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Schrama, F. N. H., Beunder, E. M., Visser, H. J., Sietsma, J., Boom, R., & Yang, Y. (2019). The hampering effect of precipitated carbon on hot metal desulfurization with magnesium. *Steel Research International*, 91 (2020)(11), Article 1900441. <https://doi.org/10.1002/srin.201900441>

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# The Hampering Effect of Precipitated Carbon on Hot Metal Desulfurization with Magnesium

Frank N. H. Schrama,\* Elisabeth M. Beunder, Hessel-Jan Visser, Jilt Sietsma, Rob Boom, and Yongxiang Yang

Carbon may precipitate during the hot metal desulfurization (HMD) process as a result of carbon oversaturation because of temperature decrease. The precipitated carbon flakes form a layer between hot metal and slag. It is postulated that this carbon layer hampers desulfurization with magnesium by preventing MgS particles from reaching the slag phase. At Tata Steel in IJmuiden, the Netherlands, carbon in hot metal is measured in 657 heats after reagent injection. With this data, it can be determined whether the hampering effect of precipitated carbon on MgS flotation has a significant effect on the performance of the industrial HMD process. Plant data show a correlation between the precipitated carbon and the specific magnesium consumption for hot metal with a low initial sulfur concentration (below 225 ppm). This correlation cannot be found for hot metal with a higher initial sulfur concentration (above 275 ppm). Furthermore, a sulfur mass balance is made over the converter process, that shows no effect of carbon precipitation during HMD on resulfurization in the converter. The limited experimental accuracy of the plant data prevents a quantitative description of the hampering effect. The measurements do suggest that the effect is small.

## 1. Introduction

Hot metal desulfurization (HMD) is a common practice in most steel plants worldwide today, as hot metal from the blast furnace (BF) contains too much sulfur, typically 0.02–0.08 wt%, for the final product. From an economic perspective, the sulfur in hot metal can be best removed, prior to the converter process, because of a low oxygen concentration, which is typically 3 ppm, and low hot metal temperatures (1300–1450 °C). Co-injection of

magnesium and lime is the dominant HMD process in Europe. In this process, metallic magnesium and lime are injected via a lance into a ladle filled with hot metal from the BF. The reagents react directly or indirectly with sulfur to form sulfides which float to the slag layer. After reagent injection, the sulfide containing slag is skimmed off, so that sulfur is removed from hot metal. The desulfurized hot metal is then charged to the converter.<sup>[1–3]</sup>


In the modern BF process, hot metal typically is not saturated with carbon when it is tapped,<sup>[4]</sup> as in the BF, the carbon concentration in the hot metal is determined by kinetics, rather than thermodynamics. During transport from the BF to the steel plant and during tapping into the ladle, the hot metal temperature will decrease, which enhances carbon saturation of the hot metal, because a lower temperature leads to a lower carbon solubility. Dust of

precipitated carbon, called kish, is often observed during filling of the hot metal ladle. Studying samples taken from the top layer of the hot metal bath, Visser<sup>[1]</sup> found that during the HMD process, graphite flakes, probably formed due to (local) oversaturation of carbon in the hot metal, accumulate in the top layer of the hot metal, just below the hot metal–slag interface. Visser postulated that these graphite flakes could possibly obstruct the rising MgS particles to be absorbed in the slag. By remaining in the metal, MgS is not removed during slag skimming, so the desulfurization efficiency decreases due to this phenomenon. This leads to higher reagent consumptions and a lower reliability of the HMD process.

The proposed effect of carbon oversaturation of the hot metal on the desulfurization efficiency was not validated before in an industrial process, as in steel plants the carbon content is typically not measured but calculated, assuming carbon saturation. With this assumption the effect of carbon saturation on HMD cannot be studied. In the steel plant of Tata Steel in IJmuiden, the Netherlands, a trial was conducted in which the carbon content of the hot metal was measured in 657 heats. Wavelength dispersive X-ray fluorescence spectroscopy (WD-XRF) was used to analyze the samples. For the heats in which carbon was measured, the effect of carbon (over)saturation on HMD can be studied. The first results of this study have shown a correlation between graphite precipitation and desulfurization efficiency.<sup>[5]</sup> However, this correlation was weak and

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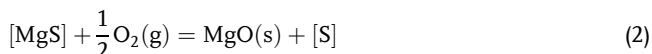
DOI: 10.1002/srin.201900441

further investigation was required to determine if the correlation can confirm the postulated effect of carbon precipitation on HMD efficiency.

## 2. Theoretical Evaluation

### 2.1. HMD Reactions

When injecting magnesium and lime into hot metal, the main desulfurization reaction takes place between dissolved magnesium and dissolved sulfur (reaction (1)). The solid MgS that is formed then floats to the slag layer. Since MgS in the slag will react with oxygen from the air, thereby leading to resulfurization of the hot metal (reaction (2)), lime is added to form the more stable CaS via reaction (3). The injected lime can also directly desulfurize the hot metal via reaction (4), but due to kinetic constraints, this reaction only contributes for roughly 5% to the total desulfurization.<sup>[2,6,7]</sup>



MgS formed through reaction (1) coalesces and, as these MgS particles grow, their buoyancy increases, so they rise to the slag layer. There MgS reacts with the lime present in the slag by means of reaction (3). MgS particles that remain in the hot metal will not be removed during skimming and thus do not contribute to desulfurization.<sup>[6,8,9]</sup>

### 2.2. Specific Magnesium Consumption

In HMD through the co-injection of magnesium and lime, desulfurization via magnesium (reaction (1)) is most important, and this determines the performance of the process. Therefore, one way to measure the desulfurization efficiency is by determining the specific magnesium consumption ( $\dot{m}_{\text{Mg}}$ ) of the process<sup>[10]</sup>

$$\dot{m}_{\text{Mg}} = \frac{M_{\text{Mg}}}{M_{\Delta\text{S}}} \quad (5)$$

where  $M_{\text{Mg}}$  and  $M_{\Delta\text{S}}$  are the mass of the injected magnesium and the mass of the removed sulfur, respectively. Equation (5) neglects the effect of lime (via reaction (4)). This equation does not show the effect of the initial sulfur content either (if the hot metal has a higher initial sulfur content, desulfurization is more efficient in terms of specific reagent use<sup>[10]</sup>). Neither does it include the final sulfur concentration (desulfurizing to lower sulfur concentrations is less efficient<sup>[2]</sup>). This means that Equation (5) is not useful if there is a large variation in initial or final sulfur concentrations. Furthermore, when magnesium is injected, an equilibrium has to be established in the hot metal, meaning that a certain amount of magnesium has to dissolve in the hot metal before MgS is formed. This magnesium

capacity ( $C_{\text{Mg}}$ ) of the hot metal depends on the temperature and sulfur concentration: for low final sulfur concentrations, more magnesium has to dissolve before MgS is formed. Ender et al.,<sup>[11]</sup> Turkdogan,<sup>[12]</sup> and Yang et al.<sup>[13]</sup> came up with slightly different equations for  $C_{\text{Mg}}$ . All equations are based on the principle that there is a temperature-dependent solubility product of MgS ( $P_{\text{MgS}}$ ) for reaction (1)

$$P_{\text{MgS}} = [\text{Mg}] \cdot [\text{S}] \quad (6)$$

Here the concentrations are in parts per million. Ender's equation<sup>[11]</sup> is based on calculations with plant conditions. Under HMD conditions, the difference between Ender's equation and the equations of Turkdogan and Yang et al. is minimal.<sup>[1]</sup> In this study,  $C_{\text{Mg}}$  is calculated with Ender's equation

$$C_{\text{Mg}} = \frac{10^{-14.3 + 0.00679T}}{[\text{S}]} \quad (7)$$

where  $T$  is the temperature of the hot metal in degree Celsius. Equation (7) can then be corrected for the amount of magnesium that has to dissolve in the hot metal before desulfurization takes place, via the following equation

$$\dot{m}_{\text{Mg,cor}} = \frac{M_{\text{Mg}} - C_{\text{Mg}} \cdot M_{\text{HM}}}{M_{\Delta\text{S}} \cdot 100} \quad (8)$$

where  $\dot{m}_{\text{Mg,cor}}$  is the corrected specific magnesium consumption and  $M_{\text{HM}}$  is the total mass of the hot metal in kilogram.

### 2.3. Carbon Saturation of Hot Metal

The carbon solubility and concentration in the hot metal depend on the composition and temperature of the hot metal. The carbon concentration increases when the hot metal sulfur, silicon, and phosphorus concentrations are low or when the manganese concentration is high. Furthermore, a high temperature enhances carbon dissolution in the hot metal. Sulfur delays the reaching of an equilibrium for carbon dissolution in the hot metal during the BF process which, in practice, leads to lower carbon concentrations at higher sulfur concentrations.<sup>[4,14]</sup> This also works vice versa, so if the carbon concentration in hot metal is higher, the sulfur concentration and its solubility will be lower.<sup>[4,15]</sup> Based on earlier research, Neumann et al.<sup>[16]</sup> established an empirical equation that predicts the carbon concentration of hot metal at saturation, which is the carbon capacity of the hot metal ( $C_{\text{C}}$ ) in wt%

$$C_{\text{C}} = 1.3 + 0.00257T - 0.31[\text{Si}] - 0.33[\text{P}] + 0.27[\text{Mn}] - 0.4[\text{S}] \quad (9)$$

Here, the concentrations of elements are in wt% and  $T$  is in degree Celsius. Equation (9) ignores the influence of other elements dissolved in the hot metal, so for industrial use of this equation, a plant-dependent correction factor is needed. For typical HMD conditions, the temperature factor in Equation (9) has the strongest effect; thus,  $C_{\text{C}}$  is highly temperature dependent.

## 2.4. Graphite Formation in Hot Metal

Visser<sup>[1]</sup> explains that the temperature in the ladle is not uniform. Close to the slag layer, the hot metal has a lower temperature than in the bulk, leading to a local decrease in carbon capacity which results in graphite precipitation. The graphite precipitates in the form of flakes due to the presence of the antispheroidizing element sulfur.<sup>[17]</sup> Because the density of graphite ( $2200 \text{ kg m}^{-3}$ ) is much lower than the density of hot metal ( $7000 \text{ kg m}^{-3}$ ), it will rise to the slag. As graphite cannot break through the viscous slag, which has a density of  $\approx 2700 \text{ kg m}^{-3}$ ,<sup>[18]</sup> the graphite flakes will accumulate horizontally at the interface between the slag and hot metal. Carbon-saturated hot metal with a low oxygen concentration (3 ppm) does not wet the graphite flakes. Graphite is not wetted by FeO–MnO–SiO<sub>2</sub>–CaO–Al<sub>2</sub>O<sub>3</sub> systems, components of which are typically present in HMD slag (in addition, HMD slag also contains significant amounts of MgO). This means that graphite flakes, once formed, are likely to stay between the hot metal and the slag or leave the system as kish through the slag eye, which is the gap in the slag created by escaping injection gasses.<sup>[1,17]</sup> These graphite flakes were observed by Visser in the slag–hot metal interface when he took samples from the hot metal ladle at the HMD station of Tata Steel in IJmuiden. The graphite flakes clearly differed from small graphite segregates that are formed during solidification of the sample. The samples retrieved by Visser did not only show graphite flakes, but also a high concentration of MgS precipitates. This indicates that the graphite blocks the MgS particles, preventing them from reaching the slag, which hampers the desulfurization efficiency.<sup>[1,5]</sup>

It is possible that the formation of graphite in the top layer of the hot metal bath is further enhanced by the sudden availability of nucleation sites when the reagent injection starts. In the preceding period, the top layer of the bath has little turbulence, which could lead to local carbon oversaturation as a result of the decreasing temperature and the lack of nucleation sites. When injection starts, solid lime and MgS particles quickly rise to the top layer, which creates a sudden abundance in nucleation sites. This could lead to instant graphite layer formation, which means that graphite can influence the HMD process from the start. However, there are no observations that support this theory.

## 2.5. The Hampering Effect of Graphite on HMD

Neumann's equation (9) shows that at HMD temperatures (1250–1450 °C), the temperature has the strongest influence on  $C_C$ . As higher temperatures lead to a higher  $\dot{m}_{\text{Mg}}$ <sup>[2]</sup> and a higher  $C_C$ , and as hot metal is usually close to carbon saturation,  $[C]$  is close to  $C_C$ , typically heats with a high carbon concentration will show a lower desulfurization efficiency. This is also observed in steel plants.<sup>[10]</sup> To distinguish between the effect of precipitated graphite and the effect of temperature on HMD, which is correlated with  $C_C$ ,  $\Delta C$  should be studied, where

$$\Delta C = C_{C,0} - \gamma_{[C],\text{meas}} \quad (10)$$

Here,  $C_{C,0}$  is the carbon capacity of the hot metal prior to HMD, calculated via Neumann's equation (9), and  $\gamma_{[C],\text{meas}}$  is the measured carbon content of the hot metal after HMD. A large

$\Delta C$  means that the hot metal is far from carbon saturation; thus, little graphite precipitation is expected. The smaller  $\Delta C$  gets, the closer the hot metal is to carbon saturation, so a smaller (local) decrease in temperature or change in composition can cause graphite precipitation. In this study,  $\Delta C$  is used as an indication for the amount of expected precipitated graphite in the hot metal, without quantifying the amount of graphite.

**Figure 1** shows an overview of the different processes inside the ladle that play a role in HMD. 1) The injected magnesium dissolves in the hot metal. 2) The dissolved magnesium reacts with sulfur via reaction (1) and then further reacts with lime via reaction (3). 3) Alternatively, the sulfur directly reacts with lime via reaction (4). 4) Because of the lower temperature at the slag–hot metal interface (the top layer), dissolved carbon precipitates as graphite. The effect of a lower sulfur concentration at the interface is not strong enough to avoid graphite precipitation, as the effect of sulfur on  $C_C$  is smaller than the effect of temperature, according to Neumann's equation (9). 5) It is expected that these precipitated graphite flakes block MgS, thus preventing it from reaching the slag layer. MgS staying in the hot metal means a lower desulfurization efficiency (and thus a higher  $\dot{m}_{\text{Mg}}$ ). It is expected that the hampering effect of graphite on  $\dot{m}_{\text{Mg}}$  becomes relatively stronger when more graphite is present. The expected relation is therefore not linear.

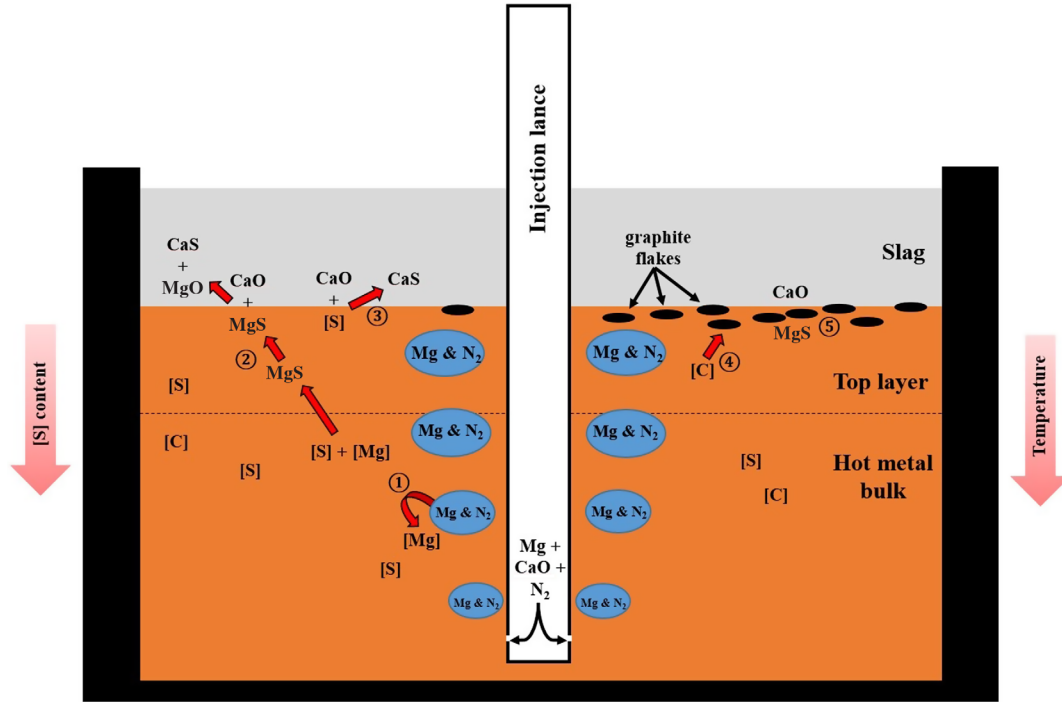
The graphite blocking MgS to reach the slag layer is comparable with the mechanism proposed by Street et al.<sup>[19]</sup> for Ti(C,N) particles that can form a layer between the hot metal and the slag, which blocks MgS during HMD.

## 3. Measurements and Discussion

### 3.1. Plant Measurements

In 2018, at Tata Steel's plant in IJmuiden (the Netherlands), a trial was executed to measure the carbon content of the hot metal at the magnesium–lime co-injection HMD station, immediately after reagent injection. In addition to the standard sample and temperature measurements, hot metal samples of 657 heats were taken for this trial. The sample was taken with an automatic sampling lance at a fixed height: 60 cm below the slag surface. It is assumed that when the sampling lance breaks through the slag layer and the graphite–MgS layer below, some MgS will be dragged down with it and ends up in the sample, leading to a higher sulfur concentration in the sample. Retrieved samples were air cooled before they were sent to the laboratory. At the laboratory, the samples were milled and then analyzed by WD-XRF. The analysis was validated using the combustion method with infrared detection. Each sample was analyzed once. The total standard deviation for carbon measurement (the sum of all deviations) is 0.1 wt%.

The dataset of 657 HMD heats where carbon was measured, including the standard data that are retrieved for every heat and the carbon measurements, was filtered for outliers. Heats where data are missing, where  $C_{\text{Mg}} > 0.01 \text{ wt\%}$ , or with temperatures below 1350 °C or above 1450 °C, were excluded. Filtering on  $C_{\text{Mg}}$  was done because high  $C_{\text{Mg}}$  values are caused by very low sulfur concentrations, but at very low sulfur concentrations, the measurement error has a too large influence on  $C_{\text{Mg}}$ . Filtering on temperature was done because temperature has a



**Figure 1.** Schematic overview of the top part of the ladle in the co-injection HMD process, where 1) Mg is dissolving in hot metal, 2) desulfurization occurs with Mg via reactions (1) and (3), 3) desulfurization occurs with CaO via reaction (4), 4) graphite formation takes place, and 5) graphite flakes block MgS particles.

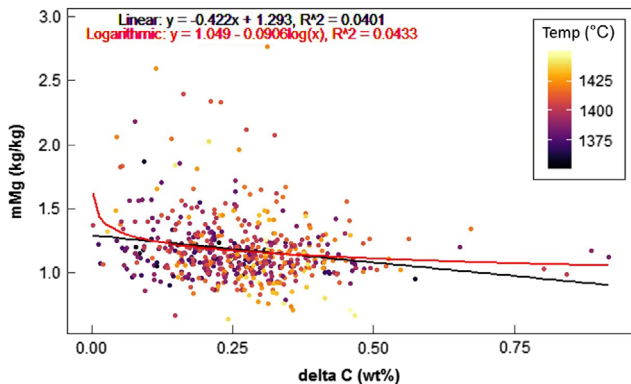
large effect on HMD efficiency, so extreme temperatures could have a disproportionate effect on the trends. After filtering 546 heats remained for further analysis.<sup>[5]</sup>

**Figure 2** shows a plot of  $\dot{m}_{Mg,cor}$  against  $\Delta C$  for the 546 HMD heats. The measured hot metal temperature (in °C) of a heat is indicated via the color of the data points, as temperature is known to have a strong effect on desulfurization efficiency. With the software package R,<sup>[20]</sup> the best fitted linear function (black line) and logarithmic function (red line) for this dataset are calculated.

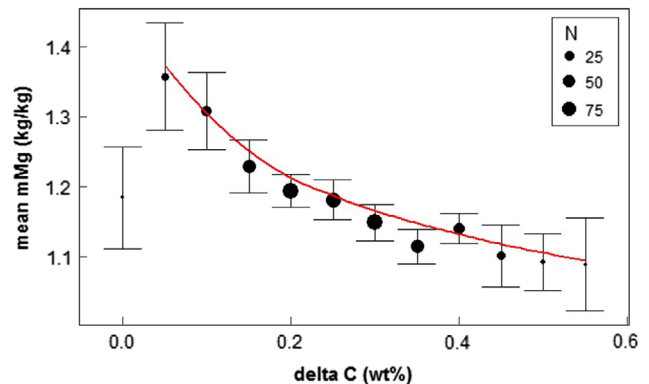
**Figure 2** shows a weak correlation between  $\dot{m}_{Mg,cor}$  and  $\Delta C$ . The slope of the best fitted linear line has a standard deviation

of 0.088 for the gradient, indicating a high probability that the correlation between  $\dot{m}_{Mg}$  and  $\Delta C$  is negative, as is expected. As the hot metal temperature seems to be scattered randomly, the data are well corrected for the temperature effect, so the observed trend cannot be attributed to temperature. A low  $R^2$  value is expected when looking at plant data, but an  $R^2$  of 0.04 indicates that other factors play a role in this correlation as well.

To make the trend better visible, the data are grouped for  $\Delta C$ , per 0.05 wt%, and for every group the average  $\dot{m}_{Mg,cor}$  is taken and shown in **Figure 3**. The error bars indicate the  $1\sigma$  standard



**Figure 2.**  $\dot{m}_{Mg,cor}$  against  $\Delta C$ . The colors of dots indicate the hot metal temperature. The black line is the linear best fit, and the red line is the logarithmic best fit.



**Figure 3.**  $\dot{m}_{Mg,cor}$  versus grouped  $\Delta C$  (per 0.05 wt%). The dot size indicates the number of measurements per group. The red line is the best fitted logarithmic function from **Figure 2**. The error bars show the  $1\sigma$  standard deviation per group.

deviation per group and the plotted red line shows the same logarithmic best fit, as shown in Figure 2.

### 3.2. Influence of the Hot Metal Composition

Figure 2 and 3 shows that there is a, albeit weak, correlation between  $\dot{m}_{Mg,cor}$  and  $\Delta C$  that is independent of temperature. However, in the HMD process, other elements in the hot metal have their influence on the desulfurization efficiency as well. In **Figure 4**, the concentrations of manganese, phosphorus, silicon, and titanium are plotted against  $\Delta C$ .

Figure 4 clearly shows there is no correlation between  $\Delta C$  and the elements' phosphorus and manganese concentrations in the hot metal. Both silicon and titanium do show a negative correlation with  $\Delta C$ , but this could be expected, as the concentrations of silicon, titanium, and carbon in hot metal are known to be correlated. However, silicon and titanium do not have an independent influence on  $\dot{m}_{Mg}$ .<sup>[4,10]</sup> The reason for the apparent two groups for manganese concentration in Figure 4 has not been investigated, as it has no influence on the graphite formation or desulfurization.

The data are not corrected for the initial sulfur concentration ( $S_{in}$ ), even though  $S_{in}$  has an impact on  $\dot{m}_{Mg}$ . The initial carbon and sulfur concentrations are correlated, as Equation (9) shows, so the apparent effect of  $\Delta C$ , and thus graphite precipitation, could also be caused by a different  $S_{in}$ . **Figure 5** shows the correlation of  $S_{in}$  with  $\Delta C$  (a) and  $\dot{m}_{Mg,cor}$  (b), respectively.

From Figure 5, it can be concluded that the correlation between  $\dot{m}_{Mg,cor}$  and  $\Delta C$  can as well be attributed to the effect

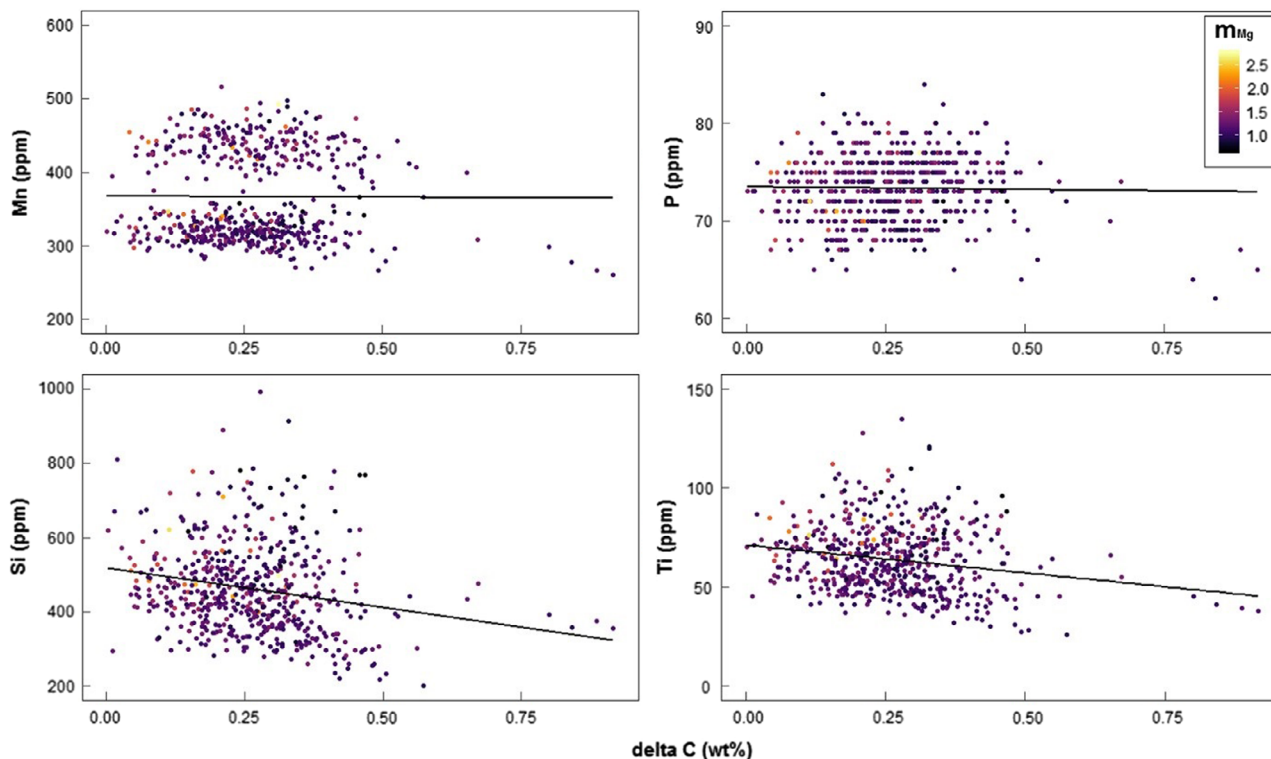
of  $S_{in}$  on  $\dot{m}_{Mg,cor}$ . Because this research is based on plant data, it is difficult to isolate the effect of a certain parameter, like in a laboratory experiment, where all parameters can be controlled. It is possible to make a selection from the available heats, grouping them based on the initial sulfur concentration. **Table 1** shows the number of heats in every  $S_{in}$  group.

**Figure 6** shows the correlation between  $\dot{m}_{Mg,cor}$  and  $\Delta C$  for  $S_{in}$  groups. For heats with a lower  $S_{in}$  (below 225 ppm), there is a correlation between  $\dot{m}_{Mg,cor}$  and  $\Delta C$ , as expected. For higher initial sulfur concentrations (above 325 ppm), there is no significant correlation. A possible explanation for this is that at higher initial sulfur concentrations, more sulfur is removed. Based on Neumann's equation, desulfurization leads to a higher  $C_C$  (Equation (9)). The higher the degree of desulfurization, which is strongly correlated with  $S_{in}$ , the more strongly  $S_{in}$  and  $C_C$ , and thus  $\Delta C$ , are correlated. This could result in no detectable separate correlation between  $\Delta C$  and  $\dot{m}_{Mg,cor}$ .

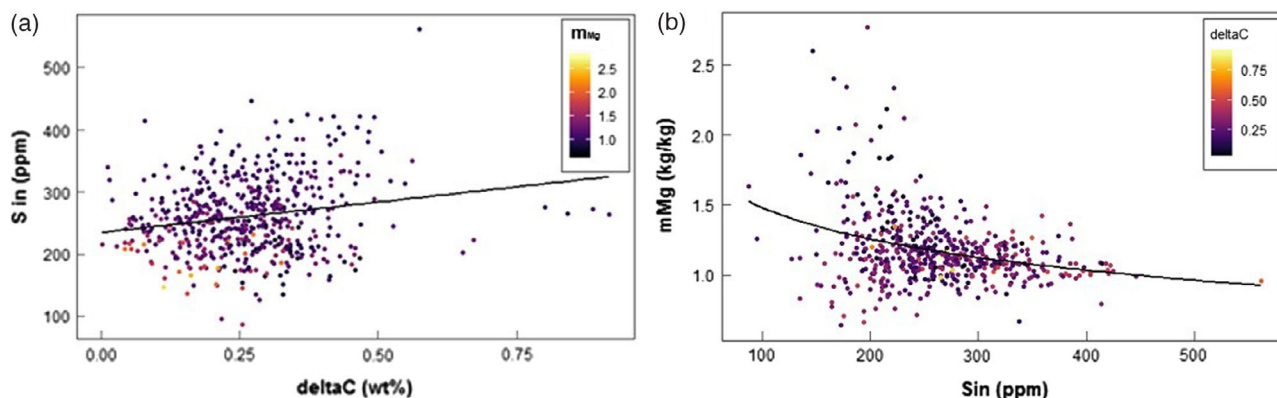
To investigate if the observed correlation can still be attributed to  $S_{in}$ ,  $\dot{m}_{Mg,cor}$  is plotted against  $S_{in}$  in **Figure 7**. It is shown that there is no correlation between  $S_{in}$  and  $\dot{m}_{Mg,cor}$ .

### 3.3. The Magnitude of the Effect

Because the effect of graphite precipitation on the desulfurization efficiency could not be clearly isolated from the HMD data, the converter data were studied for the same 546 heats. A sulfur mass balance was made, considering the measured sulfur input via the hot metal, as well as the estimated sulfur input



**Figure 4.** Correlation between  $\Delta C$  and other main elements in the hot metal (Mn, P, Si, and Ti). The black line is the linear trend line. The colors of the data points indicate  $\dot{m}_{Mg,cor}$ .



**Figure 5.** The correlation of  $S_{in}$  with  $\dot{m}_{Mg,cor}$  and  $\Delta C$ . a)  $S_{in}$  versus  $\Delta C$ , where the colors of the dots indicate  $\dot{m}_{Mg,cor}$  and where the black line is the linear trend line. b)  $\dot{m}_{Mg,cor}$  versus  $S_{in}$ , where the colors of the dots indicate  $\Delta C$  and where the black line is the logarithmic best fit.

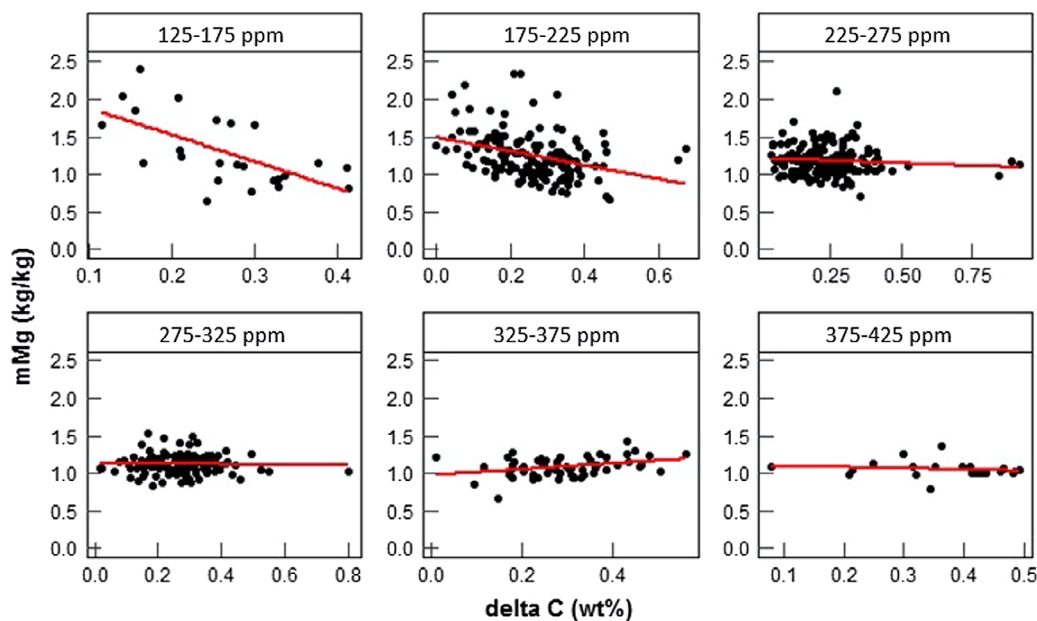
**Table 1.** Number of heats per  $S_{in}$  group.

$S_{in}$ range [ppm]	<125	125–175	175–225	225–275	275–325	325–375	375–425	>425
Count	2	25	144	172	122	56	23	2

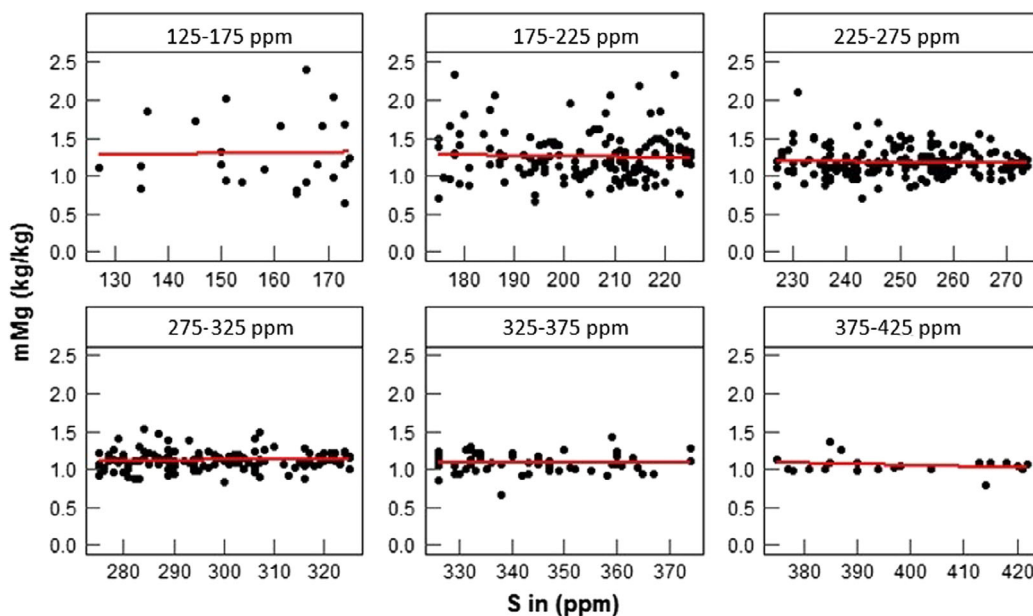
via scrap and additions, and the measured sulfur output via the liquid steel and the estimated sulfur output via the slag. Based on the theory, a significant hampering effect of graphite precipitation on HMD efficiency should lead to a sulfur concentration in the hot metal that is higher than expected and that is possibly missed by the sulfur measurement at the end of the HMD process. This should then lead to a higher resulfurization in the converter for heats that had more graphite precipitation during the HMD process. However, the sulfur mass balance over the converter did not show any correlation

between  $\Delta C$  at the HMD and resulfurization. This excludes the possibility that the effect of graphite on HMD efficiency is missed because of a systematic measurement error when measuring the sulfur concentration at the end of the HMD process. The lack of any significant correlation in the converter data shows that the postulated effect is too small to have any detectable consequences in the converter. This could be either because only a small amount of MgS is blocked by the graphite or because the graphite–MgS layer is skimmed off together with the slag in the HMD, effectively leading to successful desulfurization.

In the HMD process data, there only is a significant correlation between graphite formation and desulfurization efficiency at low initial sulfur concentrations. However, as there are many other factors that have a stronger influence on desulfurization efficiency, it is difficult to isolate this effect. This suggests that the postulated effect is small. The fact that there are hundreds



**Figure 6.**  $\dot{m}_{Mg,cor}$  against  $\Delta C$  for  $S_{in}$  groups (steps of 50 ppm). The  $S_{in}$  group is in the title of every mini figure. The red line is the linear trend line.



**Figure 7.** Correlation between  $S_{in}$  and  $\dot{m}_{Mg,cor}$  for  $S_{in}$  groups (steps of 50 ppm). The  $S_{in}$  group is in the title of every mini figure. The red line is the linear trend line.

of HMD stations worldwide, but that no correlation between graphite formation and the specific magnesium consumption has as yet been found, invigorates the suggestion that the effect is small.

Nevertheless, the high number of plant measurements, also in the low  $S_{in}$  range, makes the correlation between  $\Delta C$  and  $\dot{m}_{Mg,cor}$  significant, despite the standard deviation of 0.1 wt% per single measurement and the assumption that sulfur from the MgS-graphite layer is captured in the sample. Furthermore, it has been proven that the graphite layer between the slag and the hot metal is formed when the metal gets oversaturated with carbon.<sup>[1,5]</sup> In theory, the observed correlation between  $\Delta C$  and  $\dot{m}_{Mg,cor}$  can also be caused by carbon itself. Carbon can help to decrease the oxygen concentration of the hot metal, which will decrease  $\dot{m}_{Mg}$ . However, the oxygen concentration in the hot metal is already low (typically 3 ppm) and even at low carbon concentrations still enough carbon remains to decrease the oxygen concentration. Furthermore, carbon has an influence on sulfur concentration. In the BF, more dissolved carbon leads to a lower sulfur dissolution. However, in the HMD process, the sulfur concentration is by definition below the sulfur dissolution limit. Thus, carbon itself will not have a significant effect on HMD.

## 4. Conclusions and Recommendations

### 4.1. Conclusions

Based on the theoretical studies and the data analysis from the industrial samples, the following conclusions can be drawn:

The measurements show that there is a correlation between  $\Delta C$  and  $\dot{m}_{Mg,cor}$  for lower initial sulfur concentrations (below 225 ppm), which cannot only be contributed to the other

elements than carbon in the hot metal or the hot metal temperature. However, this effect of  $\Delta C$ , thus of graphite formation, on specific magnesium consumption, is small. For higher initial sulfur concentrations (above 325 ppm), the effect is either very small or nonexistent.

The postulated effect of graphite formation on the desulfurization efficiency has no significant influence on resulfurization in the converter. The possible increase in sulfur concentration is so small that the uncertainties of the sulfur content of the scrap and the additions make it insignificant.

The effect of precipitated graphite on HMD efficiency is larger at lower initial sulfur concentrations. Possibly a larger difference between initial and final sulfur concentrations counters the effect of graphite on  $\dot{m}_{Mg}$ .

The size and impact of graphite on the HMD process cannot be quantified from this data, because in plant data, the parameter of graphite formation (or  $\Delta C$ ) cannot be isolated from other parameters.

### 4.2. Recommendations

As the effect of graphite formation on the desulfurization efficiency is difficult to isolate from plant data, better controlled laboratory experiments should be done to confirm the existence of this effect.

Possibly graphite formation in the top layer of the hot metal bath is enhanced by the availability of nucleation sites for carbon as a result of the reagent injection. As this could lead to instant graphite formation at the start of the HMD process (assuming there is local carbon oversaturation in the top layer resulting from unavailability of nucleation sites prior to injection), the graphite could influence the process from the beginning. Further investigations are required to confirm this.

## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

carbon precipitation, carbon saturation, hot metal desulfurization, magnesium consumption

Received: August 28, 2019

Revised: October 2, 2019

Published online:

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