A KINETIC MODEL APPLIED TO PIG IRON DESULFURIZATION IN THE KANBARA REACTOR

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ABSTRACT

A model is proposed for desulfurization in the Kanbara reactor (KR) that takes into account the contribution of dispersed particles of desulfurizing agent, carry over slag from blast furnace and effects of the several operational parameters such as temperature, rotational speed of the impeller and its effect on mass transfer. Appropriate parameters such as partition coefficient of sulfur between slag and metal, extent of dispersion of solid particles (desulfurizing agent) and slag in the melt and their size distributions, mass transfer coefficient have been determined for use in the model to predict the degree of desulfurization. A comparison is provided between the results from 600 heats and those obtained from the model. The agreement is quite satisfactory.

INTRODUCTION

It is well known that desulfurization process depends on the combination of thermodynamic and kinetic parameters. Thermodynamic considerations include the type, composition and relative amount of desulfurizing agent, initial temperature of treatment, mass and composition of pig iron. Kinetic conditions depend on the distribution of the particle size of the desulfurizing agent, intensity of agitation of the bath as determined by rotational speed of the reactor, physicochemical properties of the involved phases such as viscosity, besides duration of the pretreatment.

Figure 1 gives the schematic representation of processes of desulfurization of pig iron in ladles. In the 1st case the desulfurizing agent is injected through the bottom (a). In the 2nd method injection is done through a lance introduced from top (b). In the Kanbara reactor method the dispersion of the desulfurizing agent is carried out by mechanical agitation using an impeller. All these methods have the objective of reduction of pretreatment times and specific consumption of the desulfurizing agent to attain the desired reduction in the sulfur content of the melt.

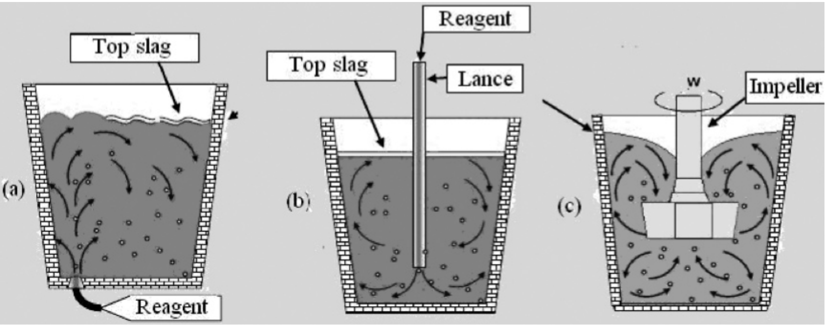

Figure 1: Desulfurization of pig iron in ladles: (a) bottom injection (b) injection with lance (c) Kanbara reactor

In the injection processes, generally the fraction of the agent dispersed in the melt is limited to ≤ 0.30 and that may limit the process yield. On the other hand in the case of Kanbara reactor one can obtain almost complete dispersion of the desulfurizing agent in the melt as a result of intense agita-tion caused by the impeller and as a result one should expect that in addition to reduction of refining times there could be a reduction in the consumption of the reagent, thus resulting in increased pro-ductivity and reduced cost of operation.

In the pretreatment process in Kanbara Reactor (KR), besides the initial temperature, mass and composition of pig iron, composition and mass of the carry over slag from blast furnace also influ-ence the desulfurization process. Operational parameters, such as: immersion depth of the impeller and its positioning, level of liquid metal also affects the desulfurization process. Hence any model that would be applicable to describe desulfurization should take into account these characteristics and specific parameters of the industrial reactor.

METHODOLOGY

Firstly a mathematical model of desulfurization in KR was developed. The kinetic model assumes that the global rate of desulfurization reaction (R) is the summation of the contributions of the slag droplets from blast furnace carry over slag (R_D) and particles of desulfurizing agent (R_P).

$$R = -\frac{1000\ M_L}{100}\frac{d[\%S]}{dt} = R_D + R_P \tag{1}$$

Where, R_D represents the rate of reaction by the slag droplets from carryover slag from blast furnace dispersed in the metallic bath due to agitation.

$$R_D = \frac{k_S^D \rho_L A_D}{100}\Big[[\%S] - [\%S]_i^D\Big] = \frac{k_S^D \rho_L A_D}{100}\left[[\%S] - \frac{(\%S)_D}{L_S^D}\right] \tag{2}$$

And, R_p represents the reaction rate of particles of desulfurizing agent dispersed in the metallic bath.

$$R_P = \frac{k_S^P \rho_L A_P}{100}\Big[[\%S] - [\%S]_i^P\Big] = \frac{k_S^P \rho_L A_P}{100}\left[[\%S] - \frac{(\%S)_P}{L_S^P}\right] \tag{3}$$

These equations imply mass transfer control at the metal side of a metal-desulfurizing agent inter-face. Thus the rate of desulfurization of the pig iron can be described by equations 1 to 3. One can notice that many of the parameters are prone to be time dependent. Also desulfurizing agents, carry over slag and lime, behave differently. A numerical procedure is required unless some simplifying assumptions are made. Some possible simplifications are as follow. These equations can be simpli-fied substituting a common %S, for the slag droplets and dispersed particles will eventually become slag.

Considering the same metal interfacial concentration regardless of the desulfurizing agent, i.e., drop-lets of carryover slag or particles of the desulfurizing agent dispersed in the melt, or in other words, same relationship $(\%S)/L_S$, and defining:

$$\lambda = \frac{L_S\left(M_{esc}^{t=0} + M_{ad}\right)}{1000} \tag{4}$$

and further assuming the same mass transfer coefficient and a total metal-desulfurizing agents inter-facial area Equation 1 can be rewritten as:

$$\frac{d[\%S]}{dt} = -\frac{k_S \rho_L A}{1000\ M_L}\left(1 + \frac{1}{\lambda}\right)[\%S] + \frac{k_S \rho_L A}{1000\ M_L}\left(\frac{[\%S]_o + \frac{M_{esc}^{t=0}(\%S)_O}{1000}}{\lambda}\right) \tag{5}$$

The above equation can be further simplified by defining the following parameters and incorporat-ing in the same to give Equation 7.

$$\alpha = -\frac{k_S \rho_L A}{1000\ M_L}\left(1 + \frac{1}{\lambda}\right) \qquad \beta = \frac{k_S \rho_L A}{1000\ M_L}\left[\frac{[\%S]_o + \frac{M_{esc}^{t=0}(\%S)_O}{1000}}{\lambda}\right] \tag{6}$$

The desulfurization treatment in the KR ladle is non-isothermal in nature, naturally the factors α and β should vary continually during the process as these parameters are temperature dependent. As magnitudes of parameters α and β vary with time hence even this heavily simplified equation should be integrated through numeric techniques, taking into consideration the effect of temperature variation during the process. Variations in the mass, composition and flux particle size distribution also induce variations in the magnitudes of the above parameters. However, if α / β can be consid-ered constant during then results:

$$[\%S] = -\frac{\beta}{\alpha} + \left[[\%S]_O + \frac{\beta}{\alpha} \right] \exp(\alpha t) \tag{7}$$

Hence the desulfurization efficiency (E) can be expressed as:

$$E = \left[1 - \frac{[\% S]}{[\% S]_O} \right] 100 = \left(\frac{\lambda}{1+\lambda} - \frac{M_{esc}^{t=0} (\% S)_O}{1000\, [\% S]_O (1+\lambda)} \right) \left(1 - exp \left(- \frac{k_S \rho_L A}{1000\ M_L} \left(1 + \frac{1}{\lambda} \right) t \right) \right) \tag{8}$$

where the term,

$$\delta = \frac{M_{esc}^{t=0} (\% S)_O}{1000\, [\% S]_O (1+\lambda)} \tag{9}$$

represents the thermodynamic parameter of the reaction, characterized by initial conditions of the treatment. This is independent of the kinetic conditions of the process and holds good for the entire duration of the process. Assuming conservation of mass that is to say there is no loss of mass in the system and if the partition coefficient does not change, GAM can be defined as a factor deleteri-ously affecting the desulfurization efficiency, and is a function of δ and is represented by

$$GAM = \delta \left(1 - \exp \left(- \frac{k_S \rho_L A}{1000 M_L} \left(1 + \frac{1}{\lambda} \right) t \right) \right) \tag{10}$$

Considering,

$$B = \frac{k_S \rho_L A\, t}{1000\ M_L} \tag{11}$$

and incorporating the same in Equation 8, results in :

$$E = \frac{\lambda}{1+\lambda} \left(1 - \exp \left(- B \left(1 + \frac{1}{\lambda} \right) \right) \right) - GAM \tag{12}$$

These simplifications allows an analytical description of the process through an equation that is es-sentially similar to that derived by Riboud et Vasse [1] for describing desulfurization process of a metal bath with top slag agitated by gas flow. It shows that for low values of the characteristic thermodynamic parameter, λ, it is necessary to further agitate the metallic bath for obtaining an increase in the desulfurization efficiency. For high values of the characteristic thermodynamic parameter, characterized by either high values of partition coefficient of sulfur or high volumes of the desulfurizing agent, one could employ lower rates of energy dissipation or larger particle sizes.

As one can see from Equation 12 for high values of characteristic thermodynamic parameter λ, $|1/\lambda \rightarrow 0$ the same gets reduced to $E \approx (1-\exp(-B))$. In this case, the efficiency of the process depends only on the characteristic kinetic parameter B, or rather conditions of agitation of the bath and of the distribution of particle sizes of the desulfurizing agent.

Model implementation requires the evaluation of some parameters. Partition coefficient of sulfur, between metal and dispersed slag of given composition and treatment temperature, depends on the activity of the oxygen and sulfur in the melt, flux composition and temperature. Sosinsky and Sommerville [2] give the following equation for the partition coefficient of sulfur between the metallic bath and the top slag:

$$\log L_S = \frac{21920 - 54640\,\Delta}{T} + 43{,}6\,\Delta - 23{,}9 + \log f_s - \log h_O \tag{13}$$

Maintenance of oxygen potential in the liquid pig iron to enable maximum distribution of sulfur between liquid metal and slag is very essential for an efficient desulfurization. The activity of oxy-gen at the reaction interface, is assumed to be established by carbon monoxide reaction formation.

For a given characteristic thermodynamic condition, the desulfurization process is affected substan-tially by the effective kinetic conditions in the reactor. The kinetic conditions depend on the state of agitation of the metal bath defined by a power number of impeller, Po, which is to be measured experimentally

$$Po = \frac{P}{r_L\,\omega^3\,D_{imp}^5} \tag{14}$$

For example Davies [3], developed the following equation for the coefficient of mass transfer:

$$k_S^P = 0{,}237\left(\frac{\mu_L}{\rho_L}\right)^{-0{,}41}\left(\frac{P_O D_{imp}{}^5}{H_{imer} D^2}\right)^{1/4} D_S^{2/3}\,\omega^{3/4} \tag{15}$$

This equation does not deal with the effect of distribution of sizes of dispersed particles. However this aspect is important as there could be a change in the magnitude of the mass transfer coefficient during agitation of melt. For that Irons, Szekely and El-Kadah [4, 5, 6] give the following equation for calculating the coefficient of mass transfer between the bath and the particles of small dimensions:

$$k_S^P = \frac{D_S}{d_P}\left[2 + 0{,}4\left[\frac{\varepsilon d_P^4\,\rho_L^3}{\mu_L^3}\right]^{1/4}\left(\frac{\mu_L}{D_S\,\rho_L}\right)^{1/3}\right] \tag{16}$$

Here the rate of dissipation of energy due to the impeller is defined as:

$$\varepsilon = \frac{P}{1000M_L} = \frac{P_O \rho_L \omega^3 D_{imp}^5}{1000M_L} \quad (w/kg) \tag{17}$$

Analysis of the Desulfurization Process in KR and Model Predictions

The relation describing variation of the concentration of sulfur in the iron melt can be written on the basis of Equation 7:

$$\frac{d[\%S]}{dt} = \alpha\,[\%S] + \beta \tag{18}$$

Which implies at equilibrium,

$$[\%S]_{eq} = -\frac{\beta}{\alpha} = \frac{[\%S]_o + \dfrac{M_{esc}^{t=0}(\%S)_O}{1000}}{1+\lambda} \tag{19}$$

and since α and β are constants, it this results in the graphical solution represented in Figure 2.

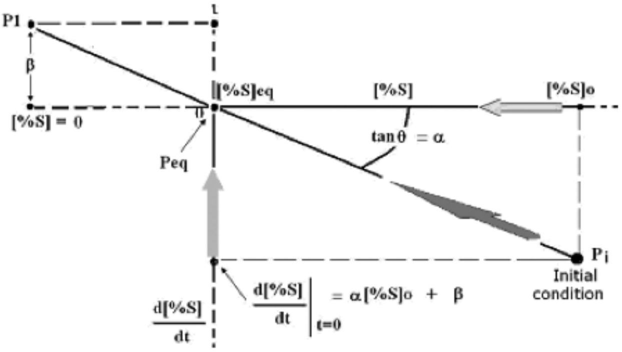

Figure 2: Evolution of the desulfurization rate with concentration of sulfur

Of course points P1 (representing initial conditions), P_{eq} (representing equilibrium) and P_1 (repre-senting the unattainable condition of complete desulfurization) lie in a straight line which can be used to characterize the rate of the process.

As a matter of fact for each operational condition defined by temperature, metal volume, type, mass, composition and particle size of flux; type, immersion depth and speed of impeller rotation; mass and composition of the carryover slag, besides the chemical potential of oxygen, at the interface of metal-dispersed particle, an operational straight line exists. It is then possible to develop a series of operational straight lines for describing desulfurization in KR for different conditions. For a typical operational condition of a given Kanbara reactor, to construct the operational line for desulfurization it is enough to determine the parameters $\left(\frac{d[\%S]}{dt}\right)_{t=0}$; [%S] o) and (0, $[\%S]_{eq}$). However proper de termination of α and β requires the evaluation of thermodynamic and kinetic parameters, according to Equation 6.

Figure 3 gives the effect of the intensity of agitation of the bath on the initial rate of desulfurization. The higher the impeller speed the higher the rate of energy dissipation which implies higher values of mass transfer coefficient and larger absolute values of α. Thus conditions 3, 2 and 1 represent decreasing rates of energy dissipation. Condition 3 exhibits larger rate of initial reaction, while the condition 1, relatively smaller rate of initial reaction.

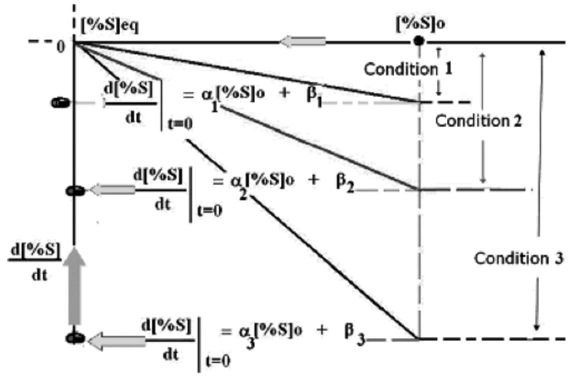

Figure 3:Family of operational straight lines for desulfurization in KR, under different conditions of turbulence (impeller speed) for the same thermodynamic conditions, that is for constant [%S]eq

The rates of desulfurization decrease with decreasing sulfur contents and as required eventually vanish close to equilibrium. The maximum efficiency of desulfurization,as has already been stated, depends on the characteristic thermodynamic parameters and the effect of carryover slag from blast furnace.

$$E_{eq} = \left(1 - \frac{[\%S]_{eq}}{[\%S]_o}\right) = \left(1 - \frac{\beta}{\alpha\ [\%S]_O}\right) = \frac{\lambda}{1+\lambda} - \delta \qquad (20)$$

Assuming absence of carryover slag or negligible sulfur contents in the same makes δ equal to zero and defines the upper value of desulfurization yield. This relationship is given in Figure 5. Geometrical modifications in the impeller may allow higher rates of energy dissipation and consequently higher values of mass transfer coefficient. Smaller particle sizes (higher interfacial area) and larger impeller speed, lead to higher initial rates of desulfurization. The maximum desulfurization efficiency can only be approximated through prohibitively large treatment times. That is so be-cause the desulfurization curve behaves assymptotically. Extending treatment times is not feasible since it implies on higher temperature losses and may result in possible operational problems.

RESULTS AND DISCUSSION

A database with values for more than 600 heats of a KR of ArcelorMittal Tubarão, Brazil, has been analyzed with this model. Typical entries are mass of pig iron, impeller rotational speed, initial sul-fur, target sulfur, final sulfur, initial and final temperature, mass of desulfurizing agent, treatment time beside other not related to this model. Slag carryover data was not provided. Desulfurizing agent was basically a 90% calcined lime/10%

fluorspar (85% CaF_2, balance SiO_2), 200 μm of di-ameter powder mixture. Ladle nominal capacity was 315 tons for an average diameter of 3.5 m. Impeller diameter was 1.5 m. Average values are seen on Table 1.

Table 1: Average data values for some 600 heats

Mass of hot metal	**300 tons**
Initial sulfur	30 ppm
Impeller rotation speed	100 rpm
Target sulfur	2 ppm
Observed sulfur	2 ppm
Initial temperature	1370 °C
Final temperature	1340 °C
Total added flux	2470 Kg
Specific flux consumption	8.1 kg/ton
Treatment time	12.3 minutes

Kirmse [5] has shown calculations of sulfur at equilibrium assuming the presence of pure and solid CaO and CaS, carbon monoxide partial pressure of 1 atm, carbon saturated pig iron such as sulfur activiy coefficient can be taken as close to 5. Accordingly at 1300°C sulfur at equilibrium can be as low as 10 ppm. The pure solid assumption may not apply on actual systems due to dilution effects from fluorspar addition (sometimes aluminum drosses) and carryover slag. Thus the true equilibrium value may difficult to assess. However as seen on Table 1 this particular plant aims at a rather low target value of final sulfur, probably very close to equilibrium values. Many database entries for observed (final sulfur) are blank reflecting poor analytical precision at such low levels. The degree of desulfurization was chosen in order to evaluate the process efficiency.

$$E = \frac{[S]_o - [S]_{final}}{[S]_o} x100 \qquad (21)$$

Figure 4 gives for each heat the ratio of *observed degree of desulfurization / predicted (by this model) degree of desulfurization*. It can be seen that there is a lot of scatter although most of the reported values lie close to unity. Overall there seems to exist a good agreement. This database was acquired during equipment start-up what may justify the dispersion. Of course a relative agreement based upon the final degree of desulfurization is no conclusive proof. For that one may need to compare the entire desulfurization curves.

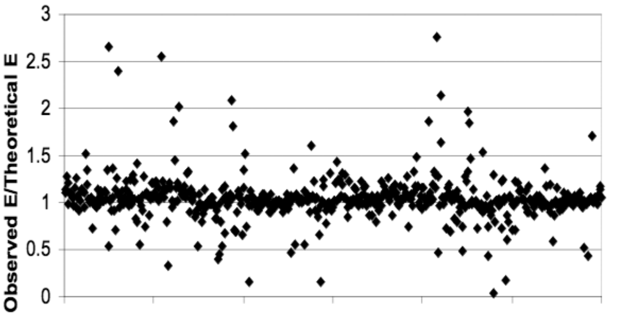

Figure 4: Ratio between observed and predicted degrees of desulfurization

According to the model presented here the sulfur equilibrium content is given by

$$[S]_{eq} = -\frac{\beta}{\alpha} \tag{22}$$

as per Equation 6. Figure 5 is a plot of sulfur equilibrium content as a function of reported sulfur content for a number of heats. One can notice that the values are quite close to each other. This may mean over-reaching since the rate of desulfurization decreases significantly close to equilibrium. As a matter of fact the target sulfur content was close to the equilibrium values as it can be seen in Figure 6. For a few heats some exceptions were observed but the reported values are mostly bellow 5 ppm.

Table 2 represents the influence of some operational parameters upon the kinetics. Thermodynamic conditions (mass of pig iron, mass and composition of the reagent, initial sulfur and temperature) are kept constant and the influence of impeller velocity, particle diameter and power number (which depends on impeller geometry), have been assessed. As can be seen by comparing the values of α and β, as per equation 54, the values of the initial rate of desulfurization are dependent on these parameters.

Effect of impeller speed on desulfurization is shown on Figure 7. As it can be seen virtual equilib-rium would be reached within 10 minutes, regardless of the rotational speed. The main effect of speed is upon the initial rate (e.g. 80 rpm; 9.0 ppm/min initial rate) and it can be shown the relation-ship to be linear. This is important since it provides a basis for judging the feasibility of shorter treatment times.

Data regarding variation of particles diameter was not included in this database, as said before. Figure 8 is to assess the influence of this parameter. Again the effect is mainly upon the initial rate of desulfurization. However the initial rate shows an inverse and quadratic relationship with particle diameter. This may have been expected since the total area for mass transfer is dependent on the diameter squared. This reflects the importance of controlling the grinding process.

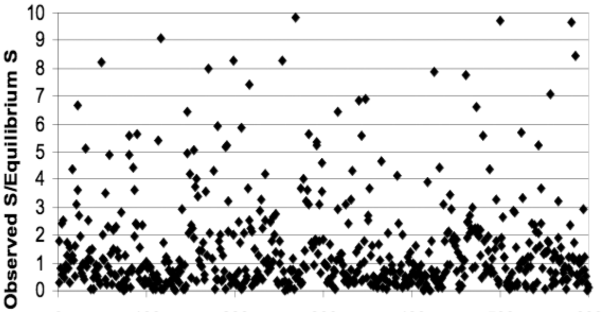

Figure 5: Comparison between reported sulfur and equilibrium sulfur contents

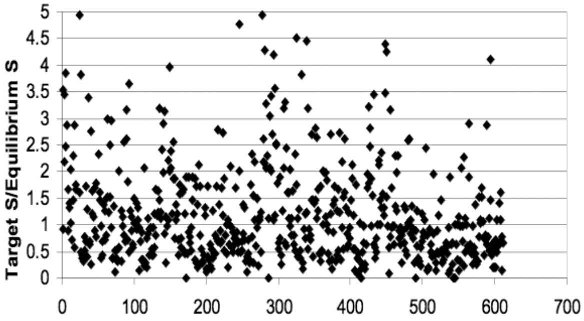

Figure 6: Ratio between target sulfur content and equilibrium values

Rate of desulfurization has been estimated using the theoretical model, since the model predictions in respect of end sulfur content for different heats are in good agreement with plant data. The model uses input data such as amount of reagent (Reag), impeller velocity (RPM), mass of pig iron (M_L), temperature (K) and initial sulfur(ppm). These data (and others) come from the data base. Multiple regression(stepwise) was carried out with MINITAB™.

It was not possible to single out a main operational parameter affecting the desulfurization. Multivariable regression yielded the following relationship for initial rate of desulfurization

$$-\frac{d[S]}{dt} = \{-12.34 + 0.0427\ \mathrm{Re}ag + 3.00\ So\ (ppm) + 0.865\ RPM - 0.532\ M_L + 0.328\ \lambda\}/10^5 \quad \mathrm{r}^2 = 96\% \tag{23}$$

with high degree of significance for all the reported variables. The particle diameter does not show because the same size was used in all heats. Thus every thermodynamic and every kinetic parameter contemplated in this model has an important role.

Table 2: Initial rate of desulfurization under different kinetic conditions; (300 tons of hot metal; 2470 kg of reagent; 30 ppm of initial sulfur; initial temperature equal to 1370 °C).

Case	**RPM**	**d_p (m)**	**Po**	**$-\alpha \times 10^3$**	**$\beta \times 10^6$**	**$-\frac{d[S]}{dt}\|t = 0$ (%/min)**
Base	100	0.0020	2	6.921	1.428	0.00116
A	120	0.0020	2	7.935	1.638	0.00133
B	100	0.0015	2	9.228	1.905	0.00155
C	100	0.0020	3	7.659	1.581	0.00128
D	120	0.0015	3	11.709	2.416	0.00196

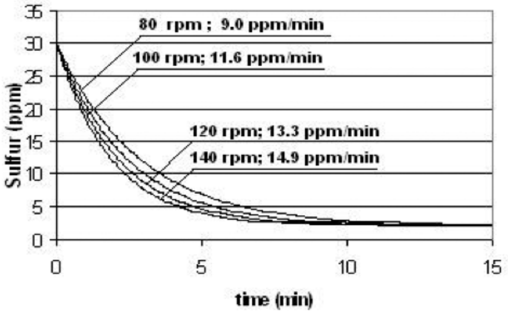

Figure 7: Influence of impeller rotation speed on desulfurization

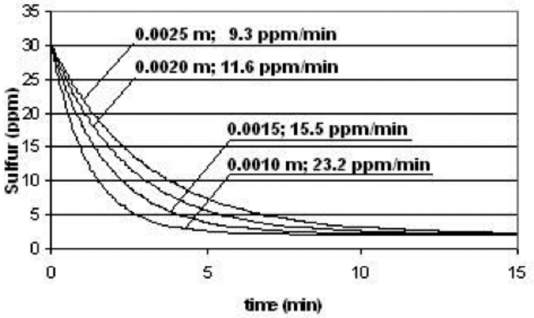

Figure 8: Influence of particle diameter on desulfurization

CONCLUSIONS

The model proposed in order to relate the progress of the desulfurization process in a KR reactor as a function of thermodynamic and kinetic parameters can be satisfactorily applied to the KR process in respect of desulfurization.

The kinetic parameters include the power input by the impeller as it is affected by ladle and impel-ler geometry and rotational speed of the latter.

The effect of particle size on the process as assessed by the model is mainly upon the initial rate of desulfurization. However the initial rate shows an inverse and quadratic relationship with particle diameter. This may have been expected since the total area for mass transfer is dependent on the diameter squared. This reflects the importance of controlling the grinding process.

Final sulfur contents as predicted by the model have been compared with those coming from a data-base including some 600 heats of an actual plant. The agreement is satisfactory.

A regression equation has been developed correlating important variables of the process for calculating the desulfurization rate in the KR reactor.

NOMENCLATURE

A = Total area of reaction, m^2.
A_D = Metal-dispersed slag droplets interfacial area, m^2.
A_p = Metal-desulfurizing particles interfacial area, m^2.
D = Diameter of the reactor, m.
D_{imp} = Impeller diameter, m.
d_p = Mean diameter of the particle, m.
D_s = Diffusion coefficient of sulfur in the liquid iron, m^2/s.
E = Efficiency of desulfurization.
f_o = Activity coefficient of oxygen in liquid iron.
f_s = Activity coefficient of sulfur in liquid iron.
H_{imer} = Depth of impeller immersion, m.
h_o = Activity of the oxygen.
K_s = Mass transfer coefficient, m/s.
$k_s{}^p$ = Mass transfer coefficient at metal-droplet interface, m/s.
$k^D{}_S$ = Mass transfer coefficient at metal-particle interface, m/s.
L_s = Sulfur partition coefficient.
$L^D{}_S$ = Partition coefficient of sulfur between liquid iron and droplets of carry over slag.
L^p_s = Partition coefficient of sulfur between liquid iron and flux particles.
$M_{esc}{}^{t=0}$ = Mass of carryover slag, kg/ton.
M_{ad} = Mass of flux addition, kg/ton.
M_L = Mass of pig iron, ton.
P = Power delivered to the impeller, W.
P_o = Power Number for impeller.
R = Overall rate of desulfurization of the iron, kg/s.
Reag = Mass of added reagent, kg.
R_D = Rate of desulfurization of iron by carry over slag, kg/s.
R_p = Rate of desulfurization of iron by flux particles dispersed in the melt, kg/s.
RPM = Impeller rotational speed, rpm.
So = Initial sulfur content, ppm.
S_{eq} = Equilibrium sulfur content, ppm.
$[\%S]$ = Sulfur concentration in iron, weight %.
$[\%S]_{eq}$ = Equilibrium concentration of sulfur in the bath, weight %.
$[\%S]_{final}$ = Final concentration of sulfur in the bath, weight %.
$[\%S]_i$ = Metal sulfur concentration at interface, weight %.
$[\%S]_i^D$ = Sulfur concentration at the metal-dispersed slag droplets interface, weight %.
$[\%S]_i^p$ = Concentration of sulfur in the metal-particle interface, weight %.
$[\%S]_o$ = Initial concentration of sulfur in iron, weight %.
$(\%S)$ = Slag sulfur concentration, weight %.
$(\%S)_D$ = Sulfur content of the dispersed slag droplets, weight %.
$(\%S)_0$ = Initial sulfur content of carry over slag, weight %.
$(\%S)_p$ = Sulfur content of desulfurizing agent, weight %.
T = Metal temperature, K.
t = Elapsed time, s.
Δ = Optical basicity.
ε = Rate of energy dissipation, W/kg.
μ_L = Viscosity of metal, kg/m.s.
ρ_L = Density of pig iron, kg/m^3.
ω = Angular velocity of impeller, Hz.

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