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Desulfurization of High-Sulfur HIsarna Hot Metal

Frank N. H. Schrama, Elisabeth M. Beunder, Ali Emami, Chris M. Barnes, Johan W. K. van Boggelen, Jilt Sietsma, Rob Boom, and Yongxiang Yang*

The HIsarna process is one of the emerging low-CO_2 ironmaking processes that could help the steel industry in achieving their carbon footprint goals. HIsarna hot metal contains 3–4 times more sulfur than hot metal from blast furnaces (BFs). Therefore, a literature study, a thermodynamic analysis, and plant data analysis from Tata Steel, IJmuiden, are used herein to investigate the consequences of HIsarna hot metal for the current hot metal desulfurization process. Although the high sulfur concentration and low temperature of HIsarna hot metal lead to a higher total reagent consumption, compared with desulfurization of BF hot metal, the specific magnesium consumption decreases. The higher oxygen concentration in HIsarna hot metal only leads to a small increase in reagent consumption.

1. Introduction

The current concern on global climate change is leading to numerous new ironmaking processes with a lower CO_2 footprint than the current blast furnace (BF) process, or even CO_2-neutral processes, being developed by industry and academia.[1,2] One new ironmaking process that is in an advanced development stage is HIsarna. HIsarna is a smelting reduction ironmaking process, which uses coal and lower-grade iron ore instead of coke and pellets as raw materials. This lowers the CO_2 footprint of the produced hot metal by 20%, compared with the BF. Furthermore, the HIsarna off gas is better suited for carbon capture and storage or carbon capture and usage, which could lead to a total CO_2 reduction of 80%.[2–6]

Due to the less reducing environment in the lower part of HIsarna, compared with the BF, the HIsarna hot metal typically contains very little silicon, low phosphorus and manganese, and slightly less carbon. In contrast, the sulfur and oxygen concentrations are higher.[5–7] **Table 1** gives a typical composition of the hot metal from HIsarna and the BF.

The tapping temperature from the HIsarna is 1400–1450 °C. This means that during tapping, HIsarna hot metal is typically 40–80 °C colder than hot metal from the BF. The hot metal is tapped separately from the slag, which implies that no hot metal–slag reactions will take place after tapping and no carryover slag is conveyed together with the hot metal to the steel plant.[2–8] Trials at the pilot HIsarna at Tata Steel in IJmuiden, the Netherlands, show sulfur concentrations between 0.03 and 0.2 wt%. High sulfur concentrations are caused by both a higher sulfur input via coal and a higher oxygen activity (a_O) in HIsarna, which hamper the desulfurization of the hot metal. Trials with low-sulfur coal led to hot metal with a sulfur concentration of 0.03–0.05 wt%, which is similar to BF hot metal. However, when the sulfur input via coal and coke is equal, HIsarna hot metal will have a higher sulfur concentration than BF hot metal.[3,5–7] This means that at an integrated steelmaking site, where a BF is replaced by the HIsarna process, more sulfur needs to be removed by hot metal desulfurization (HMD), prior to the converter process. This typically leads to a longer processing time at the HMD station. As desulfurized HIsarna hot metal is expected to be lower in all major dissolved elements, compared with BF hot metal, a shorter converter process can be expected. This shorter process time at the converter could lead to a higher pressure on the HMD process, which already will take longer.

In this study, the effect of the lower temperature and different composition of HIsarna hot metal on the processing time and reagent consumption of the Mg–CaO coinjection HMD process is investigated.

2. Theoretical Evaluations

2.1. HMD Process

The most widely used HMD process is the magnesium–lime coinjection process. In this process, the reagents magnesium and lime are injected in the hot metal via a refractory-coated lance. The magnesium dissolves and reacts with dissolved sulfur (Reaction 1). The formed MgS reacts with lime to form the stable CaS (Reaction 2).[9–12]

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Table 1. Typical hot metal composition for HIsarna and BF.

Composition [wt%]	C	Si	S	Mn	P	Ti	V	O
HIsarna	4.0	0.007	0.1	0.03	0.04	0.001	0.01	6 ppm
BF[8]	4.5	0.4	0.03	0.3	0.07	0.04	–	0.5 ppm

$$[\mathrm{Mg}] + [\mathrm{S}] = \mathrm{MgS(s)} \tag{1}$$

$$\mathrm{MgS(s)} + \mathrm{CaO(s)} = \mathrm{MgO(s)} + \mathrm{CaS(s)} \tag{2}$$

Although a small degree of desulfurization takes place via a direct reaction between lime and dissolved sulfur, typically $>95\%$ of the desulfurization takes place via Reactions 1 and 2. This means that for an industrial HMD process, the desulfurization efficiency can be expressed by the specific magnesium consumption ($\dot{m}_{\mathrm{Mg}}$).[6,13]

$$\dot{m}_{\mathrm{Mg}} = \frac{m_{\mathrm{Mg}}}{m_{\Delta \mathrm{S}}} \tag{3}$$

Here, m_{Mg} and $m_{\Delta \mathrm{S}}$ are the mass of consumed metallic magnesium and removed sulfur, respectively. In industrial HMD stations, $\dot{m}_{\mathrm{Mg}}$ values between 1.0 and 2.5 are observed.[9,10,13,14] This wide range is caused by differences in process conditions and reagent quality. However, to have a fair measure for desulfurization efficiency of industrial HMD stations, $\dot{m}_{\mathrm{Mg}}$ needs to be corrected for part of the magnesium remaining dissolved in the hot metal without reacting with the dissolved sulfur. According to Ender,[15] based on plant data, the mass fraction of magnesium in the hot metal at equilibrium ($w_{[\mathrm{Mg}]}$) can be estimated via

$$w_{[\mathrm{Mg}]} = \frac{10^{-18.3+0.00679T}}{w_{[\mathrm{S}]}} \tag{4}$$

Here, $w_{[\mathrm{S}]}$ is the mass fraction of dissolved sulfur in the hot metal and T is the temperature in °C. In this equation, carbon saturation of the hot metal is assumed. It should be noted that actual equilibrium in the hot metal is not reached during the HMD process, but according to Visser,[10] the estimated $w_{[\mathrm{Mg}]}$ from Equation (4) is in agreement with industrial observations. This leads to the following adjusted specific magnesium consumption ($\dot{m}'_{\mathrm{Mg}}$).[6,13]

$$\dot{m}'_{\mathrm{Mg}} = \frac{m_{\mathrm{Mg}} - w_{[\mathrm{Mg}]} \cdot m_{\mathrm{HM}}}{m_{\Delta \mathrm{S}}} \tag{5}$$

Here, m_{HM} is the mass of the hot metal.

2.2. Influence of Hot Metal Composition and Temperature on HMD

The theoretical influence of the different hot metal composition and temperature of HIsarna hot metal on the HMD process is summarized in **Table 2**. The column $\dot{m}_{\mathrm{Mg,\ HsHM}}$ shows how $\dot{m}_{\mathrm{Mg}}$ changes for HIsarna hot metal compared with BF hot metal for the given factor.

Table 2. Influence of different hot metal compositions and temperatures on $\dot{m}_{\mathrm{Mg}}$ by changing from BF hot metal to HIsarna hot metal. Influence ranges from a large increase (▲▲) to a large decrease (▼▼) for $\dot{m}_{\mathrm{Mg}}$ of HIsarna hot metal.

Factor	BF	HIsarna	$\dot{m}_{\mathrm{Mg,\ HsHM}}$	Source	Remarks
[O]	0.5 ppm	6 ppm	▲▲	[9,15,16]	
[Si]	0.4 wt%	0.007 wt%	▲	[10,17]	Excluding a_O
[Ti]	0.04 wt%	0.001 wt%	0	[10,13,34]	Excluding a_O
[C]	4.5 wt%	4.0 wt%	0	[10,13,29]	Excluding a_O
[Mn]	0.3 wt%	0.03 wt%	(▼)	[9,10,20]	Excluding a_O
[S]	0.03 wt%	0.1 wt%	▼▼	[7,19]	
T	1375 °C	1325 °C	▼▼	[9,19,25]	Temperature at HMD

2.2.1. Hot Metal Composition

The oxygen activity in the hot metal and the slag is important for the HMD process. A higher a_{O} in the hot metal causes less sulfur to go to the slag and more sulfur to remain dissolved in the hot metal, at equilibrium.[9,16] This implies that the amount of dissolved sulfur in the hot metal can be lowered by either lowering the amount of dissolved oxygen in the hot metal (lowering a_{O}) or by increasing the amount of oxygen in the slag phase (increasing the slag basicity). Therefore, $\dot{m}_{\mathrm{Mg}}$ will decrease with decreasing a_{O}. However, in industry, the oxygen concentration in hot metal is generally not measured. Silicon and titanium concentrations are strongly influenced by a_{O} (a high a_{O} leads to low silicon and titanium concentrations in the hot metal). The oxygen concentration prior to HMD can, therefore, best be predicted based on silicon and titanium concentrations in hot metal.

Apart from the correlation between silicon and a_{O}, silicon has a direct influence on the desulfurization process as well. Silicon enhances the direct desulfurization with lime, via the following reaction.[10,17]

$$2[\mathrm{S}] + 2\mathrm{CaO(s)} + [\mathrm{Si}] = 2\mathrm{CaS(s)} + \mathrm{SiO_2(s)} \tag{6}$$

Typically, in the coinjection process, the direct desulfurization via lime only contributes for only a fraction of less than 5% of the total sulfur removal. Therefore, the influence of silicon on the HMD process is limited. However, in some steel plants, the HMD process depends more on Reaction 6, if the Mg-to-CaO ratio is low, for example, 1:5. For HMD processes which fully depend on lime, like the Kanbara reactor (KR) process, silicon in hot metal is even more important.[9] The KR process is an alternative HMD process that uses only lime (or $\mathrm{CaC_2}$ or $\mathrm{CaF_2}$) as reagent to desulfurize the hot metal.[9,11,18] As a result, the coinjection HMD process is better suited to desulfurize HIsarna hot metal, which contains almost no silicon, than the KR process. For the coinjection HMD process, the absence of silicon in hot metal will lead to an even lower contribution of the direct desulfurization via lime, but this will have only a small influence on $\dot{m}_{\mathrm{Mg}}$.

As HIsarna hot metal has a higher sulfur concentration than BF hot metal, the HMD process will take longer and the total reagent consumption will be higher. Consequently, the costs for the HMD process will increase when HIsarna hot metal is introduced. However, the specific magnesium consumption ($\dot{m}_{Mg}$) will decrease as a result of the higher sulfur concentration, as it is easier to remove sulfur when sulfur is present at a higher concentration.[7,19]

Carbon, manganese, and titanium do not have a large influence on the $\dot{m}_{Mg}$ of the HMD process. Manganese helps increasing the sulfide capacity of the slag.[10,20] Therefore, a small negative effect on the desulfurization of HIsarna hot metal, which contains less manganese than BF hot metal, is expected in theory. Furthermore, the lower carbon concentration, which is below the saturation point, in HIsarna hot metal implies that less carbon precipitation takes place compared with BF hot metal. This means that less kish formation can be expected. Finally, a high concentration of titanium in hot metal (more than 0.1 wt%) leads to the formation of Ti(C,N) during the HMD process. Ti(C,N) particles lead to a "sticky slag," which can result in high iron losses. These Ti(C,N) particles do not influence $\dot{m}_{Mg}$.[13]

2.2.2. Temperature

Temperature has a significant effect on the magnesium-based HMD process. The desulfurization reaction with magnesium is enhanced at lower temperatures. Lower $\dot{m}_{Mg}$ values are observed in industrial HMD stations when the hot metal temperature is lower.[9] Magnesium solubility in hot metal decreases at increasing hot metal temperatures. This is because the increasing temperature increases the vapor pressure of magnesium gas, making it thermodynamically favorable for magnesium to be in the gas phase, rather than being dissolved in hot metal.[11,18,21–23] Although desulfurization of hot metal with magnesium gas is possible under HMD conditions, the homogeneous reaction between dissolved magnesium and dissolved sulfur (Reaction 1) is kinetically favorable. Irons and Guthrie[24] found that more than 90% of the magnesium-based desulfurization is via dissolved magnesium rather than via magnesium gas. Thermodynamically, Reaction 1 is favored at lower temperatures.[9,25]

It should be noted that the desulfurization efficiency increases with increasing temperature, when the reagents are calcium based (CaO or CaC_2). The reaction between dissolved sulfur and lime or calcium carbide is thermodynamically favored at higher temperatures.[9,25] This is supported by industrial observations.[19] However, as in the magnesium–lime coinjection HMD process is governed by the desulfurization reaction via magnesium, the overall HMD process is more efficient and faster at low hot metal temperatures, which is also observed in industry.[9,18]

Based on this analysis, a lower $\dot{m}_{Mg}$ can be expected at the HMD for HIsarna hot metal compared with BF hot metal. However, due to the higher sulfur concentration, the total reagent consumption would increase.

2.3. Slag

As HIsarna hot metal is tapped without any carryover slag, the slag composition at the HMD depends only on the HMD process itself. When Mg and CaO are injected, the slag will consist of the formed sulfides and oxides: CaS, MgO, and CaO. Such a slag would be solid at HMD temperatures, which is undesired. In addition, compared with desulfurization of BF hot metal, more sulfides and oxides are formed (more sulfur needs to be removed) and the temperature is lower, which further enhances the slag's solid fraction. A slag with a low liquid fraction has a high apparent viscosity, which leads to high iron losses.[6,26–28] Furthermore, a high solid fraction decreases the reaction surface and therefore the reactivity, of the slag, hampering the reaction between MgS and CaO (Reaction 2). As MgS, in contact with oxygen from the air, thermodynamically favors the formation of MgO, the sulfur would return to the hot metal, a phenomenon called resulfurization.[9,29] Therefore, the addition of synthetic slag is required. To make the slag liquid, its melting temperature should be lowered by adding acidic oxides such as SiO_2 and Al_2O_3. Also, the addition of small quantities of alkali metal oxides, like Na_2O and K_2O, could lower the slag's melting point and viscosity.[26]

It would require specific equipment to add the synthetic slag, but such a procedure would lead to lower iron losses and less slag that needs to be treated after the HMD process, eventually leading to lower costs. Alternatively, BF slag (if available) could be used instead of synthetic slag, which would lead to roughly the same slag composition as is common today at the HMD. Also basic low-sulfur slag from another steelmaking process (e.g., from secondary metallurgy) could be used to make a liquid slag, but it depends on the composition of that slag if it is suitable for that. This needs further investigation.

Although the same composition of current HMD slag could be achieved, desulfurization of HIsarna hot metal will lead to a colder slag, because of the lower temperature of the hot metal. This leads to a higher solid fraction of the slag. It is not certain that a slag modifier could completely compensate for this, as its use is limited by slag basicity (a too acidic slag would not desulfurize) and alkali metal oxide concentration (slag that is recycled at the BF cannot contain too much alkali metal oxides, because these will build up inside a BF).[26] Furthermore, the total slag volume will increase, because more reagents are added to remove the higher amount of sulfur in HIsarna hot metal. This will, despite slag modifiers, lead to higher iron losses.[26,27] Apart from the iron losses, the slag skimming time will increase when there is more slag to remove, leading to a longer total process time and higher temperature losses.

3. Experimental Section

3.1. Thermodynamic Simulations

To better understand the thermodynamic consequences of desulfurizing HIsarna hot metal, compared with typical BF hot metal, FactSage calculations were conducted. FactSage 7.3 was used for simulation of HMD with different hot metal conditions, using the FSstel-Liqu and CON3 SLAG base phases.[30] The hot metal compositions from Table 1 were assumed and a surplus of Mg was added (1.0 wt% of the hot metal, depending on the initial sulfur concentration, stoichiometrically 0.023–0.076 wt% Mg was required to remove all sulfur). In the simulation, reactions with slag, air, and lime were not considered, so only desulfurization via Reaction 1 was taken into account. As 1375 °C is a common hot metal temperature at the HMD and HIsarna hot metal is typically 50 °C colder than BF hot metal, the temperature varied from 1325 to 1375 °C.

The FactSage calculations showed no significant difference between the desulfurization of HIsarna hot metal and of BF hot metal. At equilibrium, the surplus of magnesium is large enough to remove nearly all sulfur, regardless of the initial sulfur concentration and oxygen concentration. Higher temperature does lead to higher equilibrium sulfur concentration in the hot metal. Also, the higher carbon concentration in BF hot metal slightly increases the equilibrium sulfur concentration, compared with that of HIsarna hot metal.

When instead of a surplus of magnesium, only enough magnesium for $\dot{m}_{\mathrm{Mg}}$ of 1.0 is added (so 1 kg magnesium is added per kg of sulfur present), there is a difference between HIsarna hot metal and BF hot metal. **Figure 1** shows the equilibrium sulfur concentration in the hot metal after HMD for the different initial hot metal compositions.

As was expected based on the theory, the final sulfur concentration in the HIsarna hot metal was lower than that of the BF hot metal. The reason is that more magnesium was added, as HIsarna hot metal initially also contained more sulfur (so $\dot{m}_{\mathrm{Mg}}$ remained the same). As, thermodynamically, desulfurization became harder at lower sulfur concentrations, the overall efficiency of desulfurizing HIsarna hot metal was higher than that of BF hot metal. However, when leaving the desulfurization of HIsarna hot metal until a sulfur concentration of 0.03 wt% (the initial sulfur concentration of BF hot metal) out of comparison, taking the composition of HIsarna hot metal, but with an initial sulfur concentration of 0.03 wt% (red small dashed line), the differences between desulfurization of HIsarna hot metal and BF hot metal were negligible for the same temperatures. The difference in oxygen concentration or other elements did not significantly change the equilibrium of the final sulfur concentration in the hot metal.

For desulfurization of HIsarna hot metal, extra magnesium was required to remove the surplus of sulfur, compared with BF hot metal. This sulfur was removed at a high efficiency. The real thermodynamic advantage of desulfurization of HIsarna hot metal over desulfurization of BF hot metal only lies in the lower hot metal temperature of HIsarna hot metal.

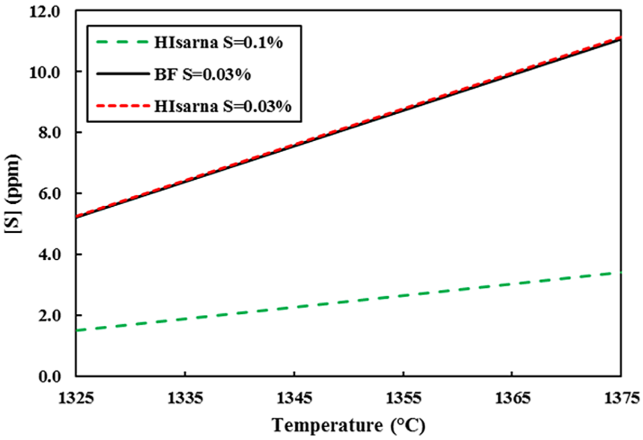


Figure 1. Sulfur concentration in hot metal equilibrium after HMD, calculated with FactSage 7.3, for BF hot metal (black solid line), HIsarna hot metal with 0.1 wt% [S] (green dashed line), and HIsarna hot metal with 0.03 wt% [S] (red small dashed line).

It should be noted that the sulfur concentrations in the hot metal at equilibrium were lower than the sulfur concentrations after HMD observed in industry. This was because kinetics plays an important role in the HMD process, impeding reaching equilibrium with an economically viable amount of reagents and within a feasible time.[9–11] This will be discussed in association with plant data analysis in Section 3.2.

3.2. Plant Data Analysis

To be able to include the kinetics in the overview of the effect of hot metal composition and temperature on the HMD process, a plant data analysis was conducted with 31 663 heats from the HMD stations for BF hot metal at Tata Steel, the Netherlands. The BF does not produce hot metal that is similar to HIsarna hot metal, so analysis of this plant data, with hot metal coming from the BF, will not directly answer the question of how HIsarna hot metal would behave. However, this plant data does give an indication of the effect of different components on the HMD efficiency. In the analysis, $\dot{m}'_{\mathrm{Mg}}$ (Equation (5)) was used to indicate the HMD efficiency. When analyzing plant data, it should be noted that a correlation does not necessarily mean causality. Furthermore, it should be noted that several parameters correlate with each other as well, like the silicon and titanium concentrations of hot metal, which are heavily correlated with each other, resulting in the fact that correlations between silicon and any other parameter will be similar to the correlation between titanium and that same parameter.

A distribution plot of the plant data, which is given in **Figure 2**, reveals the correlation between $\dot{m}'_{\mathrm{Mg}}$ and the composition and temperature of the hot metal. The plot shows the distribution of concentration of certain elements in the hot metal, temperature, and $\dot{m}'_{\mathrm{Mg}}$ for the whole dataset (black solid lines) and also the distribution for the same parameters for the data with the highest 25 % (red dashed lines) and lowest 25 % (blue dotted lines) of $\dot{m}'_{\mathrm{Mg}}$. The initial sulfur concentration clearly showed the highest correlation with $\dot{m}'_{\mathrm{Mg}}$. Temperature and silicon (and titanium and vanadium) were in correspondence with the predictions from Section 2 as well. It is remarkable that manganese showed a clear negative correlation with $\dot{m}'_{\mathrm{Mg}}$. Low-manganese concentrations correlated with a high desulfurization efficiency (low $\dot{m}'_{\mathrm{Mg}}$). Based on the theory, a small positive effect of manganese on the desulfurization efficiency was expected. The correlation cannot be explained by a_{O}, as a low-manganese concentration would indicate a high a_{O}, but a high a_{O} would lead to a high $\dot{m}'_{\mathrm{Mg}}$. However, the opposite was found. At the BF, manganese helped desulfurizing the hot metal,[9,31] which led to an inverse correlation between the manganese and sulfur concentrations in the hot metal. Upon arrival at the HMD station, the manganese and sulfur concentrations were already at equilibrium, so manganese did not influence the desulfurization at the HMD. However, as lower sulfur concentration led to a higher $\dot{m}'_{\mathrm{Mg}}$, high manganese concentration was correlated with a low $\dot{m}'_{\mathrm{Mg}}$ as well.

To better understand the relative impact of the different components in the hot metal and the temperature on $\dot{m}_{\mathrm{Mg}}$, a random

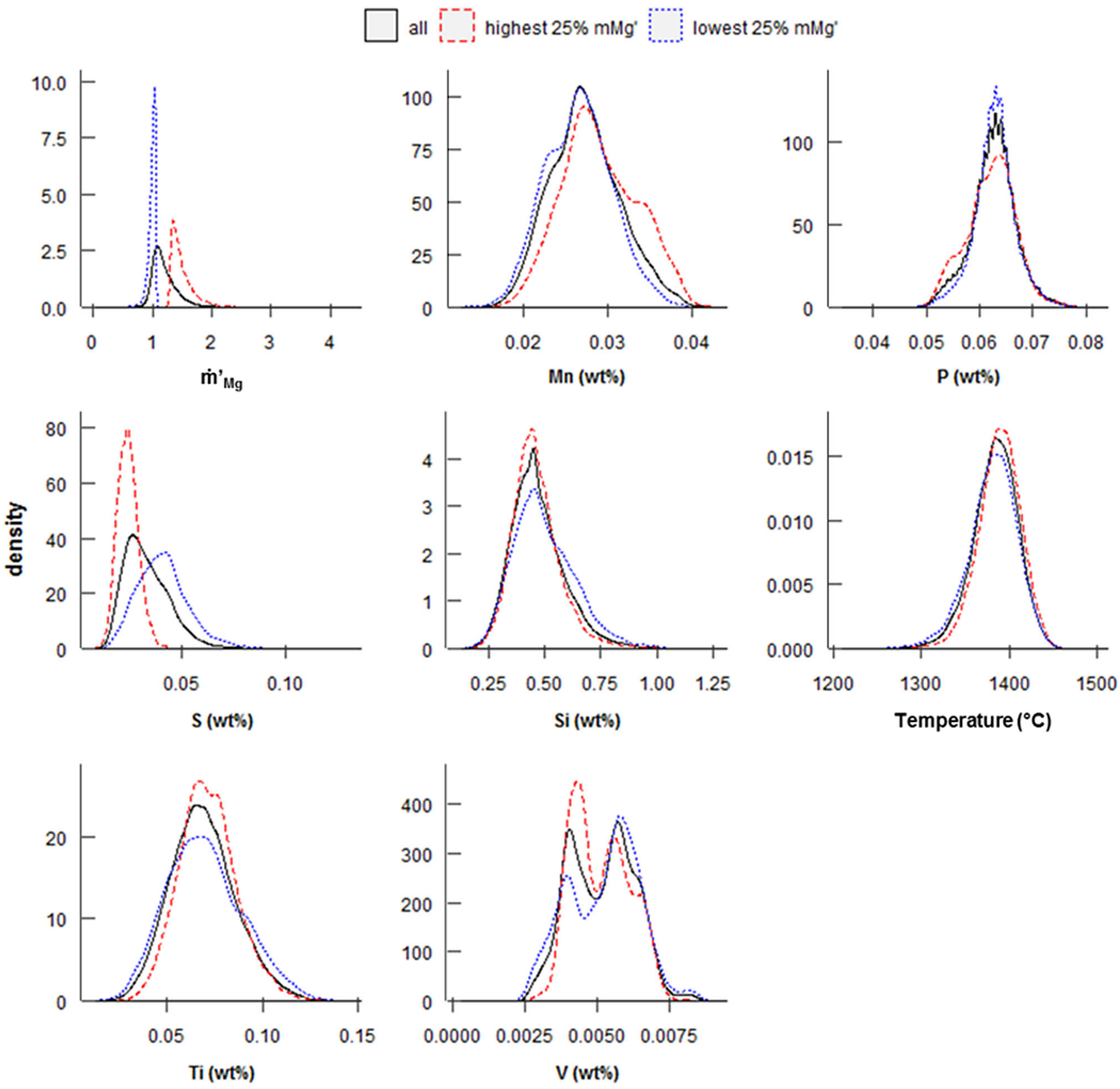
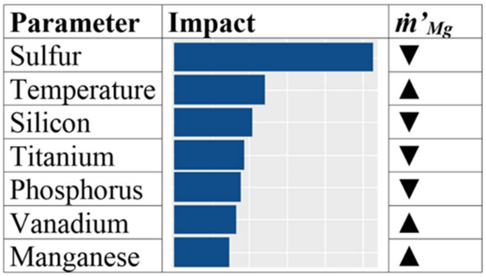


Figure 2. Distribution of the plant data from Tata Steel, IJmuiden, for the key parameters. Black solid lines show all data, the red dashed lines include only the data with the highest 25% $\dot{m}'_{\text{Mg}}$ and the blue dotted lines include only the data with the lowest 25% $\dot{m}'_{\text{Mg}}$.



Parameter	Impact	$\dot{m}'_{Mg}$
Sulfur		▼
Temperature		▲
Silicon		▼
Titanium		▼
Phosphorus		▼
Vanadium		▲
Manganese		▲

Figure 3. Relative impact of parameters on $\dot{m}'_{\text{Mg}}$, according to the RFM.

forest model (RFM) was made for the plant data. With RFM, the predicting value of the different parameters to predict $\dot{m}'_{\text{Mg}}$ in the dataset (impact) was determined.[32] In this study, the package "randomForest" within the software R was used. The RFM used 50 trees and a minimum node size of 20. **Figure 3** shows the overview of the impact of the different parameters on $\dot{m}'_{\text{Mg}}$.

The RFM showed that $\dot{m}'_{\text{Mg}}$ can best be predicted by the initial sulfur concentration of the hot metal, followed by temperature, silicon, and titanium concentrations. Despite the seemingly strong correlation between manganese concentration and $\dot{m}'_{\text{Mg}}$ based on the distribution plot, manganese proved to be a poor parameter to predict $\dot{m}'_{\text{Mg}}$. This supported the explanation that the correlation between manganese and $\dot{m}'_{\text{Mg}}$ was caused by the correlation between manganese and sulfur, rather than by an independent effect of manganese on $\dot{m}'_{\text{Mg}}$. The correlation between the silicon (and titanium) concentration and $\dot{m}_{\text{Mg}}$ cannot be fully attributed to the effect of a_{O} on the HMD process. The hot metal composition depends on the BF process. At the

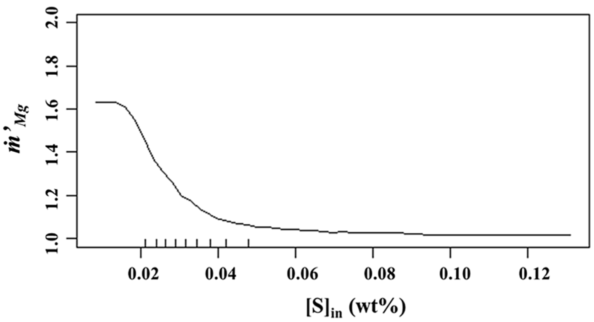


Figure 4. Partial dependency of $\dot{m}'_{Mg}$ on initial sulfur concentration, based on the RFM.

BF, a high hot metal silicon concentration correlates with a lower slag basicity,[8] which lowers the sulfur removal capacity of the slag and thus the desulfurization efficiency. A high silicon concentration in the hot metal correlates with a high sulfur concentration prior to HMD. Furthermore, a high silicon concentration at the BF indicates a low hot metal temperature, which leads to a lower $\dot{m}'_{Mg}$. Therefore, based on this plant data, it was not possible to quantify the effect of a_O on $\dot{m}'_{Mg}$, but it was clear that, in practice, the effect of a_O was smaller than the effect of sulfur concentration and temperature on $\dot{m}'_{Mg}$.

The influence of the hot metal composition and temperature on $\dot{m}'_{Mg}$ was not linear. The most important factor, the initial sulfur concentration ($[S]_{in}$), had only a significant impact up to ≈0.04 wt%. At higher sulfur concentrations, sulfur was abundant compared with dissolved magnesium anyway, so a higher sulfur concentration did not increase the desulfurization efficiency much further. This is illustrated by **Figure 4**, based on the RFM, showing the partial dependency of $\dot{m}'_{Mg}$ on the initial sulfur concentration. It should be noted that the number of datapoints at initial sulfur concentrations above 0.05 wt% was limited. However, an asymptote at $\dot{m}'_{Mg} \cong 1.0$ was in accordance with the expectations discussed in Section 2.2.

The plant data analysis showed that the higher sulfur concentration and lower temperature of HIsarna hot metal, compared with BF hot metal, will lead to a typical $\dot{m}'_{Mg}$ of 1.0. The plant data analysis supported the theory that a_O has a significant effect on $\dot{m}'_{Mg}$ but that this effect is smaller than the effect of the initial sulfur concentration and temperature.

4. Discussion

Given the much higher sulfur concentration in HIsarna hot metal, compared with hot metal from state-of-the-art BFs, desulfurization will take longer and cost more reagent. However, the high sulfur concentration and the low hot metal temperature will lead to a low $\dot{m}'_{Mg}$, in the order of 1.0. The high a_O, compared with BF hot metal, will influence the magnesium consumption, but it will only lead to a minor increase in magnesium consumption (in the order of a few kilograms per heat of ≈300 ton). All other investigated factors seem to have a much smaller influence on $\dot{m}_{Mg}$.

The fact that HIsarna hot metal has virtually no silicon will hardly influence the magnesium–lime co-injection HMD process. Silicon plays an advantageous role in the HMD process via lime (Reaction 6), but direct desulfurization via lime plays only a minor role in the magnesium–lime coinjection process. The absence of silicon in hot metal is problematic for lime-based HMD processes like the KR. Additional research would be required to determine how the KR process could be made suitable for desulfurization of HIsarna hot metal.

It should be noted that the predictions for HIsarna hot metal in both the theory and the plant data analysis are based on extrapolation of current BF hot metal data and experience. This means that certain effects of the HIsarna hot metal composition on the HMD process might be missed by this analysis. Plant trials with HIsarna hot metal would be required to rule out that certain aspects of the HIsarna hot metal composition have not been taken into account. Currently, only the pilot scale HIsarna, at Tata Steel in IJmuiden, exists, which is too small to create enough hot metal for entire heat to be processed at the steel plant. To verify whether the HMD station can effectively desulfurize HIsarna hot metal, a trial with synthetic HIsarna hot metal should be organized. Synthetic HIsarna hot metal can be produced by tapping “semi-steel” from the converter after only ≈5 min of blowing. This semisteel does not contain silicon and titanium, has low phosphorus and manganese concentrations, and contains ≈2.5 wt% carbon. Extra carbon and sulfur can be added to the semisteel, to create synthetic HIsarna hot metal, which has a comparable composition, at least for the main elements (being carbon, sulfur, phosphorus, silicon, titanium, and manganese), to HIsarna hot metal. After cooling down the synthetic HIsarna hot metal, it can be desulfurized at the HMD station and further processed at the converter and the following processes. As for this trial no actual HIsarna hot metal is required, it can be performed at any steel plant. For steelmaking companies that consider installing a HIsarna installation, this trial is a cost-effective way to investigate the consequences of HIsarna hot metal for their steel plant.

Nevertheless, the HMD process cannot only be rated on $\dot{m}_{Mg}$. The fact that more sulfur needs to be removed means that the HMD process will take longer. This can lead to the HMD becoming the bottleneck in the steel plant, resulting in a lower plant capacity. Furthermore, more slag will be produced as a result of more sulfur being removed, leading to higher iron losses. Because hot metal from the HIsarna does not come with any carryover slag, slag, or slag components, it should be added to keep the slag liquid during the HMD process. A synthetic slag (containing SiO_2 and Al_2O_3 and some K_2O or Na_2O) can be added, but as that could have too high costs, recycling slag from another process in the steelmaking route (containing high concentrations of SiO_2 and Al_2O_3) seems more likely. Given the current experience with BF carryover slag, slag from the BF would be a good candidate. However, it should be noted that due to the lower temperature of HIsarna hot metal and the longer HMD process time, the slag will be 50 °C, or more, colder than typical HMD slag. This means that despite a slag modifier, the slag could be partly solid, resulting in higher slag viscosity and, therefore, higher iron losses than at the current HMD process with BF hot metal.

To lower the impact of the aforementioned described effects of HIsarna hot metal on the HMD process, the initial sulfur concentration in the hot metal could be lowered prior to the HMD process. One option is to decrease the sulfur input in the HIsarna, using low-sulfur coal, which can lead to hot metal with a 50% lower sulfur concentration. Another option would be to mix the HIsarna hot metal with hot metal from a BF or another ironmaking unit that produces hot metal with a lower sulfur concentration. Diluting the HIsarna hot metal in this way would lead to shorter process times and less slag at the HMD, but it would also decrease the advantages of HIsarna hot metal. As discussed already, desulfurization of HIsarna hot metal is more efficient than desulfurization of BF hot metal when looking at the reagent costs per amount of removed sulfur. Diluting the HIsarna hot metal would not lower the total amount of sulfur that needs to be removed. However, diluted HIsarna hot metal with a lower sulfur concentration will lead to shorter process times at the HMD, which limits the temperature loss and lowers the chance of production loss due to delays at the HMD. Furthermore, the variation in HMD process times for mixed hot metal heats will be smaller than the variation in HMD process times for pure HIsarna hot metal heats, and heats containing only hot metal form the other ironmaking unit. The smaller variation in HMD process time is beneficial for the plant's logistic flexibility. Mixing hot metal streams after the HMD process would make use of the efficiency advantage, but mixing hot metal after the HMD has too many practical problems as mixing two streams of hot metal by pouring it from one ladle into another has safety issues and would require at least two different ladle sizes, either a separate mixing vessel or mixing in the converter. Both solutions mean extra handling time, leading to more delays and a higher chance of production loss, and would decrease the process flexibility. In addition, diluting HIsarna hot metal can only be considered when another ironmaking unit is available.

Another way to limit the consequences of desulfurization of HIsarna hot metal is to increase the aim for the final sulfur concentration. This implies that the pressure on the secondary metallurgy desulfurization increases. In addition, sulfur removal at secondary metallurgy is more expensive than desulfurization of hot metal.[9]

Given the disadvantages of the alternatives, the most promising solution for desulfurization of HIsarna hot metal is investing in the capacity of the HMD process, preferably the magnesium–lime coinjection HMD process. This can be done by either solving the bottleneck at the HMD or by building an extra HMD station. Alternatively, desulfurization of HIsarna hot metal can already start at the tap of the HIsarna, by installing a continuous HMD (CHMD) process.[33] However, this CHMD process is at an early stage of development, like the HIsarna process, and requires more intensive development.

5. Conclusion and Outlook

5.1. Conclusion

Based on the theory, a thermodynamic evaluation, and plant data analysis, it can be concluded that the magnesium–lime coinjection HMD process is capable of desulfurizing HIsarna hot metal to final sulfur concentrations as low as the current practice with BF hot metal (that is below 10 ppm). The following conclusions can be drawn. 1) Desulfurizing HIsarna hot metal will take longer and consumes more reagents than desulfurization of BF hot metal, as a result of the higher initial sulfur concentration. 2) Desulfurization of HIsarna hot metal will have a lower $\dot{m}_{\mathrm{Mg}}$ than BF HMD, because of the higher initial sulfur concentration and lower temperature. 3) The higher oxygen concentration of HIsarna hot metal will lead to a higher reagent consumption at the HMD, but this will be in the order of a 10–50 g of magnesium per ton hot metal. 4) As a result of the very low silicon concentration in HIsarna hot metal, the lime-based KR process will be less efficient in desulfurizing HIsarna hot metal. 5) Other elements dissolved in the hot metal do not have a significant influence on the HMD process efficiency.

5.2. Outlook

Given the current energy transition, steelmakers worldwide will need to change the way they produce hot metal. As HIsarna is in a mature phase of its development, it is expected that the HIsarna process will contribute to the worldwide hot metal production around the year 2035. Whether the HIsarna hot metal will be mixed with hot metal from other sources or used in its pure form, the desulfurization of the hot metal is more challenging and requires special attention.

The current study shows that desulfurization of hot metal to the required low sulfur concentrations is possible but that it can lead to capacity problems in maladjusted steel plants. This means that in the coming years the steel industry should not only focus on new ways to produce hot metal with less or no CO_2 emission, but also on the potential consequences on efficiency and quality for the subsequent processes in the steel plant. It is expected that with relatively easy adaptations, the magnesium–lime coinjection HMD process will be ready for desulfurization of HIsarna hot metal.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

HIsarna, hot metal desulfurization, oxygen activity, plant data analyses, specific magnesium consumption, thermodynamic simulations

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[1] J. Zhao, H. Zuo, Y. Wang, J. Wang, Q. Xue, *Ironmaking Steelmaking* **2020**, *47*, 296.

[2] M. Abdul Quader, S. Ahmed, S. Z. Dawal, Y. Nukman, *Renewable Sustainable Energy Rev.* **2016**, *55*, 537.

[3] H. K. A. Meijer, C. Treadgold, C. Zeilstra, G. Keilman, C. Teerhuis, M. Ouwehand, J. W. K. van Boggelen, J. Borlée, D. Wagner, C. Grisvard, C. Feilmayr, C. Thaler, J. Lövgren, P. Sikström, K.-G. Doppler, C. Günther, A. Feiterna, M. Skorianz, Z. Taszner, A. Hirsch, A. Sgura, R. Schott, Y. Höcker, P. Goedert, HIsarna

Experimental Campaigns B and C, EUR-27515, Publications Office of the European Union, Luxembourg **2015**.
[4] H. K. A. Meijer, C. Guenther, R. J. Dry, in *InSteelCon*, Dösseldorf, Ger, **2011**, p. 1.
[5] J. W. K. van Boggelen, H. K. A. Meijer, C. Zeilstra, Z. Li, in *Scanmet V*, Luleå, Swe **2016**, 008.pdf.
[6] F. N. H. Schrama, PhD thesis, Delft University of Technology, **2021**.
[7] F. N. H. Schrama, E. M. Beunder, J. W. K. van Boggelen, R. Boom, Y. Yang, in *Science and Technology of Ironmaking and Steelmaking*, Kanpur, Ind **2017**, p. 419.
[8] M. Geerdes, R. Chaigneau, I. Kurunov, O. Lingiardi, J. Ricketts, *Modern Blast Furnace Ironmaking*, IOS Press, Delft, the Netherlands **2015**.
[9] F. N. H. Schrama, E. M. Beunder, B. van den Berg, Y. Yang, R. Boom, *Ironmaking Steelmaking* **2017**, *44*, 333.
[10] H.-J. Visser, PhD thesis, Delft University of Technology, **2016**.
[11] S. Kitamura, in *Treatise On Process Metallurgy* (Eds: S. Seetharaman), Vol. *3*, Elsevier, Oxford, UK **2014**, Ch. 1.3.
[12] H.-J. Visser, R. Boom, *ISIJ Int.* **2006**, *46*, 1771.
[13] F. N. H. Schrama, E. M. Beunder, H.-J. Visser, J. Sietsma, R. Boom, Y. Yang, *Steel Res. Int.* **2020**, *91*, 1900441.
[14] W. Ma, H. Li, Y. Cui, B. Chen, G. Liu, J. Ji, *ISIJ Int.* **2017**, *57*, 214.
[15] A. Ender, H. Van Den Boom, H. Kwast, H.-U. Lindenberg, *Steel Res. Int.* **2005**, *76*, 562.
[16] U. B. Pal, B. V. Patil, *Ironmaking Steelmaking* **1986**, *13*, 294.
[17] P. K. Iwamasa, R. J. Fruehan, *Metall. Mater. Trans. B* **1997**, *28*, 47.
[18] P. J. Koros, in *The Making, Shaping and Treating of Steel* (Eds: R. J. Fruehan), AISE Steel Foundation, Pittsburgh, USA **1998**, Ch. 7.
[19] R. Samanta, A. Ganguly, A. Kumar, S. Pathak, in *Proc. of the 6th Int. Congress on the Science and Technology of Steelmaking*, Beijing, Chn **2015**, p. 67.
[20] R. W. Young, Use of optical basicity concept for determining phosphorus and sulphur slag–metal partitions, EUR 13176 EN, Publications Office of the European Union, Luxembourg **1991**.
[21] P. J. Guichelaar, P. K. Trojan, T. McCluhan, R. A. Flinn, *Metall. Mater. Trans. B* **1971**, *2*, 3305.
[22] G. A. Irons, in *Int. Magnesium Association Meeting*, Prague, CZ **1999**.
[23] N. A. Voronova, *Desulfurization of Hot Metal by Magnesium*, The International Magnesium Association, Dayton, USA **1983**.
[24] G. A. Irons, R. I. L. Guthrie, *Metall. Trans. B* **1981**, *12*, 755.
[25] E. T. Turkdogan, *Fundamentals of Steelmaking*, The Institute of Materials, London, UK **1996**.
[26] F. N. H. Schrama, E. M. Beunder, S. K. Panda, H.-J. Visser, E. Moosavi-Khoonsari, J. Sietsma, R. Boom, Y. Yang, *Ironmaking Steelmaking* **2021**, *48*, 1.
[27] F. N. H. Schrama, E. M. Beunder, S. K. Panda, H.-J. Visser, E. Moosavi-Khoonsari, A. Hunt, J. Sietsma, R. Boom, Y. Yang, *Ironmaking Steelmaking* **2021**, *48*, 14.
[28] M. Magnelöv, PhD thesis, Luleå University of Technology, **2014**.
[29] J. Yang, M. Kuwabara, T. Teshigawara, M. Sano, *ISIJ Int.* **2005**, *45*, 1607.
[30] CRCT, GTT, FactSage 7.3, www.factsage.com (accessed: June 2021).
[31] Y. Yang, K. Raipala, L. Holappa, in *Treatise On Process Metallurgy* (Eds: S. Seetharaman), Vol. *3*, Elsevier, Oxford, UK **2014**, Ch. 1.1.
[32] K. Fawagreh, M. M. Gaber, E. Elyan, *Syst. Sci. Control Eng.* **2014**, *2*, 602.
[33] A. Emami, F. N. H. Schrama, J. W. K. van Boggelen (Tata Steel Europe), WO2020/239554A1, **2020**.
[34] S. Street, R. P. Stone, P. J. Koros, *Iron Steel Technol.* **2005**, *2*, 65.