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Publication date

2019

Document Version

Final published version

Published in

Proceedings of METEC & 4th ESTAD

Citation (APA)

Schrama, F., Beunder, E. M., Visser, H-J., Boom, R., Sietsma, J., & Yang, Y. (2019). Effect of graphite on hot metal desulphurisation. In *Proceedings of METEC & 4th ESTAD* [P308] VDeH Verlag Stahleisen.

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Effect of graphite on hot metal desulphurisation

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Summary

During the magnesium-lime co-injection process for hot metal desulphurisation, graphite can precipitate as a result of carbon oversaturation. The formed graphite is known to form a layer between the slag and the hot metal. This potentially blocks the sulphides, that are formed during the desulphurisation process, to reach the slag phase thus hampering the desulphurisation efficiency.

In this research it was aimed to obtain experimental evidence for the postulated hampering effect of graphite on the hot metal desulphurisation efficiency at an industrial process. In 2018 at Tata Steel in IJmuiden, the Netherlands, the carbon concentration in the hot metal was measured after the reagent injection, instead of being calculated assuming carbon saturation of the hot metal. This provides the opportunity to predict graphite formation during the process. Although a correlation is found between graphite formation and specific magnesium consumption, which is a measure for desulphurisation efficiency, the effect could not be directly proven, as too many other parameters could have influenced the desulphurisation process. Data analysis does show that the observed correlation could not be attributed to temperature and initial sulphur concentration of the hot metal, which are the two most important factors for the desulphurisation efficiency. The observed correlation between graphite formation and desulphurisation efficiency is significant at low initial sulphur concentrations (<225 ppm) and insignificant at high initial sulphur concentrations (>225 ppm).

Key Words

Hot metal desulphurisation, magnesium consumption, graphite precipitation, kish

Introduction

It is considered best practice in modern steelmaking worldwide to desulphurise the hot metal from the blast furnace prior to the basic oxygen furnace (BOF) converter process. In the western world the magnesium-lime co-injection process is the state-of-the-art hot metal desulphurisation (HMD) method. Typically, when the hot metal is tapped from the blast furnace, it is not yet saturated with carbon. This is because the dissolution of carbon in hot metal at the blast furnace is controlled by kinetics rather than thermodynamics [1]. Due to temperature losses during transport and pouring the hot metal from the torpedo transport vessel into the hot metal ladle, the hot metal is most likely saturated with carbon when it reaches the HMD station. Visser [2] showed that during the HMD process graphite precipitates and forms a layer in between the hot metal and the slag. He postulated that this graphite layer can hamper the desulphurisation efficiency.

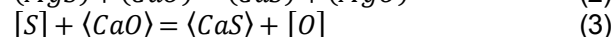
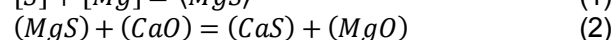
However, in the industrial process no direct evidence was found yet for the hampering effect of graphite on the HMD efficiency, because the carbon is not measured but calculated in the hot metal. In 2018, at

the steel plant of Tata Steel in IJmuiden, the Netherlands, the carbon was measured in the hot metal after the reagent injection for 657 heats. This provided the opportunity to validate the postulation of Visser [2] with plant data, which is done in the present paper.

Theoretical analysis

Magnesium-lime co-injection

In the magnesium-lime co-injection process most sulphur is removed via a reaction with dissolved Mg (reaction 1) to MgS, followed by a reaction with lime (reaction 2). Alternatively (typically 5% of desulphurisation) the hot metal is directly desulphurised via a reaction with lime (reaction 3) [3]:



Most of reaction 2 takes place within the slag. As magnesium is the main desulphuriser in the HMD process, the efficiency can be quantified by the specific magnesium consumption (\dot{m}_{Mg}) [4]:

$$\dot{m}_{Mg} = \frac{M_{Mg}}{M_{\Delta S}} \quad (4)$$

Here M_{Mg} and $M_{\Delta S}$ are the mass of the injected magnesium and removed sulphur respectively. When using \dot{m}_{Mg} to compare different heats, the solubility of magnesium (C_{Mg}) should be taken into account. Before the injected magnesium reacts with sulphur first a certain amount will dissolve in the HM; this influences equation 4 if C_{Mg} changes for different heats. According to Ender [5] C_{Mg} depends on temperature and sulphur concentration of the hot metal:

$$C_{Mg} = \frac{10^{-14.3+0.00679T}}{[S]} \quad (5)$$

Here the temperature of the hot metal T is in °C and the sulphur concentration, $[S]$, and C_{Mg} are in wt%. With this a net specific magnesium consumption ($\dot{m}_{Mg,net}$) can be calculated via:

$$\dot{m}_{Mg,net} = \frac{M_{Mg} - C_{Mg} \cdot M_{HM}}{M_{\Delta S} \cdot 100} \quad (6)$$

Here M_{HM} is the total mass of hot metal in kg.

Effect of graphite on HMD

The thermodynamic carbon saturation (C_C) in HM can be calculated with Neumann's equation [6]:

$$C_C = 1.3 + 0.00257T - 0.31[Si] - 0.33[P] + 0.27[Mn] - 0.4[S] \quad (7)$$

Here the temperature T is in °C and the concentrations of the elements are in wt%. In this equation, for typical industrial conditions, temperature has the strongest effect on C_C .

Typically hot metal leaves the blast furnace below carbon saturation [1]. During transport and pouring of hot metal from the torpedo-shaped transport vessel into the HM ladle, certain heat is lost, which brings the hot metal close to or even at its carbon saturation point. To precipitate, graphite needs nucleation sites. The MgS that is formed via reaction 1 can act as a nucleation site for the graphite. The graphite will precipitate in a laminar form (flakes), due to the high local sulphur activity, as sulphur is an anti-spheroidising element [7], [8]. Some graphite will escape from the ladle via the slag eye in the form of kish, the greyish black glistening dust at the primary metallurgy side of the steel plant [2].

Visser [2] showed in his work that graphite forms a layer between the HM and the slag. Figure 1 shows the cross section of a sample from the top layer of the hot metal after slag skimming. The upper 5 mm is rich in graphite and MgS.

Based on this observation Visser postulated the theory that precipitated graphite hampers the desulphurisation process by blocking the MgS particles, thus preventing them to reach the slag layer. MgS that does not reach the slag layer and is not skimmed off, leads to resulphurisation in the converter. Figure 2 gives a graphical overview of how graphite hampers the HMD process.

Detecting graphite formation in plant data

In the industrial HMD process it is extremely difficult to directly detect and quantify the precipitation of graphite. In some cases it is possible to see kish escaping the ladle with the naked eye, but this will not give a reliable overview of graphite formation per heat. In theory graphite formation could be predicted by the difference between the carbon concentration of the hot metal prior to HMD and the calculated C_C after HMD, assuming homogeneous conditions. However, in this study only the measured carbon content in the hot metal after HMD is available. As

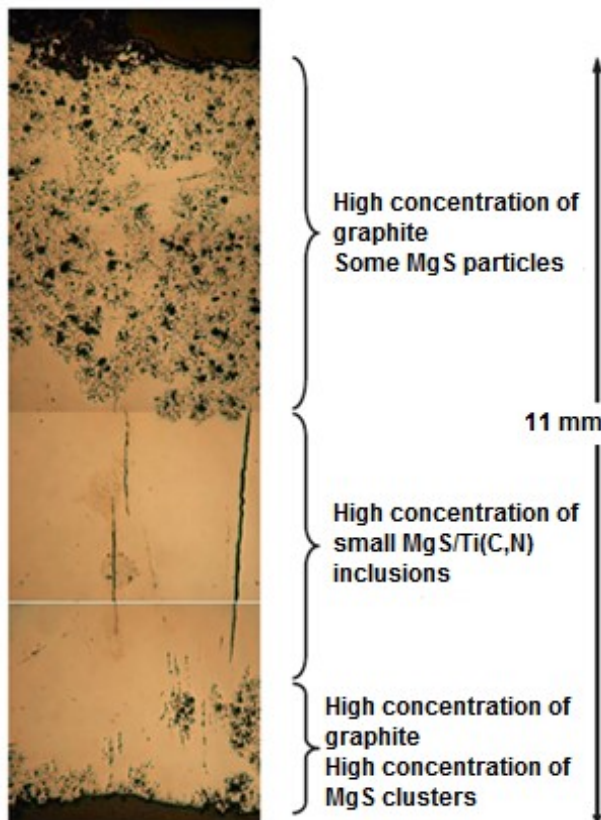


Figure 1: Top layer sample of hot metal after skimming at Tata Steel, the Netherlands [2]

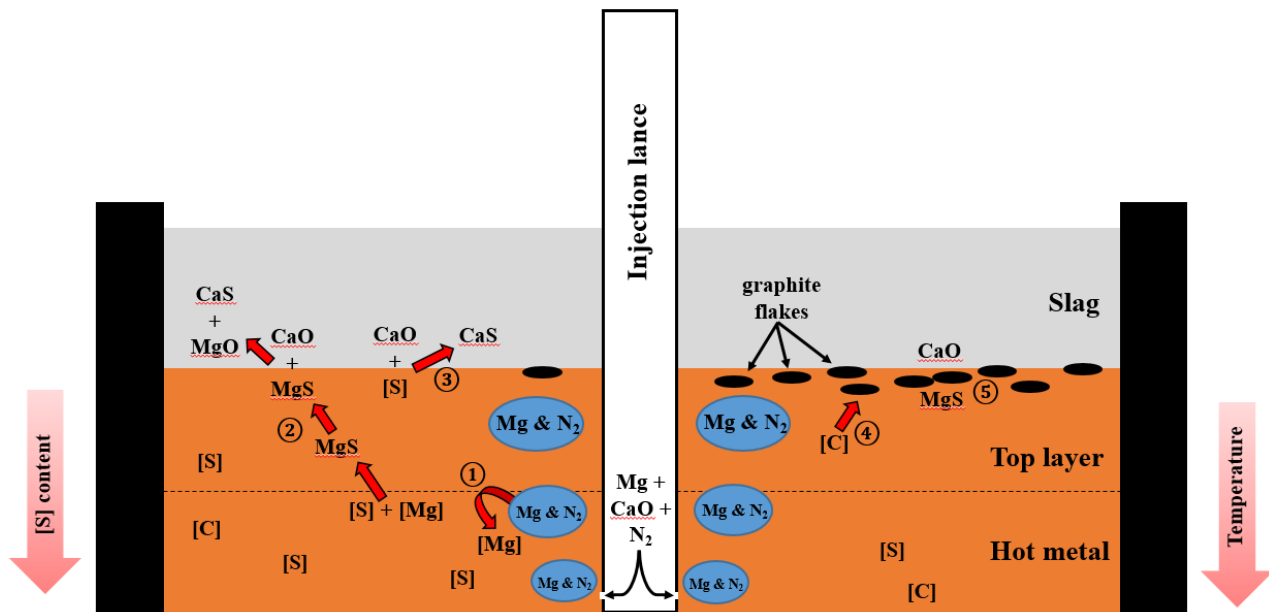


Figure 2: Hampering effect of graphite on HMD. Injected magnesium dissolves in HM (1), it then reacts with sulphur and the formed MgS reaches the slag layer (2), where it reacts following reaction 2 to CaS and MgO (3). In the top layer dissolved carbon precipitates to graphite (4), which then blocks the MgS to reach the slag (5)

the carbon content of the hot metal before HMD is unknown, the likeliness of graphite formation can best be estimated by the difference between the measured carbon content after HMD ($\gamma_{[C],meas}$) and the carbon capacity of the hot metal before HMD ($C_{c,0}$), where the hot metal is still quite homogeneous, as it has just been poured into the ladle:

$$\Delta C = C_{c,0} - \gamma_{[C],meas} \quad (8)$$

For a certain heat a small ΔC indicates that it is likely that more graphite is formed, as then the hot metal is close to carbon saturation, so only a slight, local, decrease in temperature leads to oversaturation and precipitation of carbon. Note that ΔC should never be negative, as that would imply that more carbon is dissolved in the hot metal than thermodynamically possible (the abundance of nucleation sites during HMD will prevent oversaturation). Based on the hypothesis, an increased \dot{m}_{Mg} is expected at a lower ΔC .

Plant measurements and results

In 2018 Tata Steel measured the carbon content of the hot metal, immediately after the reagent injection, in their plant in IJmuiden, the Netherlands, for 657 heats. The carbon was measured by taking a hot metal sample at a fixed height measured from the ladle bottom after reagent injection in the HMD. Because the samples were inhomogeneous as a result of graphite precipitation during cooling, the samples were milled prior to analysis by wavelength dispersive X-ray fluorescence spectroscopy (WD-XRF). The samples were also analysed by

combustion method with infra-red detection to validate the WD-XRF analysis. The total standard deviation (the sum of all deviations) for the carbon measurement was 0.1 wt%.

Outliers from the dataset of the 657 HMD heats were filtered out by excluding heats for which data was missing, temperatures outside the 1350-1450 °C range and/or $C_{Mg} > 0.01$ wt%. After filtering 546 heats remained.

To investigate the direct correlation between graphite precipitation, represented by ΔC , and \dot{m}_{Mg} , they are plotted in Figure 3.

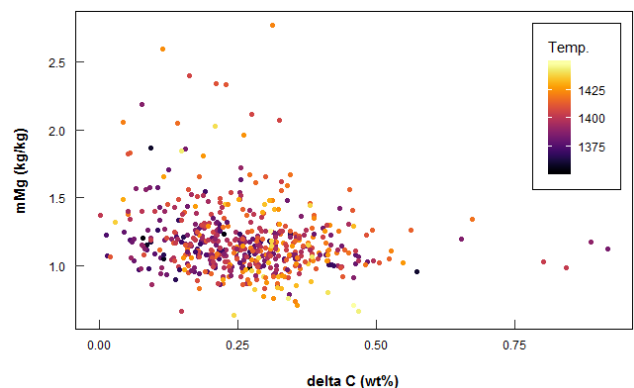


Figure 3: $\dot{m}_{Mg,net}$ versus ΔC . Colour of dots indicate the hot metal temperature (in °C)

To make the trend better visible, Figure 4 shows the same data grouped for ΔC , per 0.05 wt%, and the average \dot{m}_{Mg} is calculated per group. The trendline (a

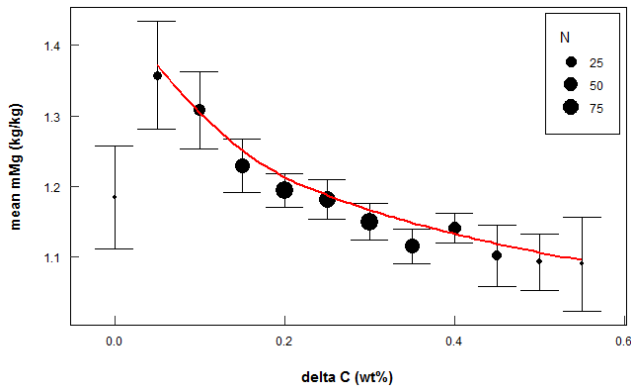


Figure 4: $\dot{m}_{Mg,net}$ versus grouped ΔC . The dot size indicates the number of measurements per group. The red line is the best fitted logarithmic function. The error bars show the 1σ standard deviation per group

logarithmic best fit) shows that the average specific magnesium consumption increases for a decreasing ΔC , thus when more graphite is expected to have precipitated.

As the initial sulphur content (S_{in}) of the HM has a large impact on the desulphurisation efficiency, the data is also grouped per S_{in} . Table 1 shows the number of data points that are available per S_{in} group.

Table 1: Data distribution per S_{in} group

S_{in} [ppm]	<125	125-175	175-225	225-275
count	2	25	144	172
S_{in} [ppm]	275-325	325-375	375-425	>425
count	122	56	23	2

For the six largest S_{in} groups Figure 5 shows the correlation between ΔC and \dot{m}_{Mg} .

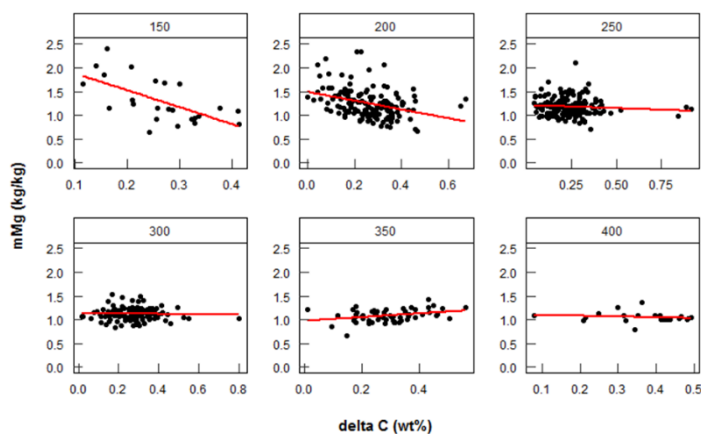


Figure 5: $\dot{m}_{Mg,net}$ against ΔC per S_{in} group. The red line is the best fitted linear trendline

The plot shows that only for lower S_{in} groups the correlation between ΔC and \dot{m}_{Mg} is significant.

Discussion

Visser [2] already observed that precipitated graphite can form a layer in between the slag and the hot metal bath during the HMD process. However, no industrial evidence for his postulation that this graphite layer actually hampers the desulphurisation efficiency was ever found. The reason for that is that other factors, like temperature, hot metal composition or injection quality, have a larger influence on the desulphurisation efficiency, so research tends to focus there. Furthermore doing proper extensive sampling is technically difficult and leads to many practical complexities.

Ideally graphite formation was directly measured for this research, but that was not possible under industrial conditions. The more homogeneous calculated carbon before injection and the measured carbon content after injection are the two most reliable estimates of the carbon concentration in the hot metal. By this definition a small ΔC can also be caused by a high carbon concentration. In theory the carbon concentration can influence the oxygen activity of the hot metal, but under HMD conditions the oxygen activity is already very low, typically 3 ppm. This low oxygen activity is a result of the strong reducing conditions caused by the abundance of carbon (even when it is considered 'low') and silicon in the hot metal. It is therefore unlikely that dissolved carbon directly influences the desulphurisation.

Finding the effect of one specific parameter on the process efficiency by using plant data is difficult, as it is impossible to completely isolate one parameter from all others. The plant data used in this study clearly shows a trend that a smaller ΔC correlates with a larger \dot{m}_{Mg} . To prove that this correlation is caused by the precipitated graphite, as was the hypothesis, the effect of other parameters on \dot{m}_{Mg} has to be filtered out.

From literature it is known that temperature has the strongest influence on \dot{m}_{Mg} [3]. Figure 3 shows that \dot{m}_{Mg} was corrected well for the effect of temperature, as the different temperatures seem to be scattered evenly across the plot. Figure 5 shows that for an S_{in} below 225 ppm there is a significant correlation between ΔC and \dot{m}_{Mg} , but at higher sulphur concentrations there seems to be no correlation. It is unclear why the correlation is only visible for low initial sulphur concentrations. One possible explanation is that for a low S_{in} , little sulphur is removed, which means that the effect on C_c , according to Neumann's equation (equation 7), is small. When the initial sulphur concentration is higher, more sulphur is removed, leading to a significant influence on the C_c , allowing more carbon to stay dissolved in the hot metal, thus decreasing the graphite formation and its assumed effect on \dot{m}_{Mg} .

Whether the observed correlation is caused by any of the other elements present in the HM has yet to be investigated. However, according to literature, only silicon and titanium are mentioned to influence the HMD process. Silicon and titanium contents are strongly correlated with each other in hot metal. Earlier research suggested that the independent effect of silicon was small as compared to that of carbon [4]. This has to be further investigated though.

Conclusions

Analysis of the hot metal samples from 546 HMD heats where carbon was measured after injection at Tata Steel in IJmuiden, the Netherlands, indicate that there is a correlation between the graphite formation and the specific magnesium consumption that cannot be attributed to the temperature or initial sulphur concentration of the hot metal. However, the correlation is only significant for lower initial sulphur concentrations. These results support the hypothesis that graphite that precipitates during hot metal desulphurisation has a hampering effect on the desulphurisation efficiency. However, more research is required to further prove the hypothesis.

Future research should focus on:

- The influence of other elements in the hot metal (like silicon and titanium) on the observed correlation
- Why a correlation could only be found for initial sulphur concentrations below 225 ppm
- The actual impact of the hampering effect on industrial hot metal desulphurisation

Abbreviations

BOF Basic oxygen furnace (converter)
HMD Hot metal desulphurisation

Symbols

C_x Thermodynamic capacity of x in hot metal (wt%)
 M_x Mass of x (kg)
 \dot{m}_{Mg} Specific magnesium consumption (kg Mg per kg removed S)
 $\dot{m}_{Mg,net}$ Specific magnesium consumption corrected for dissolved Mg (kg Mg per kg removed S)
 T Temperature (°C)
 γ_x Concentration of x in hot metal (wt%)

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