industrial data from El Teniente slag-cleaning furnace. Good results for the model can be appreciated when predicting evolution of copper content in the slag. At the end of the sedimentation time, there is a residual copper contained in the slag which can not be eliminated by sedimentation because drops have smaller size than critical one given by (5), and therefore are entrapped by surface tension matte/slag.

For industrial applications, this model could determine the best time for slag sedimentation. Hence, time both for reduction as sedimentation stage could be programmed. This is because when reduction time τ_R is known to obtain a slag with a residual viscosity η_S, then the sedimentation time to obtain a level of residual copper in the slag can be calculated. These results can be seen in Figure 3, in which three different scenarios were simulated, for three slag viscosities. Then, if the lower copper level in slag given by (5) want be obtained, for a slag with 6% magnetite, a sedimentation time τ_{S1} = 3600s must be used. For 10% magnetite, sedimentation will be τ_{S2} = 5310s. Finally, for 14.6% magnetite, sedimentation must be τ_{S3} = 7710s. Obviously, magnetite content will be given by the reduction stage condition.

The slag-cleaning furnace operates in batch mode for a given amount of slag. After some time, usually 2 or more hours, phase separation between matte and slag is ensured following sedimentation mechanism of matte-droplets, leaving a residual concentration of matte in the slag due to entrapment by surface tension of the drops, with sizes less than critical value given by (5). Other reason for residual matte in slag could be that 1 or 2 hours may be insufficient time for sedimentation (see Figure 3). However, for industrial practical purposes, not long periods of sedimentation are possible, then, it is assumed a critical copper concentration of around .

NOMENCLATURE

ϕ = Concentration of matte in the slag (droplets).
v = Hindered sedimentation velocity [m/s].
v_∞ = Terminal velocity of sedimentation, [m/s].
y = Spatial variable (thickness of slag) [m]
t = Time in the sedimentation stage, [s].
τ_R = Total time of the reduction stage, [s].
q = Flux function of the sedimentation, [m/s].
r_c Critical radii [m].
$\sigma_{sl/mt}^{\mathrm{mod}}$ = Surface tension (modified due to chemical composition) [J/m^2].
ρ, ρ_{sl} = Matte and slag density [kg/m^3].
g = Gravitational acceleration [m/s^2].
η, η_s = Slag viscosity and residual viscosity slag [kg/(m.s)].
C = Content magnetite in slag [% weight].
i=l,…,n = Index for the control volume (spatial step).
j=l,…,m = Index for the integration time (temporal step).
A = Surface of the transversal section of furnace [m^2].

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APPENDIX

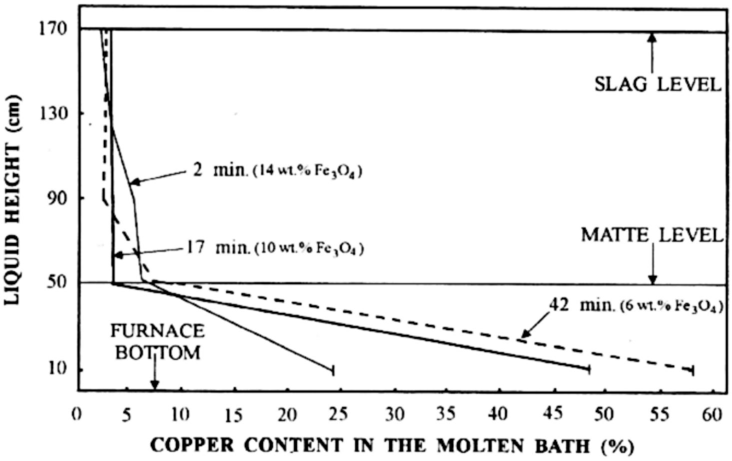

Figure 4: Industrial data (Slag-cleaning furnace, El Teniente)