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DESULPHURISATION OF HISARNA HOT METAL – A COMPARISON STUDY BASED ON PLANT DATA

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Abstract: HIsarna is a smelting reduction ironmaking process that is currently in the pilot plant development phase. HIsarna produces hot metal with higher sulphur, lower phosphorus and manganese, almost no silicon and titanium and a lower temperature compared to the blast furnace. Because of that, desulphurisation of the HIsarna hot metal is one of the challenges to ensure its use for steelmaking. Plant data from different Tata Steel plants in Europe and India was used to study the effect of carbon, silicon, phosphorus, manganese, titanium, chromium and temperature on hot metal desulphurisation by magnesium lime co-injection. The analysis of the plant data implies that the composition of HIsarna hot metal will be in favour of sulphur removal. Furthermore significant correlations were found between carbon, silicon and desulphurisation efficiency, that needs further research.

Keywords: HIsarna, hot metal desulphurisation, magnesium consumption, hot metal composition

1 Introduction

At the site of Tata Steel in IJmuiden (the Netherlands), a novel iron production process, called HIsarna, is developed in close cooperation with ULCOS (a European Union programme) and Rio Tinto. HIsarna aims for a reduction of at least 20% in CO_2 emissions for steel production, through improving the energy efficiency of iron making by replacing several processes (coke oven, sinter plant, pellet plant and blast furnace (BF)) with a single process. The process is designed to enable efficient CO_2 capture and storage, which will reduce emissions by 80% [1].

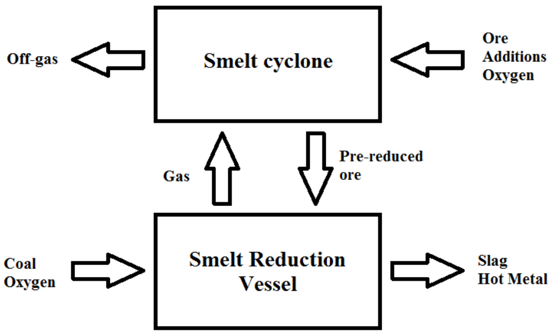

Figure 1: HIsarna process scheme.

Figure 1 shows a schematic overview of the HIsarna process, which consists of two parts. The pre-reduced (10-20 % reduction) and molten ore from the Smelt Cyclone will dissolve entirely into the slag, which leads to a high metal-slag interface in the emulsion. The turbulence created by the formation of CO gas further increases the metal-slag contact, which leads to a higher FeO content (~6%) in the emulsion than in BF slag.

In the Smelting Reduction Vessel (SRV) the pre-reduced ore is further reduced by the injected coal. O_2 is injected to partly oxidise the carbon to form CO. The temperature in the SRV (1400-1450 °C) is lower than in a BF because the strongly endothermic reduction of FeO takes place in the SRV, while part of the exothermic carbon oxidation takes place at the top. This also means that the hot metal (HM) is tapped at a lower temperature. The HM is tapped separately from the slag, resulting in no HM-slag reactions after tapping [1], [2].

Table 1: Typical HM compositions for BF and HIsarna.

Element	BF range [%]*	HIsarna range [%]**	HIsarna vs BF
C	4.5-5.0	3.7-4.3	lower
S	0.02-0.06	0.1-0.2	higher
Cr	0.009-0.013	0.03-0.10	higher
P	0.06-0.08	0.02-0.06	lower
Mn	0.25-0.4	0.02-0.05	lower
V	0.05-0.07	0.005-0.013	lower
Si	0.3-0.7	0.003-0.013	Close to 0
Ti	0.05-0.11	0-0.002	Close to 0

* typical data from Tata Steel IJmuiden.
** data from HIsarna campaign D, 2014.

Due to the less reducing environment in the SRV, compared to the BF, the HIsarna HM (HsHM) typically contains very little Si, low P and Mn. HsHM also contains slightly less C. On the other hand it contains more S, since HIsarna is not a good desulphuriser compared to the BF due to the higher oxygen potential. Because coal is used instead of coke, the S input is higher per tonne produced HsHM. However, since [S] is still mainly controlled by the input, the use of low sulphur coal can partly make up for the lower desulphurisation capacity of HIsarna. An industrial HIsarna will be able to produce HM with less S than is depicted in Table 1 [1], [3].

2 Theoretical analysis

2.1 Desulphurisation with Mg and CaO

The mechanism of hot metal desulphurisation (HMD) via co-injection of Mg and CaO has been well described in literature [3]–[5]. Dissolved Mg reacts with [S], forming MgS (reaction 1) that precipitates on nucleates (e.g. CaO, Ti(C,N)), leading to larger MgS-containing particles that rise to the slag layer. In the slag the MgS reacts with lime to form the more stable CaS (reaction 2). A small part of the desulphurisation takes place directly between CaO and dissolved S (reaction 3).

$$[Mg] + [S] = MgS(s) \qquad (1)$$

$$MgS(s) + CaO(s) = MgO(s) + CaS(s) \qquad (2)$$

$$CaO(s) + [S] = CaS(s) + [O] \qquad (3)$$

The formation of CaS (via reactions 2 and 3) is controlled by kinetics, in particular the contacts of the reactants. CaO can get blocked by CaS, graphite and $2CaO.SiO_2$. This decreases the desulphurisation efficiency [3], [5], [6].

$$[S] + (O^{2-})_{slag} = (S^{2-})_{slag} + [O] \qquad (4)$$

Equation 4 shows the general desulphurisation reaction between HM and slag. A low oxygen activity ($a_{[O]}$) and a high sulphur activity ($a_{[S]}$) in HM is beneficial for HMD. The $a_{[S]}$ and $a_{[O]}$ in HM are influenced by other elements. The presence of C, Si and P (in decreasing order) all have a positive influence on $a_{[S]}$ (and a negative on $a_{[O]}$). According to thermodynamics, the partial pressure of O_2 at lower temperatures (below 1850 °C) is controlled by [Si] rather than [C] [4]. Mn and Cr (in decreasing order) have a negative influence on $a_{[S]}$ [3], [6], [7].

2.2 Desulphurisation of HIsarna HM

The lower C, Si, P and Ti concentrations and higher Cr concentration in HsHM will lead to a higher $a_{[O]}$, which has a negative effect on HMD [6]. The lower Mn in HsHM should have a slight positive effect on HMD. However, since Mn reacts with S, it also contributes to HMD. Furthermore the absence of Ti and Si and the lower [C] leads to less nucleation sites for MgS, which hampers the HMD.

On the other hand the lower C and Si concentrations in HsHM will decrease the graphite and silicate layers around CaO, which enhances reactions 2 and 3. Furthermore, Visser [5] found that in the HM just underneath the slag the temperature is lower, which leads to a local oversaturation of C. This C precipitates as graphite flakes that prevent the MgS to reach the CaO for reaction (2). A higher [C] would enhance this effect and thus decrease the HMD efficiency.

The lower temperature of HsHM will lead to an increased desulphurisation efficiency with Mg, since lower temperatures have a positive effect on the thermodynamics of reactions 1 and 2 [3].

2.3 Desulphurisation efficiency

To compare the HMD efficiency for different produced heats in one plant, the specific magnesium consumption ($\dot{m}_{Mg}$) is used:

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

M_{Mg} and $M_{\Delta S}$ are the total mass of injected magnesium and removed sulphur, respectively. Using $\dot{m}_{Mg}$ to measure efficiency neglects the influence of lime. However, since most steel plants use a fixed ratio between Mg and CaO and the influence of Mg is much larger than of CaO, $\dot{m}_{Mg}$ gives a good indication of the HMD efficiency. Due to differences in reagent purity and Mg:CaO ratios, equation 5 cannot be directly used for comparison between different plants.

3 Plant data

For this study a set of 9484 heats with [S]>500 ppm, produced at Tata Steel IJmuiden between 2014 and 2016 was used. As a reference a set of 584 heats from LD1, produced in 2016 at Tata Steel Jamshedpur and a set of 228 heats with [S]>700 ppm produced in 2016 at Tata Steel Port Talbot were used.

Carbon in HM is not directly measured in the steel plants, but calculated via an equation. For this paper the equation of Neumann is used [8]:

$$[C] = 1.3 + 0.00257T - 0.31[Si] - 0.33[P] + 0.27[Mn] - 0.4[S] \qquad (6)$$

Where T is the temperature in °C and the concentrations of the elements are in wt%.

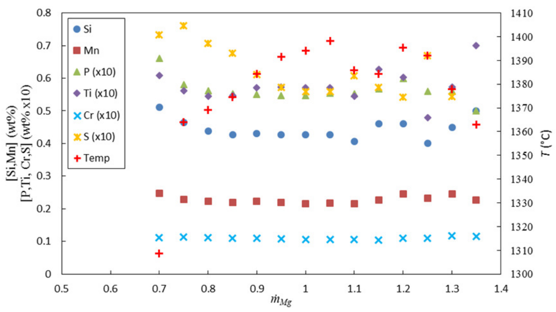

Figure 2: Average HM composition (P, Ti, Cr and S x10) and T per $\dot{m}_{Mg}$ group for the IJmuiden heats.

Figure 2 shows the change in HM composition for different $\dot{m}_{Mg}$. It shows the strong correlation between [Si] and [Ti]. Also efficiently desulphurised HM contained on average more Mn and P. This can be contributed to the temperature effect. Lower temperatures increase HMD efficiency, which is also supported by the data. However, at higher $\dot{m}_{Mg}$ values the average temperature is decreasing again. Since temperature in the BF has a strong effect on the [C] and [Si] [9], the average [C] and $\dot{m}_{Mg}$ are set against the [Si] in Figure 3 (all points contain at least 6 measurements; between 0.25-0.7% [Si] at least 100 measurements).

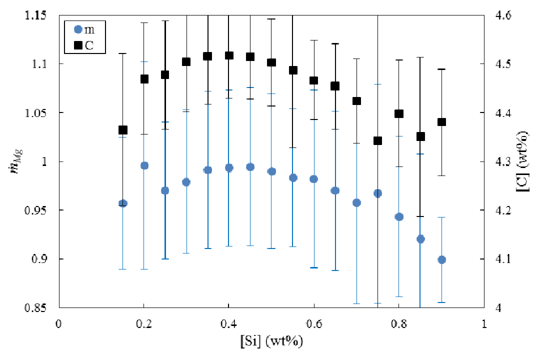

Figure 3: Average $\dot{m}_{Mg}$ and [C] for different [Si]. Error bars indicate standard deviation (σ) of the distribution.

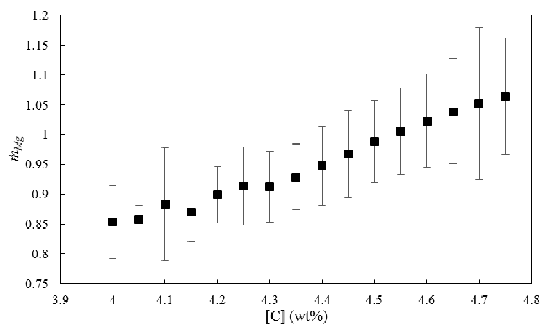

Figure 4: Average $\dot{m}_{Mg}$ for calculated [C]. Error bars indicate σ of distribution.

The data shows that HMD is more efficient for low or high [Si] heats, while for heats with an average [Si], HMD is less efficient. This same 'arc' appears when plotting [C] (calculated via equation 5) versus [Si]. The plant data also shows that there is a linear correlation between [C] and $\dot{m}_{Mg}$ (Figure 4). This correlation is strong and supports the theory of Visser [5].

In the data from Jamshedpur (Figure 5) the same trend can be found, that HMD is more efficient at low and high [Si]. However, the data set is too small and the measurement error too large to draw conclusions from this figure.

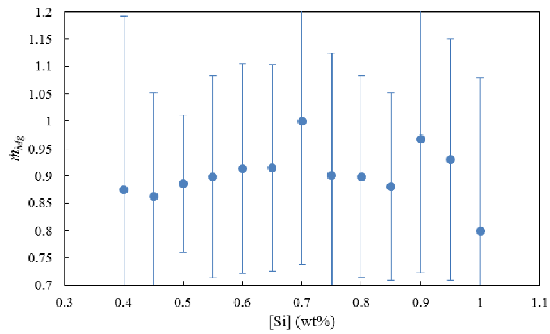

Figure 5: Average $\dot{m}_{Mg}$ vs [Si] in Jamshedpur. Error bars indicate σ of distribution.

The data of Port Talbot does not show the decrease in $\dot{m}_{Mg}$ at high [Si] (Figure 6). The average [C] decreases a little above 0.5% [Si], but the decrease is smaller than σ. [C] is calculated and $\dot{m}_{Mg}$ is derived from in-blow measurement of [S] in the oxygen steelmaking converter.

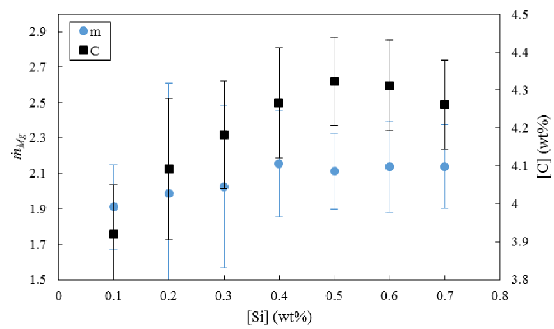

Figure 6: Average $\dot{m}_{Mg}$ and [C] vs [Si] in Port Talbot. Error bars indicate σ of distribution.

4 Discussion

The most remarkable trend in the IJmuiden data is the correlation between [Si] and [C], and $\dot{m}_{Mg}$. At low [Si] and [C], a lower $\dot{m}_{Mg}$ can be explained by the fact that these heats have on average a lower temperature and a higher [S] values. For high [Si] the data shows no influence of temperature or [S], because the [C] and $\dot{m}_{Mg}$ follow the same trend when plotted against the [Si]. A possible explanation is that at low [Si], [C] and [Si] are controlled by temperature and [S] (see equation 6), and thus follow the same trend (these correlations are well described in literature). However, at high [Si], Si and C start competing, which leads to a lower [C]. The carbon concentration, together with temperature, is the main controlling factor for HMD efficiency.

For HsHM this would have no influence, since HsHM contains only little Si and is possibly not C saturated. In fact, the low [C] could even mean that the effect of local oversaturation (causing a higher $\dot{m}_{Mg}$) is decreased or even avoided. However, the lower temperature of HsHM would again enhance this effect.

At the same time the effect of $a_{[O]}$ cannot be confirmed by the data. If $a_{[O]}$ would play a major role in HMD, high [Si] and high [C] (so low $a_{[O]}$ in HM) would have a positive effect on HMD efficiency. However, more [C] only has a negative effect on the HMD efficiency, while the seemingly positive effect of high [Si] on HMD seems to be caused by a lower [C] rather than the [Si] itself. This does not mean that $a_{[O]}$ plays no role at all in HMD; it only seems to have less influence than other factors. The small or absent negative effect of $a_{[O]}$ on HMD is beneficial for HIsarna, since the $a_{[O]}$ is expected to be higher in HsHM than HM from the BF. However, if HsHM has a significantly higher $a_{[O]}$, its influence on the process could be higher too.

The low temperature of HsHM itself will also have a positive effect on HMD efficiency with Mg. This efficiency will be further increased by the higher [S] in HsHM.

It should be kept in mind that the used IJmuiden data set contains only heats with a S>500 ppm. This could intensify or hide certain effects on HMD efficiency. Because the data sets of Port Talbot and Jamshedpur were smaller than the IJmuiden data set, their trends had a larger statistical error. These data sets were therefore only used to see if they did not contradict the IJmuiden data set.

5 Conclusion

Plant data from three steel plants was analysed to study the effect of HM composition and temperature on HMD efficiency for Mg-CaO co-injection, in order to predict the consequences for desulphurisation of HM from HIsarna. Lower [C] and almost absent [Si] are very likely to have a positive effect on HMD efficiency. The effect on HMD by the independent elements Mn, P, Ti and Cr could not be found. The fact that the influence of oxygen activity could not be found for HMD, suggests that its effect will be modest as well for HsHM desulphurisation. The lower temperature of HsHM is also beneficial for HMD with Mg. The higher [S] in HsHM will lead to a better HMD efficiency, although the total amount of Mg required to reach the same final [S] will increase.

Apart from that, the effect [C] and [Si] on the specific consumption of Mg at higher [Si] should be further investigated. Also the effect of Mg solubility needs to be investigated.

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