



## DEGREE OF PREREDUCTION WITHOUT COKE CONSUMPTION IN INDUSTRIAL FURNACES

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### ABSTRACT

*In the HC FeMn production, better utilisation of coke and electric power is vital for reducing the production costs. The higher manganese oxides in the charge are reduced to MnO in the prereluction zone, where also the Boudouard reaction is active. These gas-solid reactions are to a large extent decisive for the total consumption of both coke and electrical power in ferromanganese production. In the present work formulas for calculating the Degree of prereluction have been developed for industrial practice. It shows that the typical Degree of prereluction is between 10-40%, but it may in good periods be as high as 60%. Statistical analysis has been done in order to find how various operational parameters influence the Degree of prereluction. A few parameters were observed to have an effect on the prereluction. Comilog ore definitely had a positive influence on the prereluction, Comilog sinter and Mamatwan ore probably had a positive influence on the prereluction, all in relation to the average prereluction in the selected periods. Meanwhile, Asman ore definitely, % H<sub>2</sub>O in raw materials and increasing H<sub>d</sub> probably, had a negative influence on the prereluction. The findings for these raw materials were very much in coherence with the results of laboratory scale experiments performed, where the CO-reactivity of different ore materials was studied.*

### 1. INTRODUCTION

In the HC-FeMn production better utilisation of coke and electric power is vital for reducing the production costs. The higher manganese oxides in the charge are reduced to MnO in the prereluction zone, where also the Boudouard reaction is active. These gas-solid reactions are to a large extent decisive for the total consumption of both coke and electrical power in ferromanganese production. In particular the reduction of Mn<sub>3</sub>O<sub>4</sub> to MnO may take place by one of two reaction paths. It may be reduced either by CO<sub>(g)</sub> or be reduced directly by solid C<sub>(s)</sub>. The extent of the gas reduction of the higher manganese oxides is reflected in the CO<sub>2</sub>/(CO<sub>2</sub>+CO)-ratio of the off gases. A high degree of gas reduction (prereluction), resulting in a lower coke and power consumption, is coherent with a high gas-ratio.

It is however not the individual reactivities that are important, but the difference between the ore and coke reactivity. One way of ranking the relative reactivity of ore and coke, is to define the "Degree of prereluction". When all Mn<sub>3</sub>O<sub>4</sub> is reduced at lower temperatures before the Boudouard reaction is activated, the "Degree of prereluction" is defined to be '100%'. If all CO<sub>2</sub> from the reduction of Mn<sub>3</sub>O<sub>4</sub> is consumed in the Boudouard reaction, the "Degree of prereluction" is said to be zero. Hence, the "Degree of prereluction" is the degree of prereluction without carbon consumption.

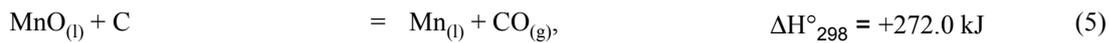
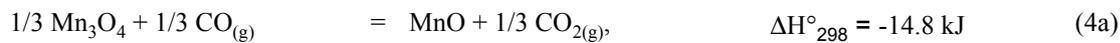
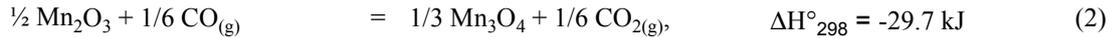
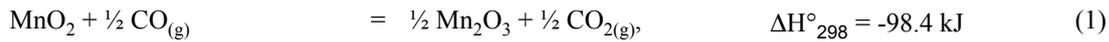
The purpose of this present work has been to investigate the variation in prereluction industrially, to find what influences the prereluction. Hence formulas for calculating the degree of prereluction have been developed, and a statistical analysis investigating what parameters influence the defined prereluction has been carried out.

In addition a series of laboratory scale experiments using a thermobalance apparatus have been carried out. The reduction rate of the raw materials was studied using particles (10-15 mm) in a gas flow of 4 Nl/min, 70%

CO + 30% CO<sub>2</sub>. Then the reactivity of the raw materials found in these experiments could be compared to their relative influence on the degree of prereduction in the industrial furnaces found in the above mentioned statistical analysis.

## 2. THEORY

In the prereduction zone the higher manganese oxides in the charge are reduced to MnO. The reaction path is presented below:



The first three reactions are exothermic, and produce energy, whilst reactions (4) and (5) are endothermic and energy consuming. Thus, high oxygen ores are preferable as the first three reactions are lowering the energy consumption of the process. However, the reduction of Mn<sub>3</sub>O<sub>4</sub> to MnO may take place by one of two reaction paths. First, it may be reduced by CO<sub>(g)</sub> in an exothermic reaction (reaction 3). Second, this reaction may take place in conjunction with the very endothermic Boudouard reaction (4b). The overall reaction becomes Mn<sub>3</sub>O<sub>4(s)</sub> + C<sub>(s)</sub> = 3MnO<sub>(s)</sub> + CO<sub>(g)</sub>, and is endothermic. This reaction will lead to a higher power- as well as coke- consumption. It is thus evident why it is of major importance that the higher manganese oxides are fully reduced to MnO before the ore has reached a temperature in the furnace where the Boudouard reaction becomes of significance.

The use of manganese ores of high reactivity, such as Comilog or BHP, may decrease the consumption of both carbon and power<sup>1,2</sup>. In addition, the power consumption will decrease due to Comilog and BHP ore being high oxygen ores, resulting in high level of exothermic gas reduction, reactions 1-3 above. The extent of the gas reduction of the higher manganese oxides is reflected in the CO<sub>2</sub>/(CO<sub>2</sub>+CO)-ratio of the off gases for closed furnaces, as is evident from the reactions given above. A high degree of gas reduction, which is high degree of prereduction, results in a lower coke and power consumption, and is coherent with a high gas-ratio. The two factors determining the CO<sub>2</sub>/(CO<sub>2</sub>+CO)-ratio are the above mentioned degree of gas reduction (pre-reduction) and the oxygen content of the charge. The relationship between the gas-ratio and the coke and energy consumption in the production process is displayed in figure 1. Since the CO<sub>2</sub>/(CO<sub>2</sub>+CO)-ratio is dependent on the charge mix, especially the total oxygen level, these curves may only be valid for one specific charge composition. However the general trends of the curves will be the same for different charges.

These above mentioned reactions may be the major cause for the actual consumption of coke to be above the stoichiometric minimum. In the production of HC FeMn the stoichiometric amount of carbon required to reduce the oxides of Mn, Fe and SiO<sub>2</sub> to their metallic components is calculated to about 275 kgC/t HC-FeMn<sup>4</sup>. This is however dependent on the Mn- and the Fe-oxides being totally reduced to MnO and FeO in the prereduction zone, before the Boudouard reaction is of significance. Industrially the consumption of carbon is usually larger, often in the range of 350 kg C/ ton HC FeMn. Previous studies have shown that the Boudouard reaction is significant first at temperatures above 1000°C and with more than 30% CO<sub>2</sub> in the gas-

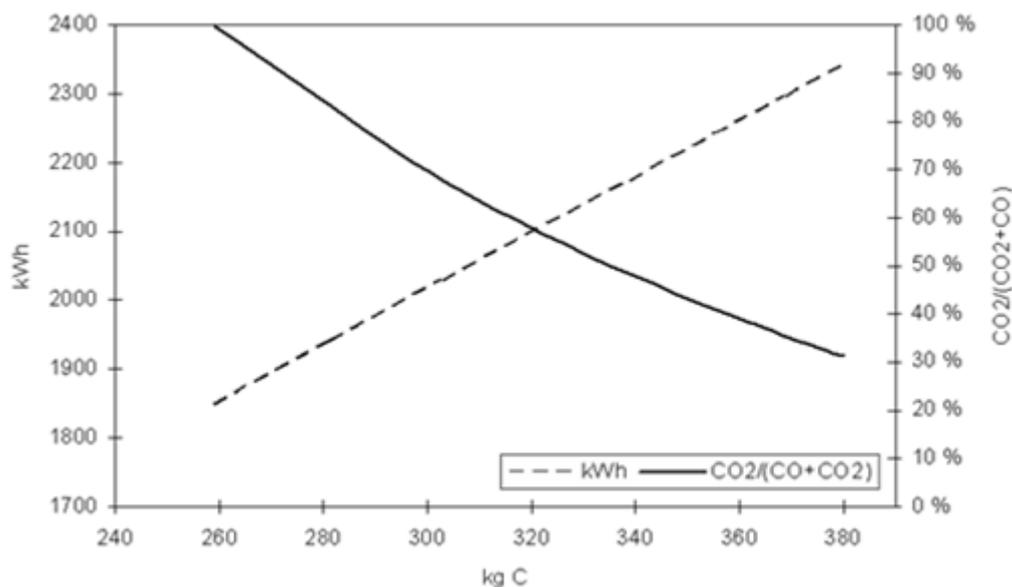


Figure 1: The relationship between the  $CO_2/(CO_2+CO)$ -ratio, the coke consumption and the consumption of electric power for the production of HC FeMn for a given charge<sup>3</sup>

atmosphere<sup>5</sup>. However alkalis have been shown to catalyse the Boudouard reaction and studies have revealed that alkalis accumulate in the furnace. Thus the Boudouard reaction becomes significant at temperatures below 1000°C, probably at temperatures down towards 800°C<sup>6</sup>.

### 3. LABORATORY SCALE EXPERIMENTS – REACTIVITY OF MANGANESE ORES

A series of laboratory scale experiments were performed to measure the CO reactivity of industrial ores. A thermobalance apparatus was used in the measurements as shown in Figure 2. The reduction rate of industrial manganese sources was studied using 10-15mm particles in a gas flow of 4 Nl/min, 70% CO + 30% CO<sub>2</sub>. A crucible with the raw materials placed on a grid inside was placed in the furnace. The crucible was suspended from a balance. The gas was released into the bottom of the crucible. During the experiments the raw materials were gradually heated up to 1100°C in reducing atmosphere. The charge weight and crucible temperature were continuously measured and logged and recorded.

In Figure 3 the results of the laboratory scale experiments are shown. The oxygen level of the ores are presented as  $x$  in  $MnO_x$ , also known as the O/Mn ratio. Hence, in a  $MnO_2$  ore the  $x=2$ , in a  $Mn_2O_3$  ore,  $x=1.5$ , in  $Mn_3O_4$  ore the  $x=1.33$  and in  $MnO$  source,  $x=1$ . The O/Mn ratio for the different raw materials has been calculated from the weight loss curves and analysis of the particles both before and after reduction.  $x$  in  $MnO_x$  has then been plotted against temperature (left axis).

Dolomite contains no manganese oxides, but still gives a weight loss due to decomposition of carbonates. Similarly Mamatwan ore gives a weight loss not only due to the reduction of manganese oxides, but also due to the decomposition of carbonates. Because of this on the right axis the % of total weight loss is plotted for these two types of raw materials (brown and green curves). For Mamatwan ore these curves are in addition to curves that are calculated considering that all of the weight loss in these tests is due to reduction of manganese oxides (red curves, left axis). The starting point of these latter curves should be positioned higher up in the diagram, simply because we know that a considerable part of the weight loss is due to carbonates (about 60 % of the weight loss, and so the curves should be “stretched out”).

In the figure a thick line displays when the temperature inside of the crucible had reached 800°C. This because we believe that in our industrial process the Boudouard reaction may be active from this temperature

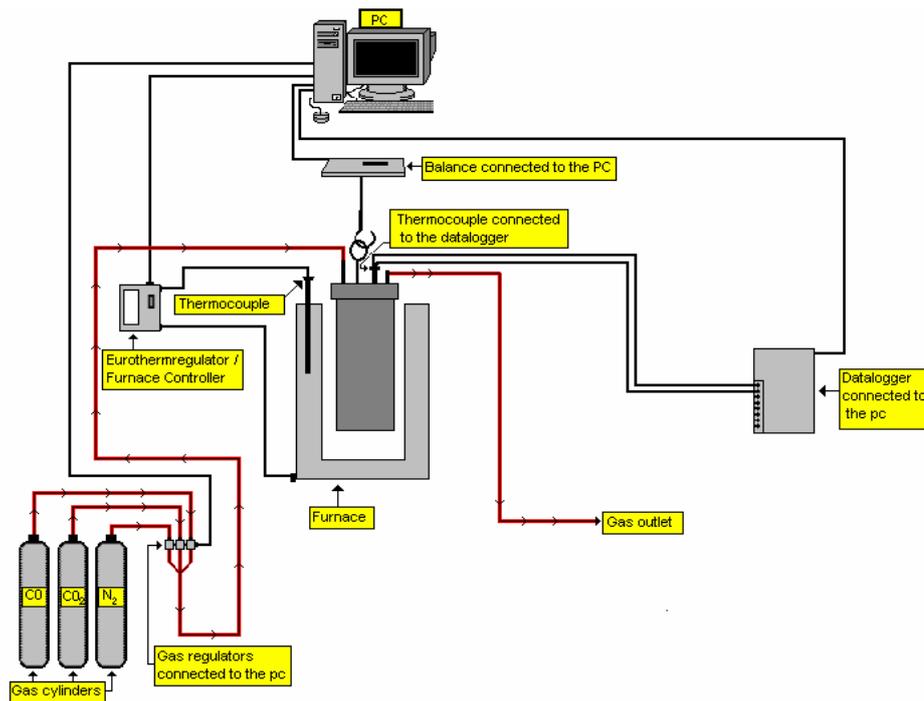


Figure 2: The thermobalance and adjacent equipment

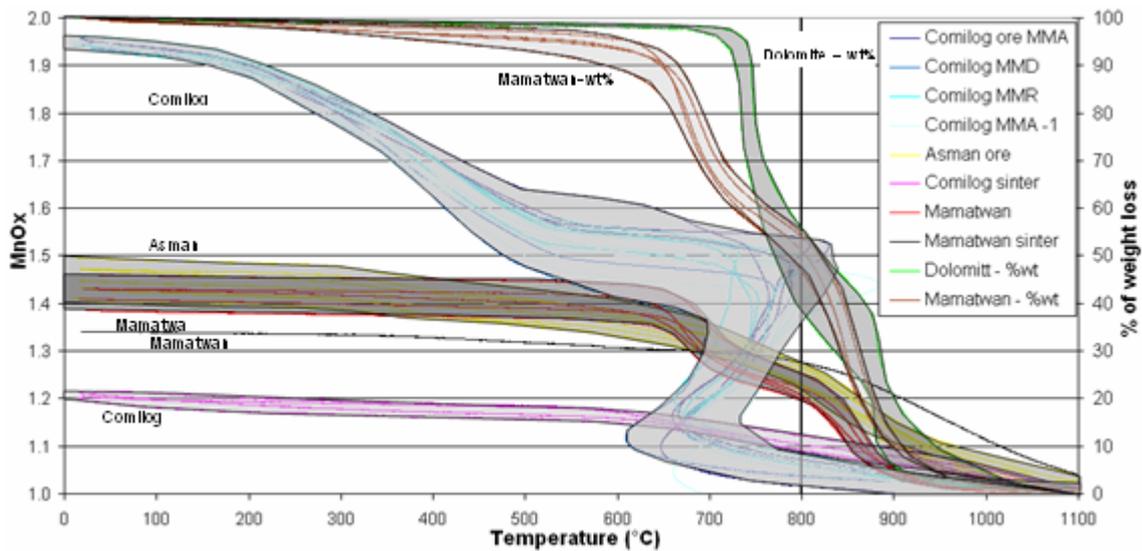


Figure 3: The reduction curves as function of temperature for several manganese sources. The reduction curves of Dolomite and Mamatwan are displayed on the right and given in total weightloss, the rest of the reduction curves are on the left ( $MnO_x$ ) axis

and above. The figure shows that at this temperature Comilog ore has the lowest oxygen level, followed by Comilog sinter, Mamatwan ore, Asman ore and Mamatwan sinter. Consequently Comilog ore should give the lowest amount of Boudouard reaction, and thus the better prereduction, followed by Comilog sinter and so on.

As mentioned above the logged weight loss for Mamatwan ore is not only due to the reduction of manganese oxides, and therefore the starting point of these red curves should be located higher up in the figure. From the

curves for Dolomite it is observed that about half of the weight loss occurs at temperatures above 800°C. This indicates that about half of the carbonates decompose above this temperature, and thus the resultant CO<sub>2</sub> is probably available to take part in the Boudouard reaction. The same might be said for the % of weight loss curves for Mamatwan ore (brown curves), but for this material one can not say if the weight loss above 800°C is due to decomposition of carbonates or reduction of manganese oxides. Either way the weight loss represents CO<sub>2</sub> that is made available for the Boudouard reaction.

#### 4. CALCULATION OF THE DEGREE OF PREREDUCTION

The off gas ratio, CO<sub>2</sub>/(CO<sub>2</sub>+CO)-ratio, will in an industrial furnace be affected by the degree of prereduction, which is the relative variation between the Mn<sub>3</sub>O<sub>4</sub> reactivity in the ore and the CO<sub>2</sub> reactivity of the coke. However, the gas ratio is also affected by the total oxygen content of the charge, and thus the gas ratio alone is not able to tell the degree of prereduction in a process. The degree of prereduction was therefore calculated based on the total mass balance of the furnace.

An example of a total mass balance producing 1 tons of HC FeMn is shown in Figure 4. When the total weights and analyses of the raw materials are known, as well as the metal and slag analyses, the theoretical metal and slag weights can be calculated. The theoretical metal weights may not always be the same as the tapped metal weight, as the furnace is not always emptied 100%. Also there may be some metal in the slag. Hence, in a mass balance of the furnace, the theoretical metal and slag weights is used.

The Degree of prereduction is calculated as the content of CO<sub>2</sub> produced from the reduction of Mn<sub>3</sub>O<sub>4</sub>, not reacting according to the Boudouard reaction. In the example shown in Figure 4, the Degree of prereduction would hence be:

$$\text{Degree of prereduction (only Mn}_3\text{O}_4) = 3.4 / (3.4+2.5) = 58\%$$

However, there are, as previously discussed, also other reactions producing CO<sub>2</sub> above 800°C; decomposition of carbonates and reduction of iron oxides. Hence the Degree of prereduction has been defined as the CO<sub>2</sub> produced from the Mn<sub>3</sub>O<sub>4</sub> reduction plus FeO reduction plus carbonate decomposition which is not reaction with C according to the Boudouard reaction. In the example shown in Figure 4, the degree of prereduction would hence be:

$$\text{Degree of prereduction} = 3.4 / (3.4+3.3+2.5_{(\text{FeO?Fe})}+2.2) = 30\%$$

The extent of the Boudouard reaction, and thus the total carbon consumption, is calculated from the weights and analyses of the raw materials, the analyses of the tapped slag and metal, the theoretical metal and slag weights, as well as the off gas ratio. The off gas ratio must of course be calibrated for any air-combustion on the top of the charge.

#### 6. DEGREE OF PREREDUCTION OF INDUSTRIAL FURNACES

The Degree of reduction was calculated for 3 furnaces over a period of 6 years, from 1998 to 2004. The Degree of prereduction is typically between 10 to 40%, however, in very good periods the Degree of prereduction is as high as 50 to 60%. Over this extensive period of time the Degree of prereduction is not below 0% which verifies that the CO<sub>2</sub> produced from the Mn<sub>2</sub>O<sub>3</sub> reduction, will never react with solid carbon industrially. The figure shows that the prereduction varies significantly both with time and for the different furnaces. These variations are believed to be both due to varying operational conditions as well as parameters such as the mix blend, the amount of moisture in the charge, the harmonic diameter and more.

These 3 furnaces have different loads and different furnace diameters. In this 5 year period also the raw materials varied. For instance, the content of Comilog ore in the charge varied from about 0 % to 50 % for all three furnaces. The same was the case for Asman ore for furnace A and B, but for furnace C the Asman content varied between 0-80 %. For furnace A and B the content of Mamatwan ore in the mix varied between 0-25 %, but only between 0-15 % for furnace C. The moisture content of the raw materials varied between 1-6

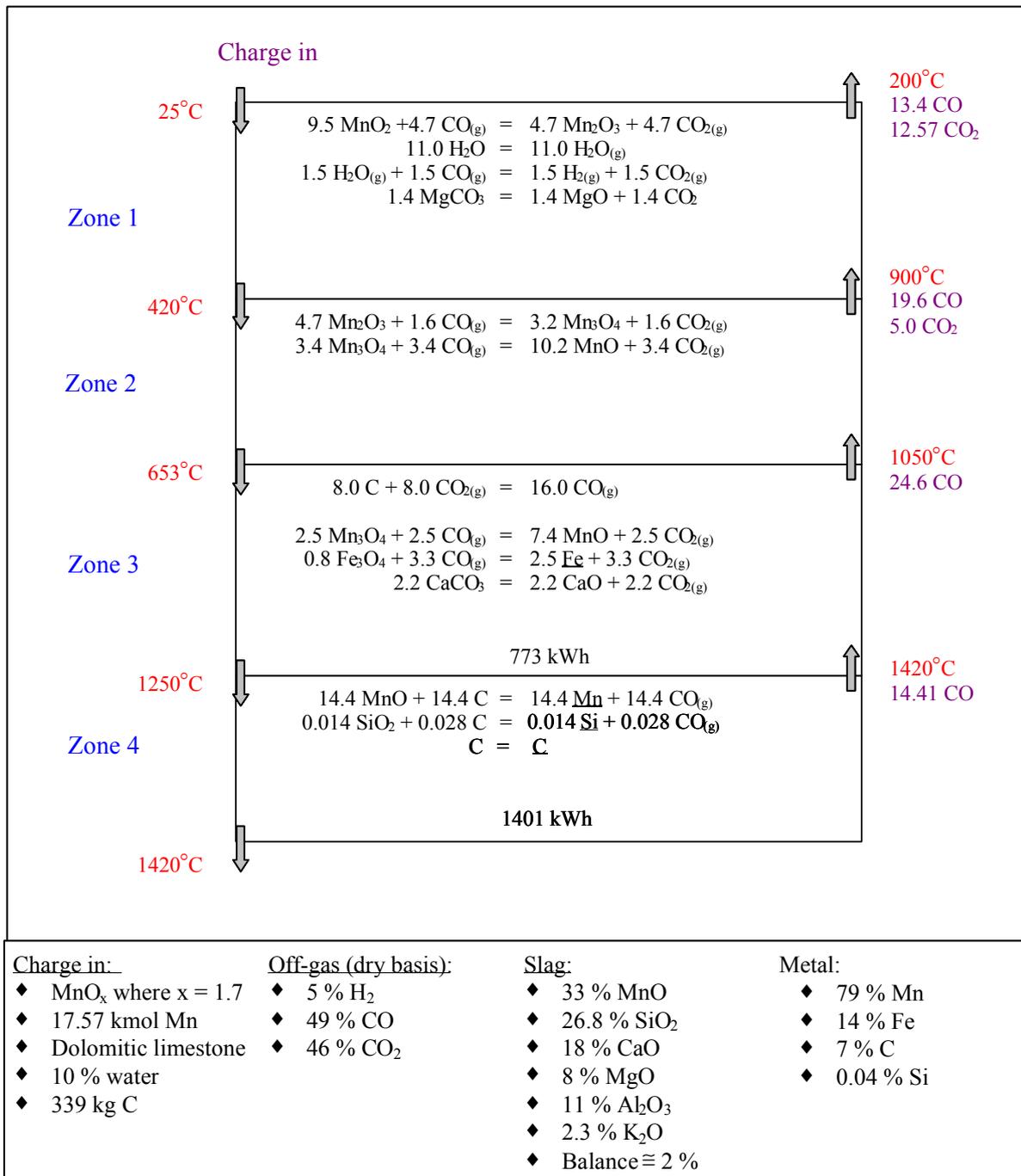


Figure 4: Staged material and energy balance. The calculations are based on the production of 1 ton of HC FeMn and 685 kg of slag. 339 kg of carbon is assumed used, the temperature of the off-gases is assumed to be 200 °C and the slag and metal temperature assumed to be 1420 °C.<sup>3</sup>

% H<sub>2</sub>O for furnace A, 1-8 % for furnace B and 4-8 % for furnace C. The harmonic diameter, H<sub>d</sub> varied between 7-12 mm for furnace A and B, and 8-13 mm for furnace C.

Figure 6 shows the average degree of prereduction for the 3 furnaces. It is observed that furnace A in general seems to have the highest degree of prereduction (29.8% on average). This is also displayed in Figure 5,

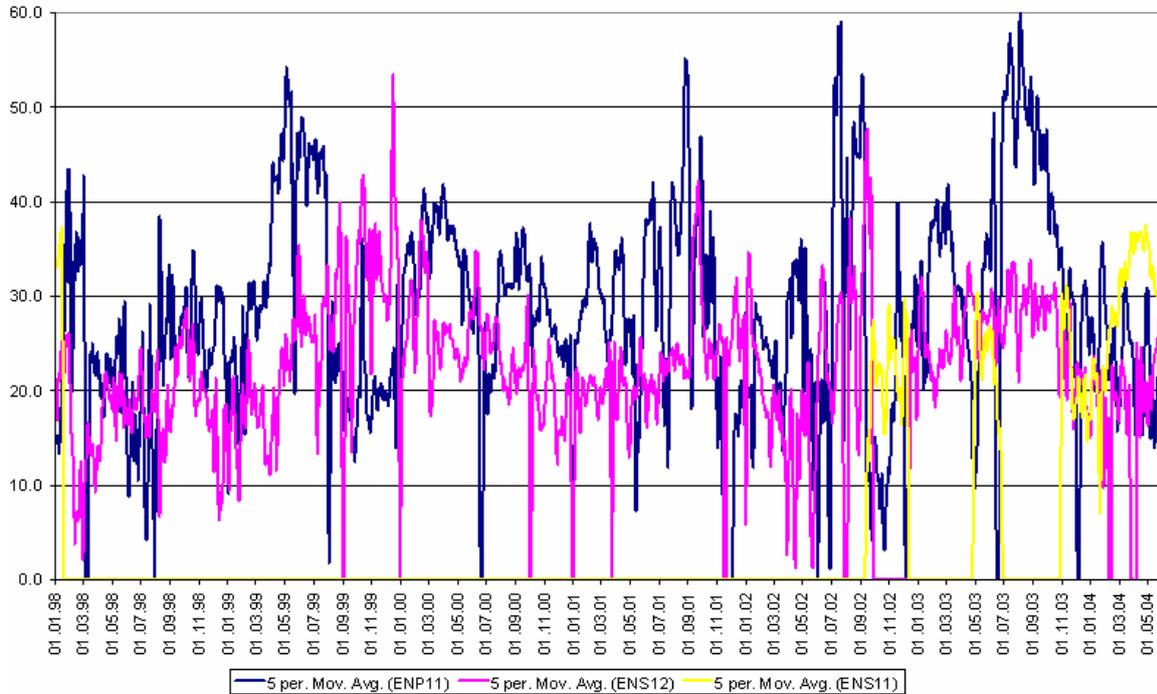


Figure 5: The calculated average Degree of prereduction over 5 days over a 5 year period of 3 industrial furnaces (A,B,C)

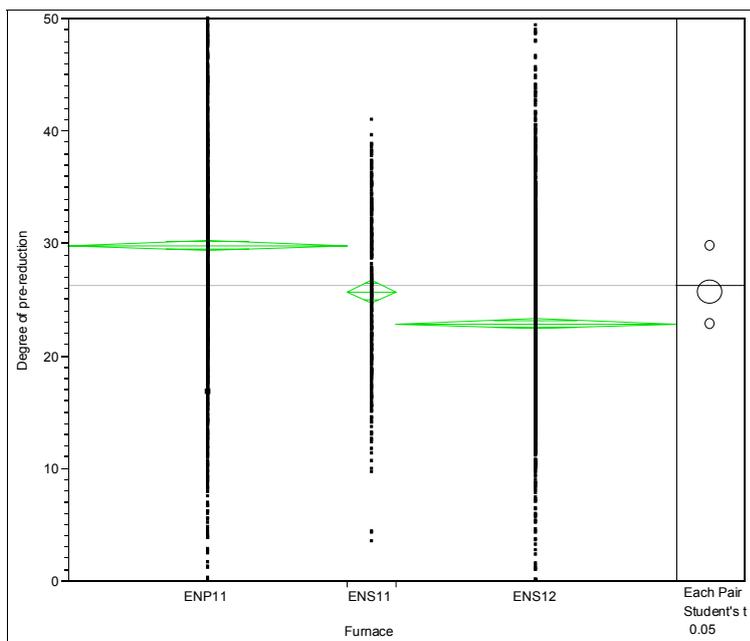


Figure 6: The average Degree of prereduction over 5 years. The height of the squares represents the 95% confidence interval, the width of the squares the amount of data used.

from which it is clear that for the specified time period on average the degree of prereduction is significantly higher for furnace A than for furnace C (25.7%) and furnace B (22.9%).

According to the laboratory test, and previous experience<sup>1,2</sup>, the various raw materials will affect the Degree of prereduction. Also the diameter of the manganese sources should affect the Degree of prereduction as the ores has been found to be reduced topochemically<sup>7</sup>. In addition operational parameters as the water content of raw materials and coke content in the furnace is believed to be of importance. A statistical analysis has been done in order to verify how much these parameters influence the prereduction.

In this statistical analysis the degree of prereduction was modeled for each furnace using the charge mix, the harmonic diameter, off gas temperature, coke balance and other furnace parameters. For furnace A and furnace B two models were made, with and without the harmonic diameter of the raw materials. Therefore 5 models were calculated in total, 1 for furnace C and 2 each for furnace A and B. In Figure 7 the correlation

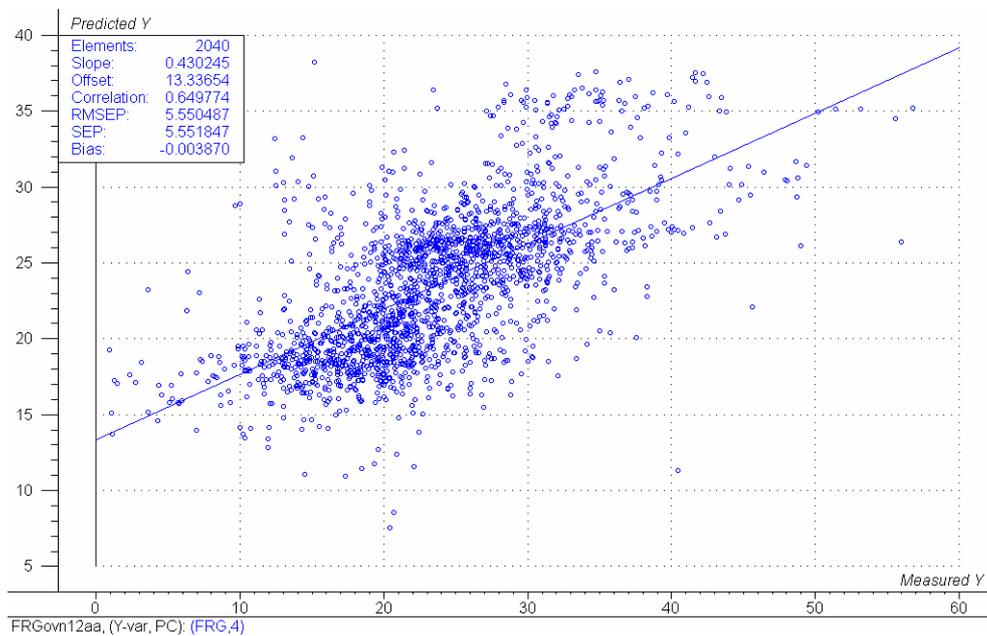


Figure 7: A plot of the correlation between predicted and calculated values for degree of prereduction for furnace B for the whole period

between predicted and calculated values for Degree of prereduction for furnace B for the whole period is plotted. The correlation is 0.65, and in industrial context, quite good.

Figure 8 displays the same modeled values together with the calculated values of Degree of prereduction in the same time period. Long term trends show good correlation, but short term trends do not always correlate that well.

The regression coefficients for this model are given in Figure 9 and show the relative importance of the various parameters. The higher absolute values, give a higher impact on the Degree of prereduction. It shows that in this model Comilog sinter, Gloria ore, Comilog ore and Mamatwan ore has a positive influence on the degree of prereduction, whilst % H<sub>2</sub>O in raw materials, BHP ore, Asman ore, oxygen level given by the x in MnO<sub>x</sub> and positive coke balance has a negative effect on the prereduction. These effects are of course relative to the average degree of prereduction.

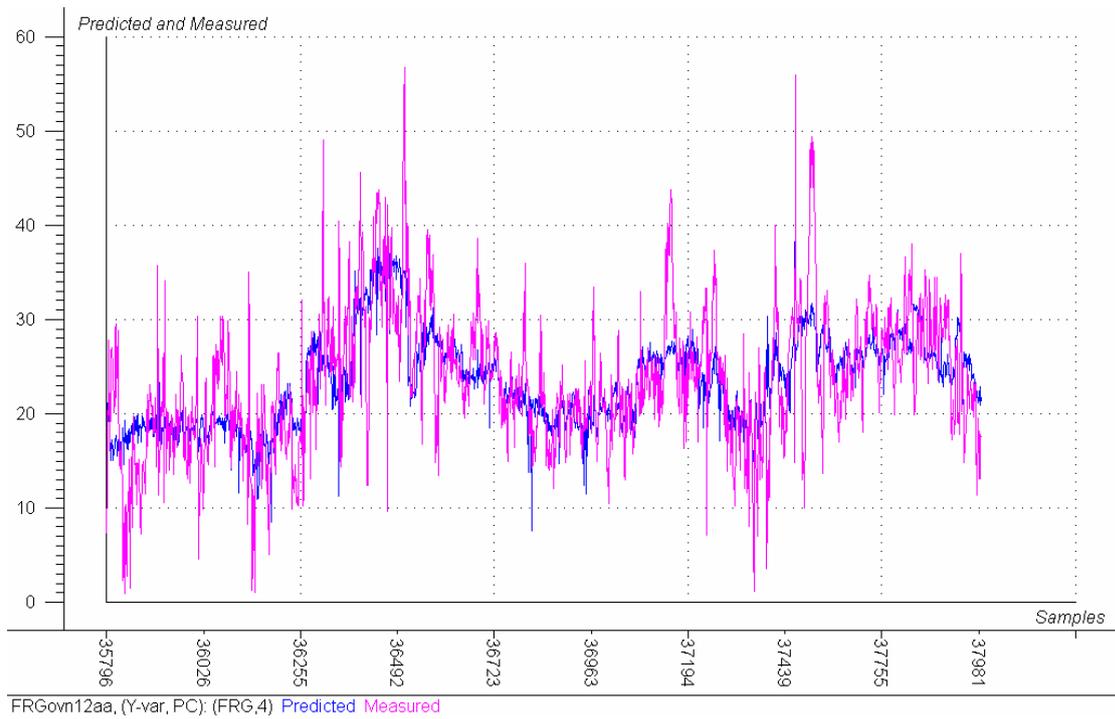


Figure 8: Displays the modeled (predicted, blue) values together with the calculated (ODS, pink) values for degree of prereduction for furnace B for the whole period

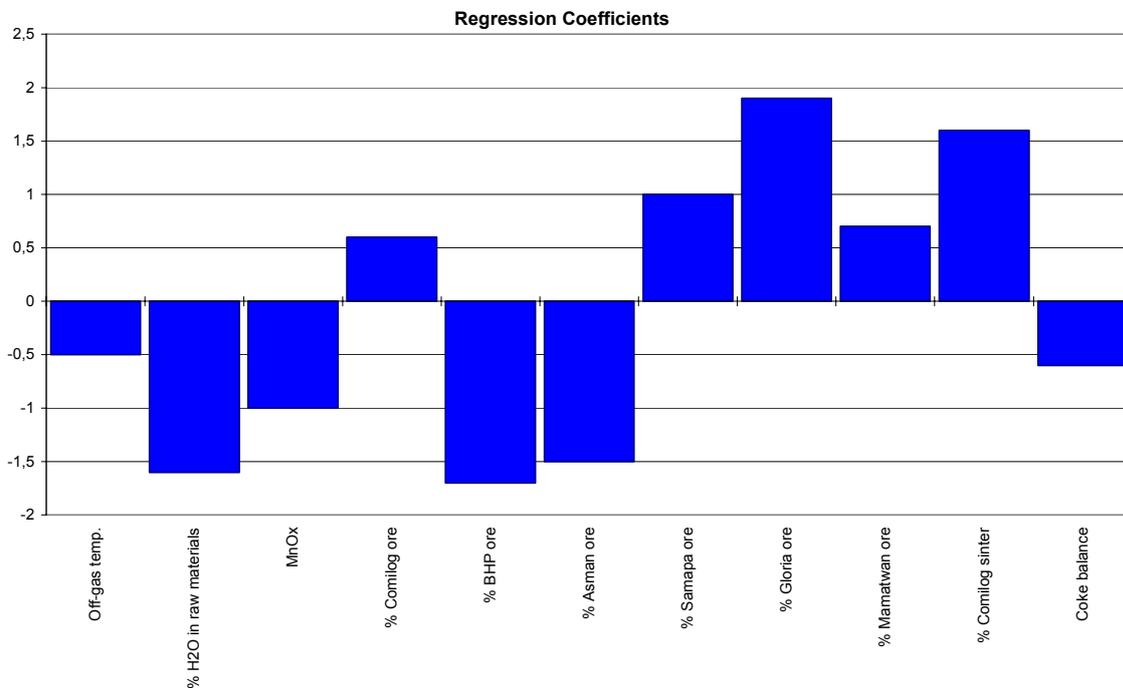


Figure 9: The regression coefficient for the model for furnace B for the whole period

## 6. DISCUSSION

In table 1 below the relative influence of the various parameters on the average degree of prereduction for the models is summarized. Addition sign (+) and subtraction sign (-) shows if the parameters show a significant positive correlation or negative correlation. When the signs are in parenthesis, the effect is not significant and question mark (?) means that it is uncertain if the effect is significant.

From the table we can read that Comilog ore definitely had a positive influence on the prereduction, Comilog sinter and Mamatwan ore probably had a positive influence on the prereduction and Asman ore definitely had a negative influence on the prereduction. This is very much in coherence with the laboratory scale experiments displayed in Figure 3, predicting that Comilog ore would give the best prereduction, followed by Comilog sinter, Mamatwan ore and Asman ore. The model made for furnace A including  $H_d$  is the only model (out of 5) that gives a negative relationship between Mamatwan ore and the degree of prereduction. And the model made for furnace B including  $H_d$  is the only model (out of 5) that gives a negative relationship between Comilog sinter and the prereduction (very small negative influence). Keep in mind that in Figure 3 the starting point for Mamatwan ore should be higher, and it probably has a higher  $MnO_x$ -level than Asman ore at  $800^\circ C$ . Also the %  $H_2O$  in the raw materials and increasing  $H_d$  was found to probably be a negative influence on the Degree of prereduction.

From the Table we see that %  $H_2O$  in the raw materials exerts a negative influence on the prereduction for all models but one. For furnace A, for the whole period, %  $H_2O$  in the raw materials actually had a positive effect. The latter may be explained by Comilog ore being a very porous ore, thus containing a lot of moisture, so that a high percentage of Comilog ore is coherent with a high %  $H_2O$  in the raw materials. And since Comilog ore definitely had a strong positive effect on the prereduction, you get a high degree of prereduction at times when also the content of moisture was high. Thus for this model moisture seemingly had a positive effect on the prereduction. However for the four other models the effect of moisture on the prereduction is found to definitely be negative.

**Table 1: The relative influence of the various parameters on the average degree of prereduction for the models are summarized**

Furnace/ Parameter	C	A (whole periode / period with $H_d$ )	B (whole periode / period with $H_d$ )	Concluded effect
Off-gas temperature	+	- / (-)	- / + ?	Undecided
% $H_2O$ in raw materials	-	+/-	- / -	Undecided, probably -
MnOx	(+)	(-) / -	- / - ?	Undecided, could be -
% Comilog ore	+	+ / +	+ / +	Definitely +
% Asman ore	-	- / -	- / -	Definitely -
% Mamatwan ore	+ ?	+ / -	+ / + ?	Probably +
% Comilog sinter	+	+ / +	+ / (-)	Probably +
Coke balance	(+)	- / + ?	- ? / (-)	???
Harmonic diameter	-	i.r. / (-)	i.r. / -	Most probably -

**Table 2: The relative influence of some parameters on the degree of prereduction for the models made including Hd are summarized**

Parameter	Effect on prereduction / Frnc. A	Effect on prereduction / Frnc. C	Effect on prereduction / Frnc B
$\Delta=1\%$ H <sub>2</sub> O	- 4.73 %	- 1.28 %	- 0.57 %
$\Delta=1\%$ Comilog ore	0.23 %	0.17 %	0.13 %
$\Delta=1\%$ Asman ore	- 0.26 %	- 0.13 %	- 0.18 %
$\Delta=1\%$ Mamatwan ore	- 0.89 %	0.21 %	0.23 %
$\Delta=1\%$ Comilog sinter	0.48 %	0.23 %	- 0.002 %
Harmonic diameter ( $\Delta=1$ mm)	- 0.78 %	- 0.80 %	- 0.97 %

In table 2 the influence on the Degree of prereduction of the parameters found to be most important to the prereduction is given. These parameters are found using the models including the harmonic diameter ( $H_d$ ). This is done to get an idea of the order of magnitude of the influence of these parameters on the prereduction, for instance in case of a change in the mix-order. The effect of increasing the content of Comilog ore, Asman ore, Mamatwan ore or Comilog sinter by 1 % is tabulated. So is the effect of a 1 % increase in moisture content and 1 mm increase in the harmonic diameter. Of course several assumptions are made in these calculations, for instance a linear relationship between all assessed parameters and the prereduction. Also the values of the parameters used in the modeling work are not the same for the three furnaces. So there is a lot of uncertainty associated with these figures.

It is of course important to keep in mind that the modeling done in this present work, and the results of these calculations, is valid only for operational parameters within the boundaries of the parameters in the dataset used for the statistical analysis. However the models are calculated using fairly ordinary operational data. To test the reliability of the models in Figure 10 and Figure 11 the modeled degree of prereduction is plotted together with the calculated values for prereduction. This was done for the first seven months of 2004, using data that had not been included in the statistical analysis done when developing the models. In these graphs the models made for furnace A and B using data including harmonic diameter are used.

From Figure 10 we see that the correspondence between the modeled values and the calculated values is quite good for furnace A, at least the first part. The model seems fairly reliable. The reason for the lack of agreement in the latter part of the graph is not known. However the peaks that clearly stands out in this period all coincide with very high Comilog sinter content in the mix. For furnace B however, we observe from Figure 11 that the agreement between the predicted prereduction and the actual prereduction is rather poor. This might of course be a strong indication of the model not being reliable. It should however be noted that the operation and operational strategy of furnace B was very variable in this period, and different from what was the common practice in the period that the data used for making the model are from.

In regards to the laboratory scale experiments it is also important to remember that in addition to contributing to increased power and coke consumption through the Boudouard reaction, the carbonates of Mamatwan ore and Dolomite also require a lot of energy for the actual decomposition. In the Mamatwan sinter, the carbonates have already been decomposed. So even though Figure 9 indicates that this raw material gives a low Degree of prereduction, it may consume less energy than both Mamatwan ore and Dolomite. Thus it may be preferable to use this sinter instead of for instance Dolomite in order to get a higher slag basicity.

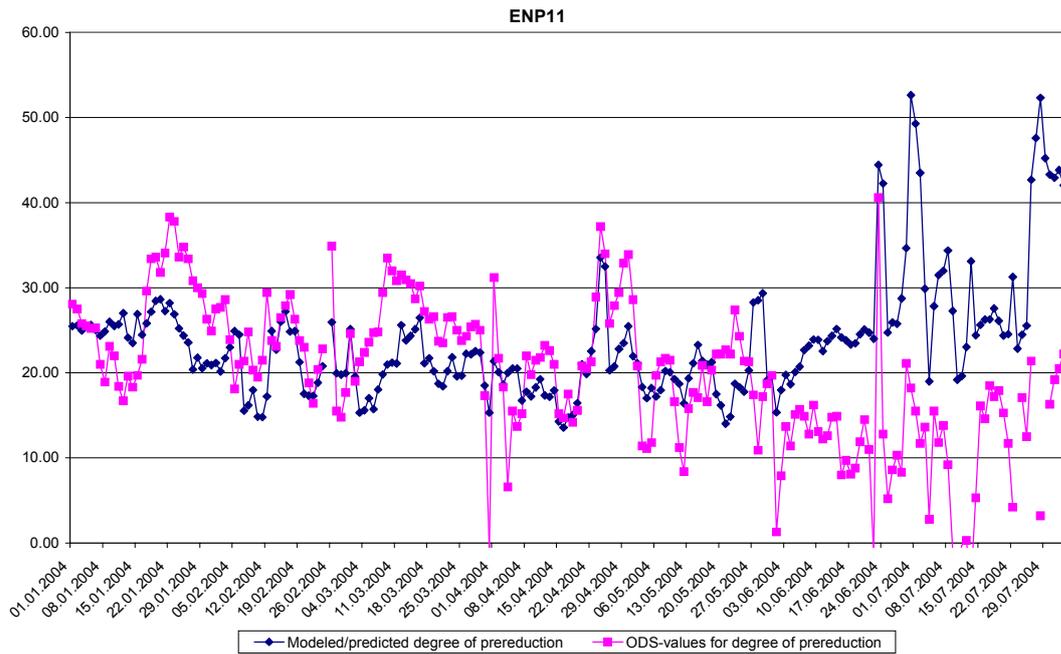


Figure 10: Calculated values for the degree of prereduction plotted together with predicted/modeled values for the prereduction for furnace A (first 7 months of 2004)

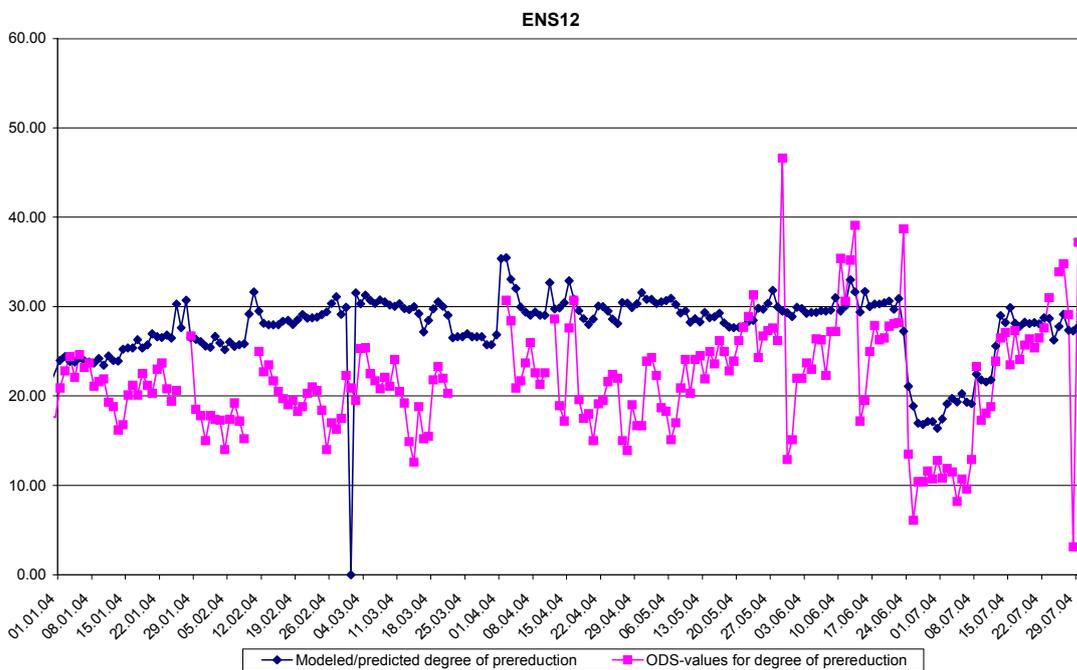


Figure 11: Calculated values for the degree of prereduction plotted together with predicted/modeled values for the prereduction for furnace B (first 7 months of 2004)

## 7. CONCLUSION

In this present work formulas for calculating the degree of prereduction have been developed for industrial practice. It shows that the typical Degree of prereduction is between 10-40%, but may in good periods be as high as 60%. A statistical analysis has been done in order to find how various operational parameters influence the Degree of prereduction. A few parameters were observed to have an effect on the prereduction. Comilog ore definitely had a positive influence on the prereduction, Comilog sinter and Mamatwan ore probably had a positive influence on the prereduction, all in relation to the average prereduction in the selected periods. Meanwhile, Asman ore definitely, % H<sub>2</sub>O in raw materials and increasing H<sub>d</sub> probably had a negative influence on the prereduction. The findings for these raw materials were very much in coherence with the results of laboratory scale experiments performed, where the CO-reactivity of different ore materials was studied.

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