Advanced Process Modelling of Hot Metal Desulphurisation by Injection of Mg and CaO

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To improve the lime–magnesium desulphurisation process at BOS No. 2 at Corus Strip Products IJmuiden, a process model is derived based on the description for the bubble plume generated by injected carrier gas and reaction kinetics of the desulphurisation agents. The model is suited to simulate variations of gas flow and injection rates of CaO and Mg during the process. A parameter study was done in order to improve the operational practice. To validate the model assumptions and to get more knowledge of the reactions of Mg, hot metal samples have been taken before, during and after desulphurisation. SEM analysis revealed (Mg, Mn)S particles with varying Mn content, often combined with Ti(C, N) accumulated in the hot metal. The morphology of the interface between slag and steel has been studied.

KEY WORDS: hot metal desulphurisation; process modelling; Mg injection; CaO injection; flotation of magnesium sulphide; slag/metal interface.

1. Introduction

In BOS No. 2 at Corus Strip Products IJmuiden hot metal is desulphurised in the transfer ladle by injection of lime and magnesium using nitrogen as a carrier gas. To reduce the treatment time high injection rates are applied: for lime 100–120 kg/min and for magnesium 20–25 kg/min. The injection system has separate dosing systems for the two reagents with the possibility to set the injection rates independently. To develop an optimum sequence of injection of the different reagents a process model based on first principles of the underlying mechanisms has been developed. This has the advantage that the model can also be applied to other desulphurisation installations within Corus Group.

During the development of the process model, the knowledge gaps in the understanding of the process became apparent. To fill these gaps further study was done and dedicated industrial experiments and measurements were performed to validate and improve the model. Application of the process model led to an improved efficiency of the desulphurisation treatment. To better understand the pick-up of reaction products into the slag layer, samples from the hot metal top layer just below the slag, taken after the injection of reagents, have been analysed.

2. Process Model

2.1. General Set-up of the Model

The desulphurisation process is modelled by simultaneously solving the mass balances of the constituents, applying the relevant thermodynamic relations and solving the

equations describing mass transfer. The following approximations, simplifications and assumptions are applied:

- The hot metal phase is modelled as a continuously stirred tank reactor of constant volume.
- The carrier gas and Mg vapour form a bubble plume in the hot metal. The upward plume velocity determines the residence time of the injected CaO in the bath.
- The reaction of CaO powder with sulphur takes place during its rise in the plume, during which the sulphur concentrations in the melt and in the plume are virtually unaltered.
- Mg dissolves upon injection and reacts with dissolved sulphur by a homogeneous reaction on nucleates in the hot metal.
- MgS particles accumulate in the melt and subsequently float to the slag layer induced by the gas plume.
- The reaction products that leave the melt accumulate in the slag layer.
- The reaction of injected Mg with dissolved oxygen is taken into account. There is no infiltration of oxygen from the atmosphere into the hot metal.
- The temperature of the system is constant.

The model has been set up using the Aspen Custom Modeller software package. A key element in the model is that injection rates of nitrogen, CaO and Mg can be varied during the process such that the actual plant injection schemes can be simulated.

2.2. Plume Model

From the energy dissipation in the bath by turbulence and the energy input by the injection of gas, Sahai and Guthrie¹⁾ derived the relation for the plume velocity:

$$U_{\text{plume}} = 4.5 \frac{\phi_{\text{vg}}^{1/3} L_{\text{im}}^{1/4}}{r_1^{1/3}} \dots\dots\dots(1)$$

Where:

L_{im} :	Immersion depth of the lance	(m)
r_1 :	Radius of the ladle	(m)
U_{plume} :	Plume velocity	(m/s)
ϕ_{vg} :	Gas volume flow rate	(m ³ /s)

The plume velocity and immersion depth determine the residence time of the injected powder in the bath:

$$\tau = \frac{L_{\text{im}}}{U_{\text{plume}}} \dots\dots\dots(2)$$

In the model the effect of the wear of the lining on the dimension of the ladle has been added such that effect of the ladle age on the immersion depth of the lance is incorporated. Based on practical experience a wear of 0.1 m in 500 heats is taken.

2.3. CaO Reactions

With Si dissolved in liquid Fe the most favourable desulphurisation reaction of lime is given by Voronova²⁾:

$$\log K_{\text{CaO}} = \frac{-66892}{T} + 1.695 \dots\dots\dots(3)$$

The equilibrium constants refer to the activities of solutes with the [1 wt%] solution as standard state. From the equilibrium constants and hot metal concentrations the sulphur concentration on the reaction interface can be calculated.

The desulphurisation rate of the injected CaO powder is given by:

$$\left(\frac{d[\%S]}{dt} \right)_p = - \frac{6f_p \dot{m}_p \tau_p \rho_{\text{HM}}}{d_p \rho_p m_{\text{HM}}} k_{\text{S,p}} ([\%S] - [\%S]_p) \dots\dots(4)$$

where:

$[\%S]$:	Sulphur concentration in hot metal	(wt%)
$[\%S]_p$:	Sulphur concentration on powder surface	(wt%)
f_p :	Fraction of particles entrapped in the hot metal	(-)
$\dot{m}_p$:	Powder injection rate	(kg/s)
τ_p :	Residence time of powder in the plume	(s)
ρ_{HM}, ρ_p :	Density of hot metal and powder	(kg/m ³)
d_p :	Powder particle size	(m)
m_{HM} :	Mass of hot metal bath	(kg)
$k_{\text{S,p}}$:	Mass transfer coefficient of S to CaO	(m/s)
T :	Temperature	(K)

2.4. Magnesium-reactions

Magnesium and CaO (lime) powder is injected in the hot metal bath using nitrogen as carrier gas. Magnesium partly dissolves in the hot metal. Subsequently magnesium and sulphur react to MgS on the surface of nucleates in the melt.^{3,4)} Both components diffuse towards the nucleate surface where Mg, S and MgS are in equilibrium. The MgS particles grow due to reaction and agglomeration with other

particles and float to the slag layer induced by the gas plume. The desulphurisation reaction of magnesium is given by Turkdogan⁵⁾:

$$\log K_{\text{MgS}} = \log f_{\text{Mg}}^{\text{C}} [\% \text{Mg}] f_{\text{S}}^{\text{C}} [\% \text{S}] = - \frac{17026}{T} + 5.161 \dots\dots\dots(5)$$

For carbon saturated liquid iron at 1260°C the following activity coefficients are given: $f_{\text{Mg}}^{\text{C}} = 0.22$ and $f_{\text{S}}^{\text{C}} = 4.4$.⁵⁾

The molar fluxes of the reactants towards the reaction interface are equal and are given by:

$$J = k_{\text{Mg}} ([\text{Mg}] - [\text{Mg}]^*) = k_{\text{S}} ([\text{S}] - [\text{S}]^*) \dots\dots\dots(6)$$

where:

J : Mole flux towards inclusion surface (mol/m²/s)

$k_{\text{Mg}}, k_{\text{S}}$: Mass transfer coefficients of Mg and S to inclusion surface (m/s)

$[\text{Mg}], [\text{S}]$: Concentration of Mg and S in hot metal bath (mol/m³)

$[\text{Mg}]^*, [\text{S}]^*$: Concentration of Mg and S on reaction interface (mol/m³)

The reaction rate of magnesium in kg/s is given by:

$$n_{\text{r,Mg}} = J a v_{\text{HM}} M_{\text{Mg}} \dots\dots\dots(7)$$

where:

M_{Mg} : Molar mass of magnesium (kg/mol)

a : Specific surface area of nucleates in the hot metal bath (m²/m³)

v_{HM} : Volume of the hot metal bath (m³)

Converting to wt% scale the consumption rate of dissolved magnesium by the desulphurisation reaction is described by:

$$\left(\frac{d[\% \text{Mg}]}{dt} \right)_{\text{MgS}} = - k_{\text{Mg}} a ([\% \text{Mg}] - [\% \text{Mg}]^*) \dots\dots(8)$$

where:

$[\% \text{Mg}], [\% \text{Mg}]^*$: Mg concentration in hot metal, on reaction interface (wt%)

The desulphurisation rate of the reaction with magnesium is derived in the same way:

$$\left(\frac{d[\% \text{S}]}{dt} \right)_{\text{MgO}} = - k_{\text{S}} a ([\% \text{S}] - [\% \text{S}]^*) \dots\dots\dots(9)$$

where:

$[\% \text{S}]^*$: S concentration on reaction interface (wt%)

In the model the equations describing the reaction rate, the requirement of stoichiometry and the equilibrium constant are solved simultaneously.

In various publications the role of dissolved oxygen in hot metal desulphurisation is described.⁶⁻⁸⁾ Injected magnesium will initially consume the dissolved oxygen. The de-oxidation by magnesium is given by Turkdogan⁵⁾:

The deoxidation reaction of magnesium is assumed to proceed similar to the desulphurisation reaction and the conversion rate is modelled the same way as the desulphurisation reaction.

2.5. Mass Balances

The mass balances for the solutes sulphur, oxygen and magnesium are given by:

$$\frac{d[\%S]}{dt} = \left(\frac{d[\%S]}{dt} \right)_p + \left(\frac{d[\%S]}{dt} \right)_{\text{MgS}} \dots (11)$$

$$\frac{d[\%O]}{dt} = \left(\frac{d[\%O]}{dt} \right)_{\text{MgO}} \dots (12)$$

$$\frac{d[\%Mg]}{dt} = f_d \dot{m}_{i,Mg} + \left(\frac{d[\%Mg]}{dt} \right)_{\text{MgS}} + \left(\frac{d[\%Mg]}{dt} \right)_{\text{MgO}} \dots (13)$$

Where:

f_d : The fraction of injected magnesium that dissolves in the hot metal (—)

$\dot{m}_{i,Mg}$: Injection rate of magnesium (kg/s)

After formation, the MgS and MgO particles accumulate in the hot metal bath and subsequently float to the slag layer by buoyancy, primarily induced by the gas plume. The rate of floatation of the particles follows from growth, agglomeration, the flow pattern of hot metal in the ladle and pickup by the slag. As a first approximation the rate of floatation from the hot metal to the slag is set proportional to the concentration. The mass balance of MgS in the hot metal is given by:

$$\frac{d[\%MgS]}{dt} = - \frac{M_{\text{MgS}}}{M_{\text{Mg}}} \left(\frac{d[\%Mg]}{dt} \right)_{\text{MgS}} - C_f [\%MgS] \dots (14)$$

where:

C_f : Flotation rate constant (1/s)

$[\%MgS]$: Concentration of MgS as separate phase in the hot metal (wt%)

From analysis of heats and experimental data it is noted that after a 2 min period of post injection of CaO and N₂ the MgS content in the bath is approximately halved. This results in a flotation rate constant of: $C_f = 0.006$ (1/s). It is assumed that when no CaO and N₂ are injected, the rate of floatation is much lower and in the model it is set to 0. For MgO the same mass balance and flotation rate constant are used.

The total hot metal sulphur content is composed of dissolved sulphur and sulphur bound to MgS accumulated in the hot metal:

$$[\%S]_{\text{tot}} = [\%S] + \frac{M_S}{M_{\text{MgS}}} [\%MgS] \dots (15)$$

The total hot metal magnesium content is composed of dis-

Fig. 1. EBS image of particles in hot metal sample, taken before injection.

Fig. 2. EBS image of multi phase particle in hot metal sample, taken after injection of magnesium and lime.

solved magnesium and magnesium bound to MgS and MgO accumulated in the hot metal:

$$[\%Mg]_{\text{tot}} = [\%Mg] + \frac{M_{\text{Mg}}}{M_{\text{MgS}}} [\%MgS] + \frac{M_{\text{Mg}}}{M_{\text{MgO}}} [\%MgO] \dots (16)$$

where:

$[\%MgO]$: Concentration of MgO as separate phase in the hot metal bath (wt%)

3. Validation of the Model

3.1. SEM Analysis of Hot Metal Samples

To study the hot metal composition before and after desulphurisation, several samples were taken from the bath at a depth of 50–60 cm below the surface. These samples have been examined by SEM/EDS.

Figure 1 shows two phases commonly found in hot metal samples taken before injection of desulphurisation reagents: Ti(C, N) and MnS. Ti(C, N) originates from the addition of TiO₂ to the blast furnace. Li, Li and Fruehan⁹⁾ have studied the formation of Ti(C, N) from hot metal and have derived the accompanying thermodynamics. It follows that under average hot metal conditions Ti(C, N) is a stable phase whereas MnS is formed upon cooling of the sample and is not present in liquid hot metal as a separate phase. Figure 2 shows a cluster of two different phases as often encountered

Fig. 3. Element mappings of multiphase particle in Fig. 2.

Fig. 4. Element mappings of (Mg,Mn)S particle in hot metal sample, taken after injection of magnesium and lime.

Fig. 5. EBS/spot EDS image of cluster of particles in hot metal sample, taken after injection of magnesium and lime.

in the hot metal samples taken after injection of magnesium.

Figure 3 shows the distribution of the most abundant elements found in the multiphase particle indicating it is composed of MgS surrounded by some smaller parts of Ti(C,N) enriched with vanadium. EDS analysis of a large number of particles showed that often vanadium and niobium are dissolved in the Ti(C,N) phase, effectively forming the solid solution (Ti, V,Nb)(C,N).

Figure 4 shows the distribution of the most abundant elements in an MgS particle found in hot metal after the injection of magnesium. It indicates that the MgS phase is enriched with manganese. MgS and MnS form a completely miscible solid solution (Mg,Mn)S above 500°C of which the melting point is above 1100°C.¹⁰ Due to the homogeneous distribution of manganese it seems it has been incorporated into the MgS lattice at the same time as magne-

Fig. 6. EBS/spot EDS image of MgS/MgO particle in hot metal sample, taken after injection of magnesium.

sium. It therefore seems unlikely that MgS present in the liquid hot metal has been covered with MnS upon cooling of the sample. Detailed calculations on the formation of this phase can not be made due to lack of thermodynamic data. Suppose the excess Gibbs energy of the formation of the solid solution is significant, this could lead to a lower activity of both MgS and MnS in the solid solution (Mg,Mn)S which could affect the equilibrium constants of reactions of formation of the sulphides.

Figure 5 shows another example of a cluster of these phases with the results of spot EDS analysis. These results show that oxygen is also present, with this combination of elements most likely bound to MgO. Furthermore manganese is present in some spots, probably forming (Mg,Mn)S with sulphur and magnesium.

Figure 6 shows a particle composed of MgS and MgO as found in a hot metal sample taken immediately after finishing of the injection of magnesium. These MgO containing particles have not been found in hot metal samples taken after completely finishing the desulphurisation treatment

which includes post-injection of, in this case, CaC_2 and deslagging. These observations confirm the assumption that injected magnesium reacts with dissolved oxygen.

The particles shown are examples of particles encountered in large concentrations in the samples. Summarizing these results, observing hot metal samples on the reaction products of desulphurisation the following phases are encountered:

- pure stoichiometric MnS , formed upon the cooling of hot metal with a high sulphur content;
- pure stoichiometric MgS , the reaction product of the desulphurisation reaction of injected magnesium;
- solid solution $(\text{Mg}, \text{Mn})\text{S}$, formed in liquid hot metal or during solidification of the sample;
- solid solution $\text{Ti}(\text{C}, \text{N})$, present in hot metal before desulphurisation takes place and also extra formed with solidification of the sample;
- multiphase particles composed of a combination of $\text{Ti}(\text{C}, \text{N})$ with one of the sulphides.

Analysing these hot metal samples, no CaO containing particle has ever been found. This supports the assumption that injected powder floats to the surface in the plume and is collected in the slag layer and is not entrained in the liquid hot metal. Furthermore these observations could indicate that the carbo-nitrides play a role in the agglomeration and therefore the flotation of MgS . Finally it seems manganese affects the thermodynamics of the reaction of magnesium with sulphur. These observations have led to better understanding of the desulphurisation reactions and support modelling assumptions. Due to the high concentration and wide range of types of particles present, a large number of observations is required before general conclusions can be derived. This has led to the application of an automated technique to analyse the samples.

3.2. Automated Inclusion Analysis of Hot Metal Samples

The SEM as used has a tool that automatically identifies and measures inclusions. This has been applied in the investigation of alumina inclusions in steel.^{11,12)} This tool has great potential in addressing the major questions in the research on magnesium desulphurisation:

- How fast do MgS inclusions grow in time and how quick do they float to the surface of the hot metal bath?
- How are the MgS inclusions distributed in the hot metal ladle at certain moments during the treatment?
- Is $\text{Ti}(\text{C}, \text{N})$ formed as a result of the injection of N_2 ?
- Do $\text{Ti}(\text{C}, \text{N})$ particles act as nucleates for MgS ?
- What is the role of Mn in the desulphurisation process?

The automated inclusion analysis has been applied on two hot metal samples taken from the ladle after the desulphurisation process. One sample has been taken from the top layer, the other from a depth of approximately 0.5 m below the surface. The result of the analysis is a list with all particles detected on the surface with their size, shape and chemical composition. The particles of interest for the magnesium desulphurisation reactions can be described as a combination of MgS , MnS and $\text{Ti}(\text{C}, \text{N})$ with varying content of either substance where MgS and MnS can form a solid solution. In Fig. 7 for each sample every particle detected that falls within this class is plotted in the composi-

Fig. 7. Composition of multiphase particles, upper: top layer, lower: bulk sample.

Table 1. Data for sampled and modelled heats.

Hot metal		Heat 1	Heat 2
$[\text{S}]_{\text{in}}$	ppm	200	250
$[\text{S}]_{\text{final}}$	ppm	7	7
Mass	tonne	288	283
Temperature	$^{\circ}\text{C}$	1370	1399
$[\text{Si}]$	wt %	0.35	0.44
$[\text{Ti}]$	wt %	0.12	0.14
Desulphurisation agents			
CaO injected	kg/tonne	2.5	2.6
Mg injected	kg/tonne	0.41	0.51

tion diagram $\text{Ti}(\text{C}, \text{N})$ – MgS – MnS . The surface area scanned was 1 mm^2 for both samples.

Figure 7 shows the differences in the phases present in the two samples. The phases in the top layer sample are for the greater part pure $\text{Ti}(\text{C}, \text{N})$ and MnS particles and to lesser extent a combination of these two, without any pure MgS , whereas the particles in the bulk sample often are multiphase particles composed of $\text{MnS}/\text{Ti}(\text{C}, \text{N})$ and also almost pure MgS is found. This measurement technique shows great potential for this research and will be further applied.

3.3. Comparison of the Model to Plant Measurements

During two desulphurisation heats hot metal samples have been taken with short intervals during the injection of CaO and Mg . The basic properties of the heats are given in Table 1. The chemical composition of the hot metal sam-

Fig. 8. Development of sulphur and magnesium concentration during injection of lime and magnesium, comparison of calculation to measurements.

ples has been analysed by XRF with an accuracy of $\pm 1\text{--}10\text{ ppm}$. XRF gives the total sulphur and magnesium content of the hot metal, i.e. including the MgS . The process model was applied to calculate the development of sulphur and magnesium concentrations during the injection process.

Initially, assuming $f_d=1$, the results for total sulphur content agreed with the measured data. On the contrary, the calculated total magnesium concentration was higher than found in the samples. This could point to exceeding the maximum solubility of magnesium in the hot metal. The solubility of magnesium in hot metal is given by the following correlation expression:

$$\log[\% \text{Mg}]_{\text{sat}} = \frac{7000}{T} - 5.1 + \log P^{13}) \dots\dots\dots(17)$$

Under the given circumstances of temperature and pressure, $T=1612\text{ K}$ and $P=1\text{ bar}$, the maximum solubility is: $[\% \text{Mg}]_{\text{sat}}=0.12$ which is well above the measured concentrations of 0.006% . Therefore it seems unlikely that the maximum solubility has been exceeded.

The model was initially based on the assumption that upon injection magnesium completely dissolves in the hot metal bath followed by part reaction with dissolved sulphur to solid MgS . If due to mass transfer limitations the injected magnesium does not completely dissolve in the hot

metal, it will leave the bath unreacted after which it will burn in the atmosphere. The model has been adjusted by the introduction of the dissolution fraction, f_d , which is set to 0.5 . This indicates that work must be done to maximise the efficiency of the injected magnesium. The calculated results are shown together with the measurement in Fig. 8. These results emphasise the important role of flotation of MgS : for these heats after $300\text{--}360\text{ s}$ the hot metal sulphur concentration is governed by MgS that remains to float out.

4. Application of the Model

After validation of the model by comparison of the data of a large number of heats it has been used for a parameter study in which the effects of individual process variables could be assessed and an improvement of efficiency of 10% has been reached by optimising carrier gas flow rate.

5. Top Layer Analysis

Hot metal samples from the top layer, including slag and hot metal after injection have been studied to investigate the hot metal–slag interface. Of particular interest are lime containing particles present in the top layer of the hot metal prior to slag removal of which Fig. 9 shows an example.

Fig. 9. EBS image of CaO particle in iron phase surrounded by a CaS product layer. In the iron phase Mg is present as MgS, in direct vicinity of CaO/CaS as MgO.

The figure shows an EBS image of a particle composed of CaO surrounded by a layer of CaS. Furthermore MgO is present in the direct vicinity of CaO/CaS whereas in the iron phase MgS is found, as also found in hot metal samples taken from a depth of 50 cm.

Irons and Celik⁴⁾ describe the thermodynamics of combined lime–magnesium desulphurisation. At the reaction interface, magnesium–vapour, CaS, CaC₂ and MgO coexist. Consequently magnesium is responsible for deoxidation and lime for desulphurisation. This coincides with the current observations. The MgS particles found in the iron phase result from the reaction of dissolved magnesium and sulphur in the hot metal bath in the absence of CaO and slag. Ender *et al.*¹⁴⁾ also found that in the desulphurisation slag no magnesium sulphide was present and explained this by analysis of the thermodynamics.

Furthermore, CaC₂ could not be detected since carbon is deposited on the sample to ensure proper conductivity of the non-metallic particles. However, no high concentrations of carbon are measured in the product layer. Whereas no calcium containing particles have been found in hot metal samples taken at a depth of approximately 50 cm, just beneath the slag layer CaO containing particles are present in

high concentration. The particles have floated to the surface of the hot metal bath properly but have not been absorbed in the slag. It is not known until what depth these particles are present and whether or not these contribute significantly to the total sulphur content of the hot metal ladle.

6. Conclusions

(1) significant amount of MgS resides in the hot metal during and after injection. This contributes to the total amount of sulphur in the hot metal and therefore must be taken into account in the model. The rate at which this MgS floats to the slag layer is estimated.

(2) Reaction products in hot metal samples are, besides MgS, for the greater part multiphase particles composed of the phases (Mg, Mn)S and Ti(C, N).

(3) Analysis of the top layer indicates lime-containing reaction products reside in this layer.

(4) The composition of the product layer on lime particles coincides with the predicted reaction products of combined magnesium–lime desulphurisation.

(5) The model has been successfully applied to improve plant practice.

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