A Study of parameters influencing desulphurization of Carbon-saturated Iron with 
Lime-based Flux Injection in Industrial Ladles

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Abstract

In this study the effect of various operational parameters have been analyzed on the desulphurization efficiency of carbon saturated iron during injection of flux mixtures containing lime, Magnesium and calcium carbonate using a kinetic model, which takes into consideration the contribution by the top slag, particles dispersed in the melt as well as particles adhering to the bubbles of the gas. Experimental data from laboratory studies as well as industrial data were used to test the validity of the model.
1- Introduction

Lime-based fluxes are used in many countries for hot metal and steel desulfurization and dephosphorization. Thermodynamic studies\(^{(1-4)}\) have shown that solid CaO can be a powerful desulfurizing agent for pig-iron as well as for steel, and that sulfur as low as 0.001\% can be achieved. However, from a kinetic standpoint the desulfurization reaction by CaO is sluggish due to formation of solid reaction products (sulfides and silicates) which deposit at the particle surface blocking the sulfur diffusion. The beneficial effect of higher sulphur activities due to high silicon contents cannot be fully realized since the SiO\(_2\) formed during the reaction affects the sulphur transport.\(^{(1,2)}\)

Lime-based fluxes with various liquid-phase fractions, have been investigated\(^{(1,2)}\). It was found the amount of liquid phase, as transport of reactants through a molten product layer is much faster compared to the solid product shell. The shrinking core model for CaO desulfurization, proposed by the same authors, highlights the importance of solid state diffusion of sulfur to the process. They argue that the slow desulfurization kinetics could be generally attributed to formation of a shell of solid reaction products (2CaO.SiO\(_2\) and 3CaO.SiO\(_2\)) on the particle surface, and so the fluxing of the product layer by fluor spar, millscale or other additives, enhances diffusion and increases the overall rate of reaction.

The extra resistance caused by this solid shell on the lime particles would decrease the importance of mixing on the overall rate of reaction\(^{(3)}\). So when the diffusion through the solid shell is the rate controlling step, increasing agitation will only benefit the process through an increasing of the residence time and depth of penetration of each particle. It is desirable to avoid the solid shell phenomena, the reactant should be associated with a liquid phase. It was found\(^{(1,2)}\) that the injection of CaO particles smaller than 1.5 mm, could lead to the formation of agglomerates as large as 20 to 30 mm, due to liquid phase formed at the particle surface. The addition of small amounts of CaF\(_2\), promotes the formation of a low viscosity, low melting primary liquid phase eutectic containing CaO - CaF\(_2\) - SiO\(_2\), which is capable of penetrating into the pores and cracks of the particles dissolving CaO, CaS and other reaction products\(^{(2)}\). However, since the CaF\(_2\) has no desulfurizing power by itself but only helps to dilute the main component, its amount should be kept to a minimum. The percolation power of a primary liquid phase CaO - Al\(_2\)O\(_3\) - SiO\(_2\) - CaF\(_2\) - CaS is limited and then in order to keep the reaction moving fresh CaO particles are necessary\(^{(4)}\). Additions of Na\(_2\)O to CaO based mixtures
promotes the formation of a liquid phase capable of dissolving the CaO, and increases the sulfur partition coefficient\(^{5-11}\). However, according to these authors, addition of CaF\(_2\) decreases the thermodynamic desulfurizing power, but improves the transport of sulfur and oxygen ions. Also the reaction system associated with sodium carbonate is very complicated, involving fusion, vaporization, dissociation, and reactions with silicon and carbon of the hot metal.

The rate of desulfurization increases with the rate of injection of solids and with decreasing particle size, if agglomeration can be avoided\(^{3,12}\). However, it is desirable to have larger CaO particles in order to assure a higher degree of penetration and lesser powder agglomeration\(^{13}\). On the other hand, high values of gas flow rate lead to decreasing residence time of particle dispersed in the melt, thus increasing gas-liquid interfacial area. An optimal gas flow rate must be chosen in order to minimize splashing and oxidation of metal.

The benefits of a gas-releasing agent, such as calcium carbonate or sodium carbonate in the flux mixture are attributed to increasing interfacial area of the bubbles and formation of small particles during decomposition, and not to decreasing mixing time. Also, for situations corresponding to high gas flow rate there would be little benefit in decreasing of particle size since the rate of desulfurization would be controlled at the melt-bubble interface. As far as the top slag reaction is concerned, it should be enhanced by gas releasing agents. It is well known that gases released during carbonate decomposition and Boudouard reactions can play an important role in bath stirring. In addition, residence time and bubble size should also play an important role. A theoretical analysis of the heat transfer phenomena\(^{14}\) concerning the particles dispersed in the melt and those entrapped in the bubbles show that, under the average conditions reported for these experiments, the carbonate decomposition should be total and between 85 to 94\%, respectively. In the present work these aspects have been taken into consideration in the simulations carried out with fluxes containing carbonates.

The desulfurization process also is dependent upon low oxygen potential conditions at the reaction interface, large reaction interface area, total amount of the powder and the gas/powder ratio, particle size, improved transport of sulfur and reaction products to and from the reaction front; control of temperature and degree of bath stirring. The effect of these variables as well as others influencing the process can be analyzed with the help of a computer model developed on the basis of the equations that describe the simulation of desulfurization in industrial ladles as well as experiments conducted in the laboratory scale. Influence of the
composition of flux powder (CaO, Na₂O, Mg etc), temperature, amount of carry over blast furnace slag etc also have been evaluated.

2- Model Equations

The overall desulphurization rate can be defined considering contributions by top slag, dispersed particles and particles entrapped in the bubbles in the transient and permanent reactors:

$$\frac{M_s}{100} \frac{d[\%S]}{dt} = R_{ts}^t + R_{s}^p + R_s^b$$  (1)

The contribution of permanent region of the reactor amounts to nearly 70-80% of total and is essentially due to the top slag. This is given by:

$$R_{ts}^t = \frac{k_{ts}^s A_{ts} \rho_s}{M_s^{100}} (\frac{[\%S] - [\%S]}{L_s^{ts}} + \frac{M_{ts}^{(t)}}{(M_{ts}^{(t)})^{[\%S]}})$$  (2)

Mass transfer coefficient in the above equation is given by:

$$\frac{1}{k_s^t} = \frac{1}{k_s^{net}} + \frac{1}{L_s^{ts} k_s^{sl}}$$  (3)

$k_s^{net}$ is the mass transfer coefficient of sulfur at the metal side of the slag metal interface under conditions of bath agitation through gas flow and can be evaluated on the basis of the surface renewal theory by Higbie as given by Riboud et al.:

$$k_s^{net} = 500 \sqrt{\frac{D_{s}^{net} Q}{A_{ts}}} \text{ m/s}$$  (4)

where the diffusion coefficient is given by:

$$D_{s}^{net} = 2.8 \times 10^{-9} e^{\left(\frac{-3774.5}{T}\right)} \text{ m}^2/\text{s}$$  (5)

Similarly, the mass transfer coefficient for the slag side for turbulent conditions is given by:
where the diffusion coefficient can be calculated using Stokes-Einstein equation\(^{16}\):
\[
D_{sl} = \frac{k_B T}{3 \pi \eta \text{d}_{ion} \mu_{sl}} \text{ m}^2/\text{s}
\]  \hspace{1cm} (7)

\(k_B\) is Stefan-Boltzmann constant for \(\text{d}_{ion}\), diameter of sulphur ion in the slag, a value of 1.84 angstrom has been considered. The proportion between the above two coefficients has been estimated as,
\[
\frac{k_{sl}}{k_{met}} \leq \sqrt{\frac{D_{met}}{D_{sl}}} < 10
\]  \hspace{1cm} (8)

This is in agreement with the value given by Kitamura et al.\(^{17-19}\)

Slag viscosity in equation 7 can be estimated using the following equation calculated using the concept of optical basicity, \(\Lambda_{cor}\),\(^{20}\)
\[
\mu_{sl} = A \cdot e^{\frac{B}{\Lambda_{cor}}} \text{ Pa.s}
\]  \hspace{1cm} (9)

where
\[
\ln A = - 232.69 \cdot \Lambda_{cor}^2 \cdot 35.732 \cdot \Lambda_{cor} - 144.17
\]  \hspace{1cm} (10)

and,
\[
\ln \frac{B}{100} = -1.77 \cdot \frac{2.884}{\Lambda_{cor}}
\]  \hspace{1cm} (11)

Partition coefficient of sulphur \(L_{sl}\) is given by\(^{21}\), where \(C_s\), sulphide capacity of slag, can be calculated using the following equations:
\[
\log C_s = \left( \frac{22690 - 54640 \Lambda}{T} \right) - 43.6 \Lambda - 25.2 \quad \text{for} \quad \Lambda = 0.8
\]  \hspace{1cm} (12)
\[
\log C_s = -13.913 \cdot \Lambda - 32.82 \Lambda^2 - \frac{11710}{T} - 0.02223 (\% \text{SiO}_2)
\]  \hspace{1cm} (13)

\[
+ 0.02275 (\% \text{Al}_2\text{O}_3) \quad \text{for} \quad \Lambda < 0.8
\]
Contribution of dispersed particles in the metal, considering that they possess the same capacity for desulphurization during the time of their residence in the plume region, is given by:

\[ R_s^b = \frac{f I L_s^b}{M_s 100} \left( 1 - e^{-\frac{2.39 k_s^b p_L T_b^0 T_P^0}{273 p_s^b d_b^t t^t}} \right) \mathrm{[\%S]} \]  

(15)

The contribution by particles entrapped inside the bubbles can be described by the following equation:

\[ R_s^p = \frac{(1 - f) I L_s^p}{M_s 100} \left( 1 - e^{-\frac{6 k_s^p p_t^t}{d_s^p d_p}} \right) \mathrm{[\%S]} \]  

(16)

The theoretical basis for the development of the above equations as well as evaluation of the parameters, has been discussed in an earlier publication by the authors.

The overall contribution from magnesium on molten pig iron desulphurization is given by two contributions: desulphurization in the bath by dissolved magnesium and desulphurization at bubble-metal surface.

\[ R_s^\text{Mg} = R_s^{\text{dis}} \cdot R_s^{\text{bab}} \]  

(17)

These contributions, \( R_s^{\text{dis}} \) and \( R_s^{\text{bab}} \), must be added to the contributions from dispersed and entrapped particles. The latter namely desulphurization at the bubble-metal interface takes place according to the following reaction involving magnesium vapor.

\[ [S] + \text{Mg}_{(v)} = \text{MgS}_{(sol)} \]

Assuming equilibrium at the bubble metal interface,

\[ R_s^{\text{bab}} = \frac{6 Q T \tau_b ^0 k_s^b p_L}{273 100 M_s d_b^t} \left( [\%S] - [\%S]^\text{eq} \right) \mathrm{kmol~S/s} \]  

(18)

Similarly, dissolved magnesium also reacts with sulphur:
\[
[S] + [Mg] = MgS_{\text{sol}}
\]

Magnesium vapor pressure at the bubble metal interface will determine the concentration of Magnesium in the bath:

\[
M_{g(v)} = [Mg]
\]

However, all the magnesium present in the form of vapor does not dissolve in the melt and this would depend on the residence time of the bubbles in the bath and hence only a fraction of the total flux of the vapor contributes to the saturation of the Magnesium in the bath. This effect is taken into account by the factor, \( \Omega_{Mg} \) which is calculated in the computer code considering the residence time of the bubble etc.:

\[
R_{g}^{\text{dis}} = \frac{6 \cdot Q \cdot T \cdot \tau_b \cdot k_{Mg} \cdot \rho_{f}}{273 \cdot 100 \cdot M_{Mg} \cdot d_{p}} \cdot (\text{[\%Mg]}_{sat} - \text{[\%Mg]}_{eq}) \cdot \Omega_{Mg} \text{ kmol S / s} \quad (19)
\]

3 - Simulation with experimental data

The computer code developed on the basis of the above equations was used for simulation of experimental results in the laboratory. Experimental work in the laboratory was carried out in a high temperature carbon resistance furnace with computer control for temperature and data collection with provision for injecting flux powder with nitrogen gas in an iron melt containing sulphur in graphite crucible. One set of experiments were carried out with top slag only with agitation of the bath with injection of nitrogen and the other set with injection of flux powder along with nitrogen. The experimental set up and the conditions of experiments are given in figure 1 and table I respectively. Two sets of preliminary experiments were carried out as shown in figure 1. In the first set the flux powder was added separately and in the second injection was done along with gas stream. As results did not differ much (probably due to very small residence time of particles in the melt) the second set up was adopted for carrying out the experiments. Samples of molten pig iron were collected in intervals of 5 minutes during the flux injection upto 25 minutes, using vacuum vitreous silica sampling tubes, and these were analyzed for sulphur.

Figure 2 shows a comparison between experimental data and predicted by model agreement between the two is fairly satisfactory. As can be seen from figure 3, with increase in the top slag mass the desulphurization efficiency increases, as the activity of the calcium sulfide formed decreases inhibiting reversion. In addition the characteristic parameter defined in terms
of \( L_{\text{t}}, M_{\text{slag}}/M_{\text{t}} \) increases with the mass of top slag resulting in better desulphurization as predicted in the model. In this case also there is a good agreement between the experimental and simulation results. However increase in the slag quantity is not desirable from the point of view of cost and environmental factors.

Figure 4 shows that the substitution of fluorite by \( \text{Na}_2\text{O} \) improves desulphurization efficiency. Simulated results also predict the same as it is evident that the partition coefficient of sulphur is increased relatively by increasing alkaline oxides as they contribute to higher sulphide capacity due to increased optical basicity.

### 4 Simulation of Industrial Data

Simulations were carried out with industrial data from a Brazilian integrated steel plant. The scheme of injection of flux for desulphurization of melts is given in figure 5. A total of 400 heats of desulfurization of carbon-saturated pig-iron through injection of powder mixtures have been analyzed. Industrial working conditions for desulphurization of the molten pig iron and data are given in table II.

For most of the simulations in industrial ladles \( f = 0.70 \) has been chosen (eqn.4). The fraction of the particles entrapped inside the bubbles (\( f \)) was not measured in these experiments. Values cited in the literature \(^{3,12}\) are in the range 0.60-0.80. Cold model studies \(^{23}\) imply that increasing values of the \( G_{\text{s}}/G_{\text{g}} \) (solid mass flowrate/gas mass flowrate) ratio result in decreasing values of \( f \) (fraction of particles entrapped inside the bubbles) whenever \( G_{\text{s}}/G_{\text{g}} < 0.5 \). Here the increase of the solid/gas ratio would produce higher desulfurization performance since the characteristic values associated with the particles dispersed inside the melt are higher than those associated with the ones entrapped inside the bubbles. However for \( G_{\text{s}}/G_{\text{g}} \) values greater than 0.5, \( f \) seems to vary little for the range of Weber Number (\( 0 < \text{We} < 8000 \)) investigated. Optimum ratio of solid/gas ratio (\( G_{\text{s}}/G_{\text{g}} \)) must be based on individual shop performance and operating philosophies, although it appears that higher ratios should achieve lower final sulfur in molten pig iron.

Sulphur content of pig iron at the end of flux injection is compared with those predicted by model simulations in fig 6. The correlation coefficient amounted to. However it should be remembered that control of all the parameters are not so rigorous in the industrial practice and this could give rise to deviations between the observed and predicted values.
5- Effect of various operational parameters (Simulated results)

a) Amount of carry over slag

Using the data given in the table an analysis of the effect of various other parameters has been evaluated. Figure 7 shows the detrimental effect of the carry-over slag from the blast furnace due to inferior sulfide capacities of these slags. This has been anticipated by the sensitivity analysis. Increase of carryover slags, other conditions remaining constant result in decreasing rates of desulphurization. However the contribution of magnesium for the desulphurization rates as evaluated in the simulation remains independent of the amount of carryover slag. For 2 and 10kg/ton., the overall initial rate calculated were - 0.0287 and -0.0216 mol of S/ton. respectively. For 2, 5 e 10kg/ton., of carryover slag the relative contribution for desulphurization amounted to 83, 76 e 68%, respectively.

b) Temperature

Desulfurization rates improve in general with the temperature as can be seen from figure 8, although with higher temperature heat losses should also increase. For treatment temperatures of 1300 and 1400°C respectively the decrease in temperature of the melt amounted to 40 to 45°C and the initial desulphurization rates amounted to -0.0077 and -0.0206 mol de S/ton//s , respectively. The contribution of magnesium amounted to -0.0049 and -0.0035 mol of S/ton/s respectively for both the above temperatures, the relative contribution being 54 and 17% for both the cases. The relative contribution of slag for the desulfurization process increased with the initial temperature of the treatment namely 30 and 76% respectively for both the temperatures and the contribution of the particles adherent to the bubbles amounted to 11 and 5%, respectively.

c) Carrier gas flow rate

Increase in carrier gas flux has no significant influence on the rate of desulphurization as is evident from figure 9. Relative contribution of the top slag for desulphurization of the molten pig iron is also not affected much by the inert gas flow rate. For flow rates of 28 and 40Nm³/h, the relative contribution of the top slag amounted to 75 and 77%, respectively. Relative contribution by magnesium decreased from 17 to 16% probably due to some decrease in the residence time of the bubbles in the melt with increase in the gas flux. For these carrier gas flow
rates the contribution to initial rate of desulfurization by magnesium amounted to -0.0216 and - 0.035 mol of S/ton/s respectively.

d) Flux injection rate

Higher injection rates of flux powder result in better desulfurization efficiency as can be seen from figure 10. For injection rates of 28 and 40 kg/min initial desulfurization rates amounted to -0.0216 and -0.0279 mol of S/ton/s respectively and the relative contribution of top slag amounted to 75 and 78% respectively, whereas that of magnesium amounted to 17 and 15% for the 2 injection rates respectively. The increase in the injection rate of powder also causes a certain decrease in the temperature of the bath which amounted to 45 and 59°C respectively for both the cases. The amount of CO₂ generated due to decomposition of the CaCO₃ improves the efficiency of desiliconization which amounted to 17 and 25% respectively for the 2 injection rates. However higher injection rates generate higher amounts of slag and loss of heat from the bath and hence this parameter has be optimized considering overall economic aspects.

e) Influence of calcium carbonate in the flux

The efficiency of desulphurization is not affected much by increasing the calcium carbonate content of the powder mixture, figure 11. This is probably due to the drop in temperature as a result of endothermic nature of decomposition of the carbonate. For 10, 20 and 30% of calcium carbonate in the mixture the temperature drop amounted to 33, 38 e 43°C, relative contribution by the top slag to desulfurization was 59, 67 e 73% and that of magnesium was 31, 24 e 19%, respectively. The decrease observed in the case magnesium is due to the fact that the mean residence time of the bubbles decrease (due to increase in the gas flow caused by CO₂ from the decomposition of calcium carbonate particle, CaCO₃, leading to increase in the magnesium loss as vapor with the gas. As such in the mixtures containing high proportion of carbonates, it is desirable to reduce the carrier gas so that the residence time of bubbles can be increased leading to less magnesium loss and increase in desulphurization efficiency.

f) Influence of magnesium in the flux mixture.

The relative increase in the proportion of Magnesium results in a certain increase in the rate of desulphurization as can be seen from figure 12. Relative contribution to
desulphurization by the top slag for 1, 2 and 3% Mg in the mixture was 76, 60 e 46%, respectively, whereas the contribution by Mg amounted to 17, 34 e 48% respectively. It can be seen that increasing the proportion of magnesium in the mixture does not necessarily result in proportional increase in the desulphurization efficiency as there is increasing loss of the element due to decrease in the residence time caused by increasing turbulence with higher rates of injection of magnesium. It is suggested that the increase in the proportion of Mg in the mixture should be accompanied by a corresponding reduction in the carrier gas rate so as to increase the residence times which should lead to better desulphurization efficiency.

6 - Conclusions

On the basis of the results of simulation of industrial trials with the desulfurization model developed the following conclusions can be reached.

i) The results of model predictions for desulfurization of iron with lime based mixtures agree fairly with the industrial trials.

ii) Under the operational conditions analyzed, powder injection rate, amount of carry-over slag and temperature have relatively a sizable influence on desulfurization.

iii) The relative contribution of top slag is significant to the desulfurization process. On the other hand the contributions of particles and bubbles are small due to inadequate residence times and powder agglomeration.

iv) Calcium carbonate in the mixture promotes higher reaction efficiency due to the increasing reaction interface provided by bubbles resulting from decomposition and also by turbulence and mixing which increases the top slag/metal reaction.

7 - Nomenclature

\( A_{\text{ss}} \) = area of the slag-metal interface (m\(^2\));
\( d_b \) = average bubble diameter (m);
\( d_p \) = average particle diameter (m);
\( f \) = fraction of particles entrapped in the bubbles;
\( h \) = depth of injection, (m);
\( I \) = rate of injection of the desulfurizing agent (kg/s);
$K_{Mg}$ = magnesium mass transfer coefficient, (m/s);
$K_{ts}$ = sulfur mass transfer coefficient through the metal-slag boundary layer, (m/s);
$K_{tb}$ = sulfur mass transfer coefficient through the bubble-melt boundary layer, (m/s);
$K_{tp}$ = sulfur mass transfer coefficient through the particle-melt boundary layer, (m/s);
$L_{ts}$ = partition coefficient of sulphur between top slag and melt;
$L_{tb}$ = partition coefficient of sulphur between entrapped particles in the bubbles and melt;
$L_{tp}$ = partition coefficient of sulphur between dispersed particles and melt;
$M_s$ = atomic mass of the sulphur, (kg);
$M_{Mg}$ = atomic weight of the magnesium, (kg);
$M_{ts}^{(t=0)}$ = mass of carry-over slag from the blast furnace, (kg);
$Q$ = total gas flow-rate, (Nm$^3$/s);
$R_{b}$ = desulphurization rate at metal-bubble interface, (kmol S/s);
$R_{bub}$ = desulphurization rate taxa by magnesium at the bubble surface, (kmol S/s);
$R_{dis}$ = desulphurization rate by magnesium in the melt bulk, (kmol S/s);
$R_{Mg}$ = desulphurization rate by magnesium, (kmol S/s);
$R_{ts}$ = desulphurization rate at metal-particle interface, (kmol S/s);
$R_{ts}$ = desulphurization rate at melt-slag interface, (kmol S/s);
$\%S_0$ = initial sulfur concentration in the melt, (weight %);
$\%S_{ts}$ = initial sulfur concentration in the carry-over slag from the blast furnace, (weight %);
$t$ = time elapsed (s);
$T$ = temperature of the melt, (K);
$\Lambda$ = theoretical optical basicity of top slag;
$\Lambda_{cor}$ = corrected optical basicity of top slag;
$\rho_L$ = specific mass of the molten pig iron, (kg/m$^3$);
$\rho_p$ = specific mass of the solid particle, (kg/m$^3$);
$\tau_{e}$ and $\tau_{p}$ = residence time of bubbles and dispersed particles in the melt, (s).

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<td><strong>Amount of molten pig iron</strong></td>
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<tr>
<td><strong>Average gas flow rate</strong></td>
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<td><strong>Average temperature</strong></td>
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<td><strong>Treatment time</strong></td>
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<td>Table II - Operational Conditions for Industrial Trials of Molten Pig Iron</td>
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<td>---------------------------------------------------------------</td>
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<tr>
<td><strong>Ladle capacity</strong></td>
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<td><strong>Ladle diameter</strong></td>
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<td><strong>Gas flow rate</strong></td>
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<td><strong>Powder rate</strong></td>
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<td><strong>Amount of carry-over slag from the Blast Furnace</strong></td>
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<td><strong>%SiO₂</strong></td>
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<td><strong>%Mn</strong></td>
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</tbody>
</table>
Figure 1 – Schematic experimental setup for desulphurization studies

Figure 2 – Comparison of the sulphur content of metal at the end of the experiment and sulphur predicted by simulation at 1300°C with top slag
Figure 3 - Effect of top slag metal ratio on the desulphurization rate at 1300°C

Figure 4 - Effect of substitution of Na₂O by CaF₂ on the desulphurization rate at 1300°C
Injection rate 20 - 40 kg/min

Particle mean diameter 150 µm

Figure 5: Simulation in industrial ladle - average conditions - injection scheme

Figure 6 - Comparison between industrial and predicted values of sulphur content during powder injection
Figure 7 - Effect of amount of carryover slag from blast furnace on the desulphurization.

Figure 8 - Effect of initial temperature on desulfurization rates.
Figure 9 – Effect of carrier gas flow rate on desulphurization.

Figure 10 – Effect of injection rate of flux powder on desulfurization rates.
Figure 11 – Effect of calcium carbonate content in the mixture on desulphurization
Figure 12 – Effect of magnesium content in the powder flux on the desulfurization rate