



# **A Study on Selected Hot-Metal and Slag Components for Improved Blast Furnace Control**

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*To My Beloved Father*



## **Abstract**

The main objective of this work was to gain an increased understanding of selected blast furnace phenomena which could be utilized for an improved blast furnace process control. This thesis contributes with both a model study and an experimental study on blast furnace tapping, and results from these findings can be used to enhance the control of the blast furnace.

The work was divided in two parts. The first part dealt with a model study for optimisation of the blast furnace burden calculation. During the second part the frequency of the hot-metal and slag sampling was increased compared to routine sampling throughout the taps of a commercial blast furnace. Thereafter, composition variation and correlation between distribution coefficients were examined.

With an optimisation of the burden calculation the first step towards controlled hot-metal production is taken, since the optimal material mixture for a desired hot-metal composition could easily be found. Due to the fact that the optimisation model uses yield factors, which are easy to calculate from material and hot-metal compositions, these values have to be accurate for a controlled process control of the furnace. The study of hot-metal and slag compositions during tapping concluded that variations exist. The large variations for C, Si, S, Mn and V in hot metal during tapping lead to the conclusion, that one single sampling of hot metal was not enough to get a representative value for the composition. The solution was to use a double-sampling practise, where the hot metal was sampled first after tap start and secondly short after slag start, and subsequently an average composition value was calculated. The following study was on the elemental distribution between hot metal and slag from a thermodynamic point of view. The major conclusion from this study was that the distribution coefficients behaved as expected when looking at the equilibrium reactions. The studied slag-metal distributions were also showing strong, trend-like relationships, which was not affected by the operational status of the blast furnace during the studied sampling period.

The overall conclusion is that with a more reliable composition of hot metal and slag from the taps, the distribution coefficients could be calculated with better precision and hence, the yield factors for the optimisation model would be more accurate. This procedure would probably lead to a more reliable burden optimisation and a therefore better and more stable blast furnace control.



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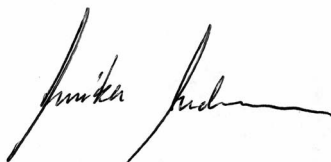
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To colleagues and friends at the Department of Material Science and Engineering: many thanks for making the coffee breaks so vital, the encouragement and the many smiles.

Sincere thanks to Mats Brämning, who made the blast furnace world understandable.

Anders for your love.

Stockholm, October 2003

A handwritten signature in black ink, appearing to read 'Annika Andersson', written in a cursive style.

Annika Andersson



# Supplements

The thesis is based on the following papers:

- Supplement 1:** The Use of an Optimisation Model for the Burden Calculation for the Blast Furnace Process  
**A.J. Andersson**, A.M.T. Andersson and P.G. Jönsson  
ISRN KTH/MSE--03/57--SE+APRMETU/ART  
Accepted for publication in Scandinavian Journal of Metallurgy
- Supplement 2:** Variations in Hot-Metal and Slag Composition During Tapping of the Blast furnace  
**A.J. Andersson**, A.M.T. Andersson and P.G. Jönsson  
ISRN KTH/MSE--03/58--SE+APRMETU/ART  
Submitted to Ironmaking and Steelmaking
- Supplement 3:** A Study of some Elemental Distributions Between Slag and Hot Metal During Tapping of the Blast Furnace  
**A.J. Andersson**, A.M.T. Andersson and P.G. Jönsson  
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Submitted to Steel Research

Parts of this work have been accepted at the following conference:

A Study of Successive Sampling During Tapping of a Full-Scale Production Blast Furnace  
**A.J. Andersson**, A.M.T. Andersson, P.G. Jönsson and B. Sundelin  
*Scanmet II, 2nd International Conference on Process Development in Iron and Steelmaking, 6-9 June 2004, Luleå, Sweden*





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# 1. Introduction

The blast furnace (BF) is a complex non-isothermal counter-current reactor, transforming iron ore to liquid hot metal at high temperatures. In the blast furnace (Figure 1) solid material, such as iron-bearing material, coke and fluxes, are charged at the top of the furnace. Preheated air with increased oxygen content and auxiliary reduction material (pulverized coal or oil) is blown into the lower part of the blast furnace, and liquid hot metal and slag are tapped at the bottom. The combustion of carbon with oxygen provides the hot reduction gases needed for the reduction of iron oxides and the energy required for the melting of oxides and metal to liquid products.

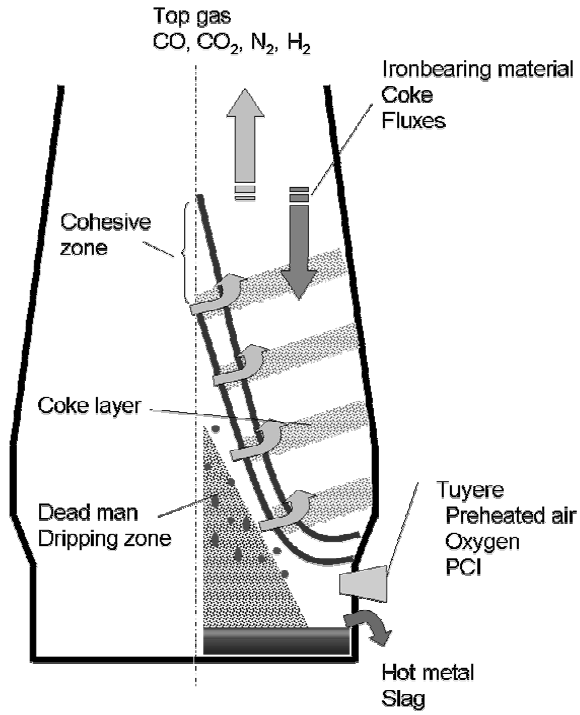


Figure 1 Schematic layout of the blast furnace process.

The reactions in the blast furnace are complicated, since they include several phases as well as occur at various temperatures, compositions and pressures. Iron oxides charged at the top meet the warm gas, heat is exchanged and reduction occurs. Solid carbon and gaseous carbon dioxide reacts through Boudouard's reaction, equation (1), to gaseous CO that is used in the indirect reduction, equation (2), of the oxides. In the upper part of the furnace, CO and also H<sub>2</sub> in the ascending gas have the ability to reduce the iron oxides (magnetite, hematite) to wüstite. In the lower parts of the BF the wüstite is reduced in the so-called direct reduction, equation (3), where solid carbon reduces the oxides.

		$\Delta H_{298}(\text{kJ}/\text{mol})^1$	
Boudouard's reaction	$\text{C} + \text{CO}_2 \leftrightarrow 2 \text{CO}$	172.5	(1)
Indirect reduction	$\text{FeO} + \text{CO} \leftrightarrow \text{Fe(s)} + \text{CO}_2$	-18.6	(2)
Direct reduction	$\text{FeO} + \text{C} \leftrightarrow \text{Fe(s)} + \text{CO}$	153.9	(3)

In the cohesive zone there are permeable coke slits, which allows the reduction gas to ascend through the layers of material. With higher temperature the material starts to soften, and at the cohesive zone the melting starts. The metal droplets and liquid slag drips down via the dead man and are collected in the hearth. The slag with its lower density stay on top of the denser hot metal, so when the furnace tap hole opens, the hot metal will flow out first, and when the level inside the furnace has decreased, the slag will come.

Despite the fact that a large number of advanced instruments have been used for monitoring phenomena and measuring operational data so far, the blast furnace is still considered as a “black box”. The methods of understanding the ongoing process have been laboratory scale experiment and excavation of quenched blast furnaces from which conclusions are drawn and applied to the production process. Since the experimental studies normally are simplified they are often proved not to be quite appropriate for the production blast furnace process.

For the blast furnace process, a simplified material balance, a so-called burden or charge calculation, is commonly used for calculating the amounts of burden materials needed for obtaining a desired quality of hot metal and slag, though the approaches used are quite different for different furnaces. The burden calculations employed for the blast furnaces are generally based on hands-on trial and error calculations<sup>2</sup> rather than optimisation models. The heat balance where the amount of reduction material needed for the reduction and heating is considered, is not within the scope of this thesis and will be left for others to study.

The quality of the product as well as the thermal conditions inside the furnace can only be clearly known, when the actual compositions of the hot metal as well as the slag are reported. In addition, some components, especially silicon, carbon and sulphur contents in hot metal, as well as the temperature of hot metal have been commonly used as main indicators of the thermal state of the furnace.<sup>3,4</sup> Consequently, the ability to take representative metal and slag samples during tapping is an important issue for the operation of the blast furnace, as well as for the control of the quality of the hot metal produced. However, only a few samples of hot metal and slag are normally taken for each tap at most blast furnaces. This is perhaps based on an assumption that the hot metal and the slag in the blast furnace are almost homogenous, or the compositions of the hot metal and slag are considered to be practically the same during the whole tapping.

One of the parameters frequently studied in laboratory experiments is the equilibrium between slag-metal-gas reactions for different elements. Studies have shown that equilibrium seldom is reached between these phases.<sup>4,5,6</sup> Another way of studying equilibrium between slag-metal-gas reactions is to look at actual production data and from them calculate actual distribution coefficients. This approach has been applied in the present thesis.

The overall aim with this work is to provide information which could improve the blast furnace control through a higher understanding of the BF process and model used. This thesis contributes with both a model study and an experimental study on BF tapping, and results from these findings can enhance the control of the BF.

The original intention was to determine if a model for material balance that optimises the burden from hot-metal and slag properties could be used with good agreement for a production blast furnace. The use of yield factors in the model raised the question if variation in hot metal and slag composition during and between taps exist. So the second purpose of this work was to make an investigation of the variations of the compositions of hot metal and slag as well as the temperature of hot metal during tapping in a commercial blast furnace. Therefore, a unique plant study was conducted on a commercial blast furnace during a 68 hour period where slag and hot-metal samples were taken with a 10-minute interval. Furthermore, based on these results, the distribution coefficients of manganese, silicon, sulphur and vanadium have been calculated.

The work was divided in two parts. The first part dealt with a model study for optimisation of the blast furnace burden calculation. During the second part the frequency of the hot-metal and slag sampling was increased compared to routine sampling throughout the taps of a commercial blast furnace. Thereafter, composition variation and correlation between distribution coefficients were examined.

## 2. Theoretical considerations

The outline of the optimisation model for the blast furnace burden calculation is first described, and thereafter the relation between the yield factor and the distribution coefficients used in this study is explained.

### 2.1. Optimisation model for burden calculation

The original model was devised in an Excel spreadsheet and the author analysed and rewrote the material balance equations so it was possible to program the model in JAVA and display it on the Internet.<sup>7</sup> The optimisation model for burden calculation solves the input amounts of materials, based on the known composition of the ingoing materials and the desired composition of the hot metal and slag that are to be produced in the blast furnace. The model always optimises the iron-bearing material, whereas the amounts of fluxes are optimised in order to meet both the desired slag amount and basicity. Basicity is defined according to equation (4).

$$\text{basicity} = \frac{(\text{wt}\%CaO)}{(\text{wt}\%SiO_2)} \quad (4)$$

Optimisation procedures for the tracer elements manganese, vanadium and phosphorus were also implemented in the model. The optimisation can be done if the maximum amount (set as the upper limit) and the minimum amount (set as the lower limit) of the ingoing materials are known. For the reductants (coke, coal and/or oil) specific amounts have to be given; if a heat balance would have been included those amounts could be calculated. When there is loss of material(s), such as dust, that material could be given a negative amount and thereafter used in the calculation.

For the optimisation of iron-bearing material, the iron content in slag and hot metal has to be known, besides the composition of material. The model use yield factors, equation (5), and desired hot metal composition for the optimisation of tracer elements.

$$\eta_i = \frac{i_{HM}^{kg}}{i_{Charged}^{kg}} \quad (5)$$

where  $i_{HM}^{kg}$  is the weight of element  $i$  in hot metal and  $i_{Charged}^{kg}$  is the total charged weight of element  $i$ . A successful optimisation of fluxes requires charging of both acid and basic slag formers.

An outline of the calculation flow for the model can be seen in Figure 2. The model uses an iterative work-order, where the new calculated material amounts are used in the next iteration. The calculated material amounts are checked

against the allowed minimum and maximum amounts before they are used in a new iteration. When the change from one iteration to another is less than  $10^{-3}$  the calculation stops and the result is presented as ingoing material amounts as well as a calculated hot metal and slag composition based on the charged material amounts. The hot metal and slag compositions are calculated with the help of a desired hot metal and slag composition and the yield factors for silicon, manganese, sulphur, vanadium and phosphorus.

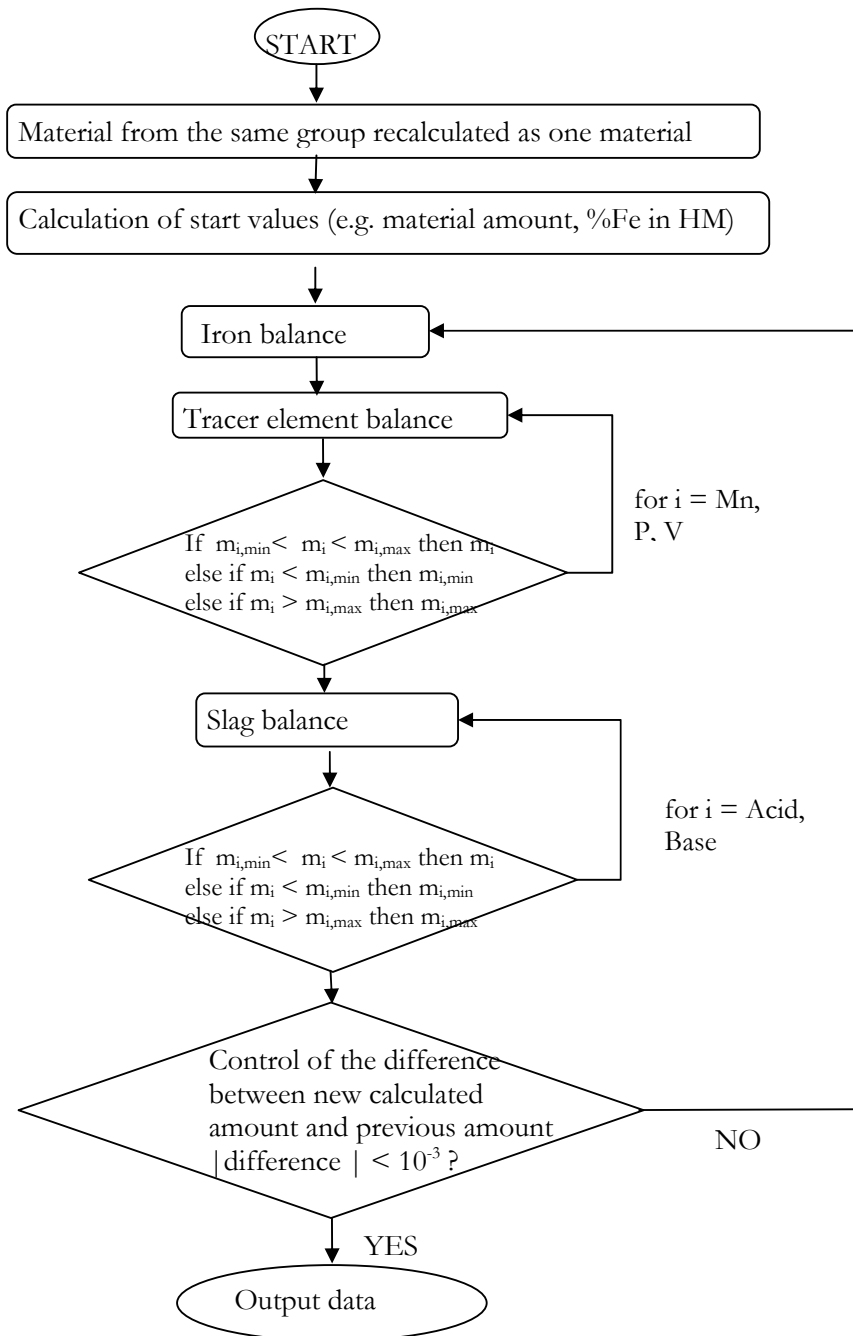


Figure 2 Flow sheet of the optimisation burden calculation



## 2.2. Yield factors and distribution coefficients

The main reactions in a blast furnace are heterogeneous slag-metal-gas reactions. Although the reactions normally go through the gas phase, a common way to present the degree of the reduction of oxides is to use distribution coefficients. This is possible due to the fact that most of the elements of interest leave the furnace through the slag or the hot-metal phase. Since the blast furnace is assumed to operate at steady state the distribution coefficient,  $L_i$ , for a general slag-metal equilibrium can be expressed on the form

$$L_i = \frac{(\%i)}{[\%i]} \quad (6)$$

where parentheses indicate slag phase and brackets indicate metal phase of element  $i$ . Theoretical and experimental studies of  $L_i$  do normally not consider all of the elements that actually existed in the blast furnace, hence, the use of empirical values are more common in practice. In the present work another approach was chosen; the yield factor  $\eta_i$ , defined in equation (5) was used. The calculation of  $\eta_i$  will be more straightforward since it only requires the material and hot-metal composition; the slag weight or composition is not necessary. When a component is assumed only to be distributed between hot metal and slag the yield,  $\eta_i$ , could easily be expressed as a function of the distribution coefficient,  $L_i$ , see equation (7)

$$\eta_i = \frac{1}{1 + \frac{m_{slag}}{m_{HM}} \cdot L_i} \quad (7)$$

where  $m_{slag}$  represent the amount of slag and  $m_{HM}$  the amount of hot metal.

It is generally accepted that the elemental slag-metal distribution is mainly influenced by (i) temperature, (ii) basicity and (iii) oxygen potential. In this study the hot metal temperature showed only a weak correlation with the hot metal elements and was therefore not investigated further. The basicity could be expressed using the activity of the oxygen ion ( $a_{O^{2-}}$ ), where a high activity is compatible to high basicity. Through equation (8)



the oxygen potential ( $p_{O_2}$ ) is correlated to activity of oxygen ( $a_O$ ).

### 3. Method

During this thesis work, two commercial blast furnaces at SSAB Oxelösund AB, Table 1, have been used as primary research targets. All the work has been done with actual production data that has been theoretically treated in different ways.

Table 1 Blast furnace information for No.2 and No.4 at SSAB Oxelösund

	BF No. 2 during 2002	BF No.4 June 2003	Unit
Annual production	550 ·10 <sup>3</sup>	1000 ·10 <sup>3</sup>	metric ton
Capacity	2000	3000	metric ton/24h
Hearth diameter	6.9	8.6	m
Working volume	760	1339	m <sup>3</sup>
Top charging	Rotating chute	Rotating chute	
Relined	1996	1996	Year

#### 3.1. Burden calculation approach

To be able to study the optimisation model behaviour, actual data from blast furnace No.2 at SSAB Oxelösund for six periods during 2002 was selected from process characteristics that were classified as normal operational conditions. The process was run on ordinary burden, see Table 2, and with no significant changes in amounts of material, blast flow, blast temperature, added moisture or oxygen enrichment.

The calculations were done in two ways:

- 1) Actual charge material from the six periods was put into the model and the hot-metal and slag composition was calculated.
- 2) The hot-metal and slag compositions from the six periods was given as input data to the model and the optimal burden mixtures were calculated.

In the second calculation, the material amounts were given minimum and maximum value to enable the optimisation procedure. Both calculations used the same yield factors, based on the calculated average composition for all the six periods.

Table 2 Production data from blast furnace No.2 and No.4 at SSAB Oxelösund

	BF No. 2 during 2002	BF No.4 June 2003	Unit
Blast volume	77400	114700	Nm <sup>3</sup> /h
Blast temperature	1010	1033	°C
Steam	9	7.5	g/Nm <sup>3</sup>
Oxygen	3	4.8	%
Production	1840	2858	metric ton/24h
Cooling effect	N/A	22796	MJ/h
Material charged			
Pellet	1308-1319	1427	kg/thm
Slag fluxes (BOF- slag and limestone)	68-79	~70	kg/thm
Mn briquettes	67, 80	65	kg/thm
Coke	379-385	~360	kg/thm
PCI	90-95	~100	kg/thm
Calculated slag (avg)	183	171	kg/thm
B2	0.92	0.96	
Hot metal (avg)			
C	4.50	4.54	wt%
Mn	0.31	0.30	wt%
Si	0.55	0.62	wt%
S	0.069	0.048	wt %
P	0.039	0.039	wt %
V	0.27	0.28	wt %

### 3.2. Successive sampling of hot metal and slag at tapping

In order to investigate variations during tapping of a blast furnace, a study was done using BF No.4 at SSAB Oxelösund, Table 1, in June 2003. The total studied period lasted nearly 3 days (68 hours) and during that time samples of hot metal and slag, as well as temperature measurements of the hot metal, were taken at intervals of 10 minutes. The location of the hot-metal sampling and temperature determination was the area directly following the skimmer. The slag sampling was performed in the first part of the slag runner. The hot metal was sampled using a lollipop sampler and a scoop was used to sample the slag. About a handful of slag was sampled and poured out on a slag shovel. After the samples had cooled down, the slag was also crushed before it and the hot metal were put into paper-bags pending later analyse. The hot-metal elemental concentrations, except for carbon, were determined with one of two automatic XRF (X-ray fluorescence) spectrometers, one ARL8680 and one Philips W2400. The carbon concentration was determined using high-temperature decomposition, which converts the carbon to gaseous carbon. The instrument

employed was a CS444 from LECO. The slag samples were analysed with the same instrument used for the hot metal.

During the study the process was running on an ordinary burden mixture, see Table 2, and under normal operational conditions. One exception was that an excess of hot metal in the steel shop caused a minor decrease in the blast of 15% for 6 hours towards the end of the study.

## **4. Results and discussion**

### **4.1. Scope of supplement 1**

#### *4.1.1. The calculation of hot-metal and slag components when the burden amounts were given*

When the optimisation model was used to perform a straight forward burden calculation from a given material charge, good agreement could be found between the actual and calculated hot-metal and slag compositions. This is seen in Figure 3, where comparisons between the hot metal values (Si, Mn, V, S and P) calculated from the model and the average composition values for six periods are shown. Note that during period 5 an input of 10 kg/thm of blast furnace slag is believed to be an explanation to the kinks in the curves.

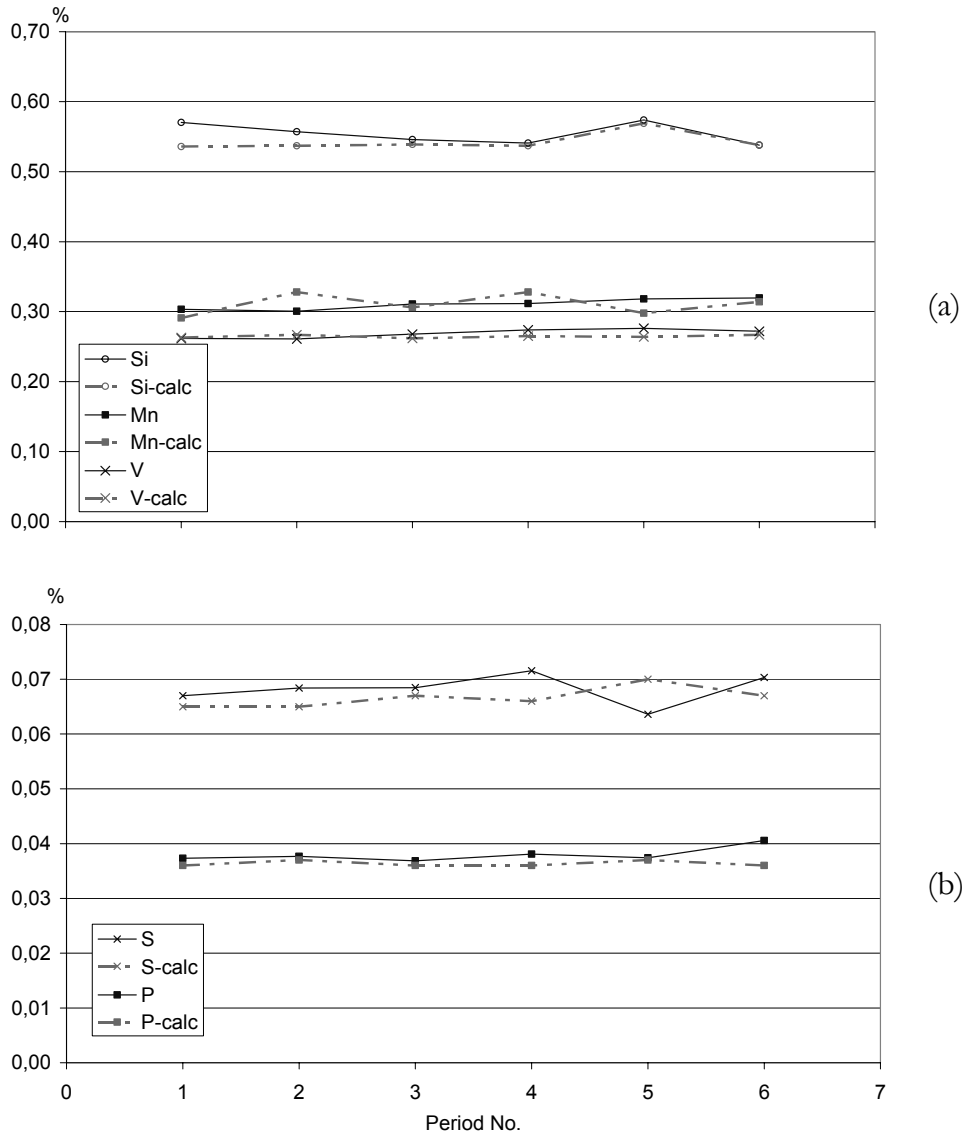
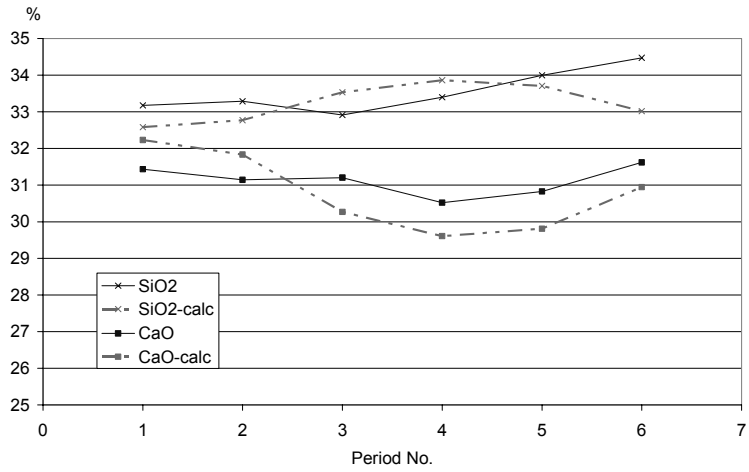
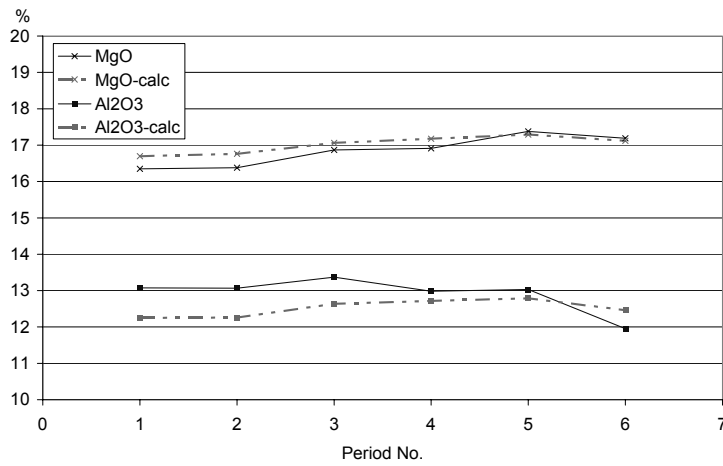


Figure 3 Comparison for calculated hot-metal composition with average composition for six periods during 2002

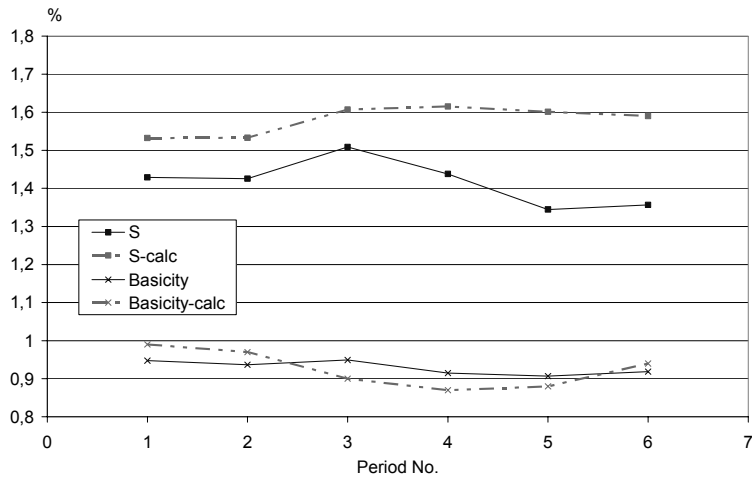
For the slag the same evaluation was done, and the result can be seen in Figure 4. Here the agreement is also good, except for sulphur that has a lower actual value than the calculated. This could be due to the loss of sulphur in the top gas, which is not compensated for in the optimisation model.



(a)



(b)



(c)

Figure 4 Comparison for calculated slag composition with average composition for six periods during 2002

The relative standard deviation, RSD, was calculated for the differences shown in Figure 3 and Figure 4. The calculated values are provided in Table 3 for hot metal and Table 4 for slag. The RSD for the analysis error for the hot-

metal and slag composition measured with the XRF-spectrometer was also calculated. For the hot metal the agreement is good for all elements except manganese, which is believed to be due to the variation in manganese content in BOF-slag and its effect on the total input of manganese. Why this variation in manganese input does not show up in the actual values is not clear. For the slag the large divergence for sulphur is due to the model not compensating for sulphur loss through the top gas. The less good agreement for Al<sub>2</sub>O<sub>3</sub> can not be satisfactory explained.

**Table 3** The relative standard deviation for the calculated hot-metal composition compared with the actual average value for six periods during 2002 for BF No.2 at SSAB Oxelösund.

Period \ Element	Mn	V	P	S	Si
1	-4.1	0.4	-3.5	-3.0	-6.0
2	9.1	2.3	-1.8	-4.9	-3.6
3	-1.6	-2.2	-2.3	-2.2	-1.3
4	5.3	-3.2	-5.5	-7.8	-0.7
5	-6.3	-4.4	-1.0	10.0	-0.8
6	-1.7	-1.8	-11.3	-4.8	0.0
Analysis error	±3.7	±2.2	±10.8	±6.4	±9.2

**Table 4** The relative standard deviation for the calculated slag composition compared with the actual average value for six periods during 2002 for BF No.2 at SSAB Oxelösund.

Period \ Component	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	S
1	2.53	-1.79	-6.30	2.14	7.21
2	2.22	-1.55	-6.20	2.32	7.55
3	-3.00	1.87	-5.49	1.15	6.51
4	-2.99	1.39	-2.04	1.57	12.31
5	-3.29	-0.86	-1.87	-0.50	19.08
6	-2.13	-4.23	4.26	-0.42	17.22
Analysis error	±2.36	±1.54	±2.12	±2.94	±1.07

#### 4.1.2. The optimisation of burden amounts

When the optimisation model uses the average hot-metal and slag composition for the six periods to calculate an optimal burden mixture, the difference between the actual amounts and optimisation amounts varies. This behaviour can be seen in Figure 5.



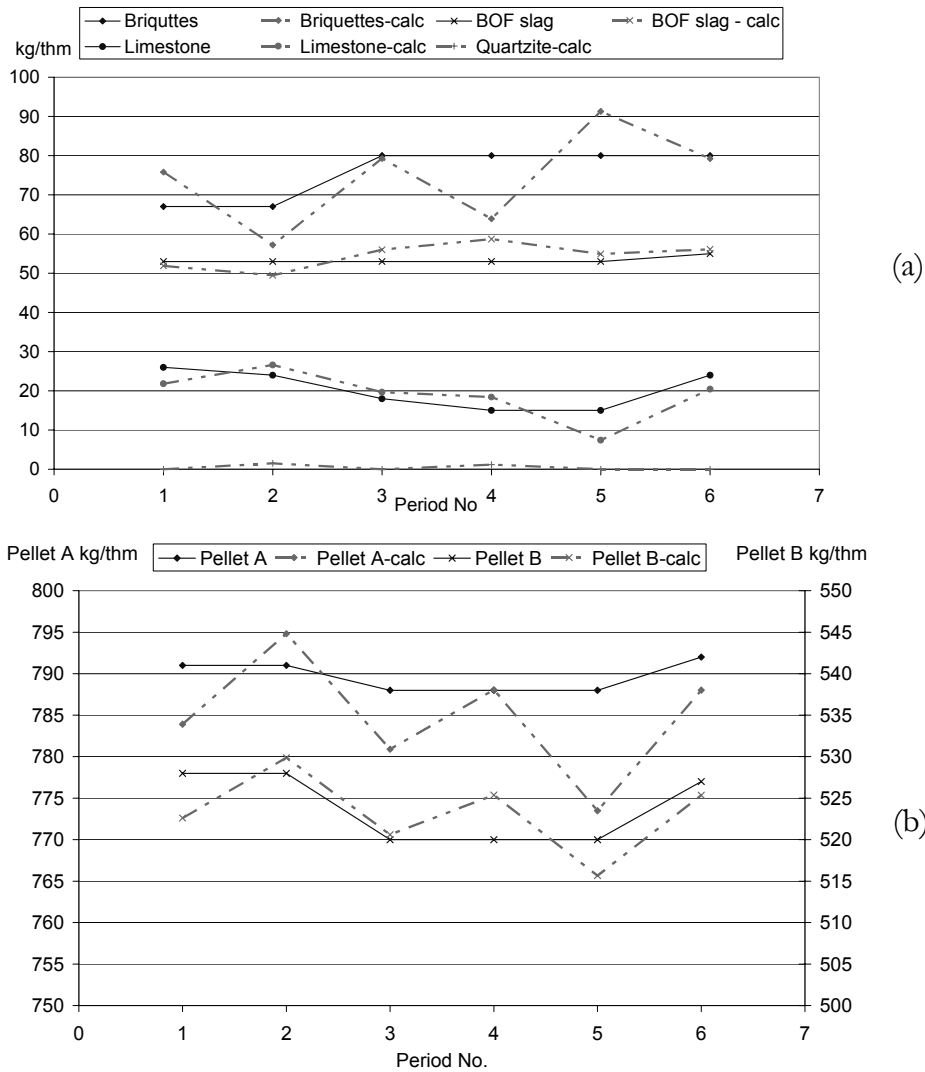


Figure 5 Comparison between actual and calculated amounts for the burden charge for six periods during 2002 for BF No.2 at SSAB Oxelösund.

The largest variation could be seen in the briquette charge and this is due to the different manganese composition within the briquettes from period to period. This variation had a great effect on the amount of briquettes that was required to fulfil the hot-metal manganese composition. However, the briquettes mostly contain residues from the pellets, an iron content of 50%, and this will have impact on the calculated amount of pellet needed to produce one tonne of hot metal.

#### 4.2. Scope of supplement 2

From the successive sampling of hot metal and slag the composition variation could be detected for various elements and components. There were variations both over the whole period and during single taps. These behaviours

are illustrated with silicon in hot metal in Figure 6 and sulphur in slag in Figure 7.

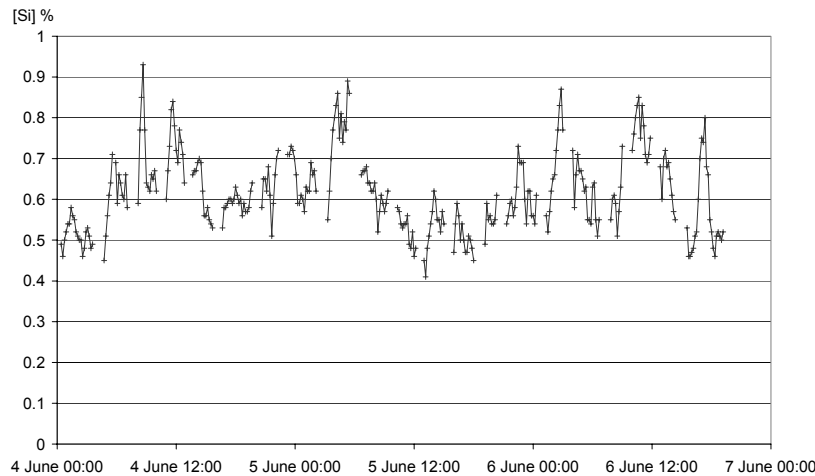


Figure 6 The variation of silicon in hot metal during tapping of BF No.4 SSAB Oxelösund

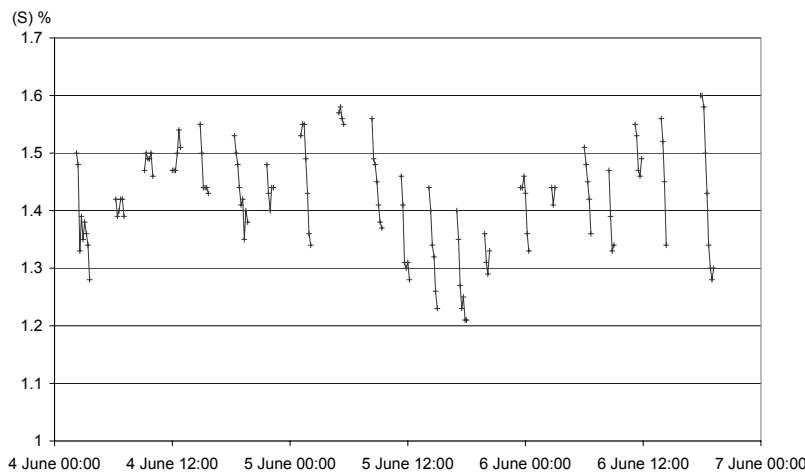


Figure 7 The variation of sulphur in slag during tapping of BF N.4 SSAB Oxelösund

Over the whole period [Si] and (S) showed similar trends. When looking at single taps, there was no general trend for the silicon in hot metal. However, for the sulphur in slag there was a decreasing drift for a single tap.

No strong relationships between the hot-metal temperature and elements in the hot metal were found. In Figure 8 this observation is displayed, with silicon in hot metal versus hot-metal temperature. The values used are the average values for each tapping.

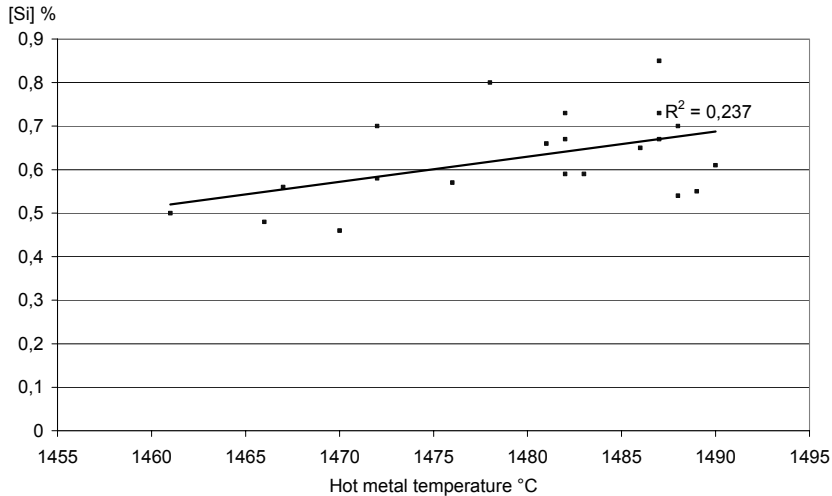


Figure 8 Silicon in hot metal versus the hot metal temperature for 21 taps as average values.

On the other hand relationships between different elements in hot metal were found, where all three elements, carbon, silicon and sulphur showed stronger correlations with each other. In Figure 9 silicon in hot metal is shown versus carbon in hot metal and it can be seen that high carbon content corresponds to high silicon content in hot metal, and vice versa.

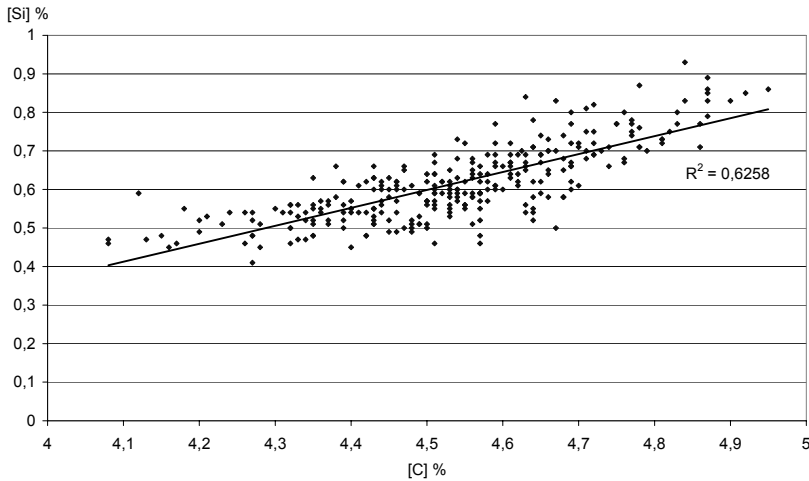


Figure 9 Silicon versus carbon in hot metal for 21 taps as average values.

Since there was a variation of the hot metal and slag composition during tapping, the composition from the routine sample was compared with the actual average for the whole tapping. This was done using equation (9)

$$\Delta_i = \frac{\%i_{routine} - \%i_{average\ trial}}{\%i_{average\ trial}} \cdot 100 \quad (9)$$

Since one single sample was not a good representative for the whole tapping, two samples were selected from the successive sampling series. The first sample was taken 30 minutes after tap start and the second was taken 20 minutes after slag start, and from these two samples a double-sampling average (dbl) was calculated. This double-sampling average was compared with the actual average value using equation (10)

$$\Delta_i^{dbl} = \frac{\%i_{double\text{-}sample\text{ average}} - \%i_{average\text{ trial}}}{\%i_{average\text{ trial}}} \cdot 100 \quad (10)$$

Illustrated in Figure 10 both  $\Delta_i$  and  $\Delta_i^{dbl}$  can be seen for [Si] and [S]. It is clear that the double-sampling average represents the composition of hot metal much better than the routine sample.

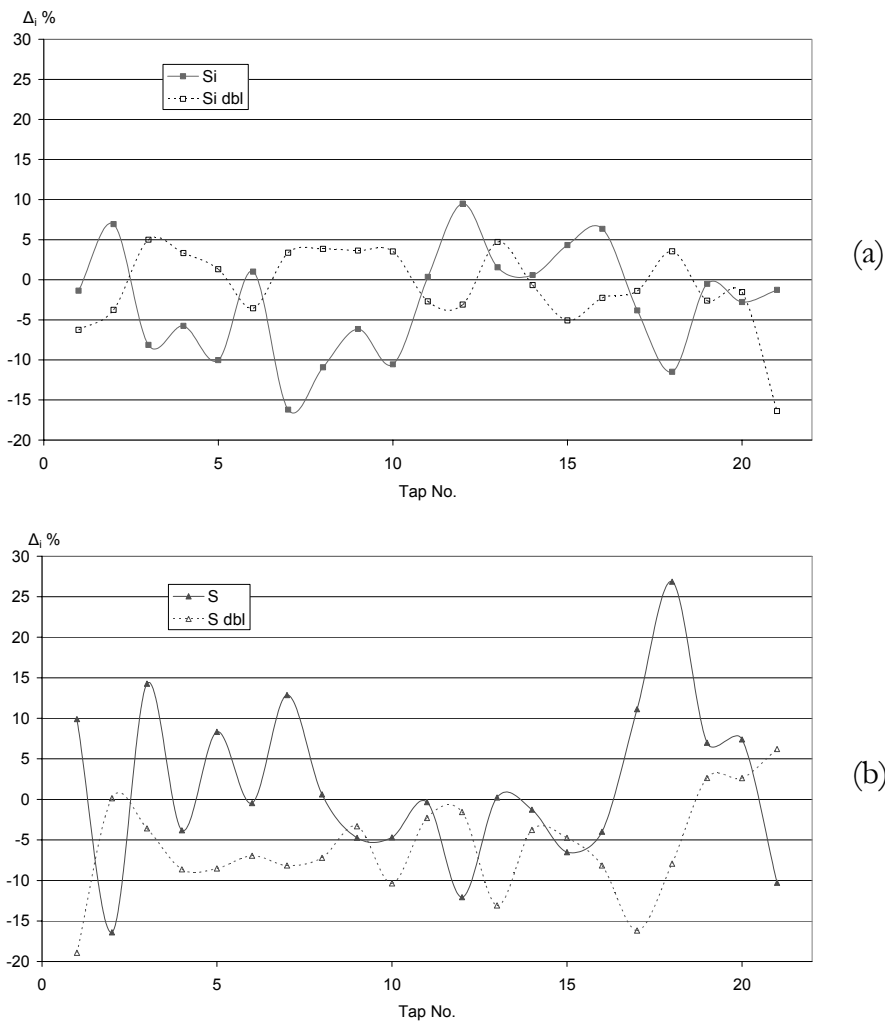


Figure 10 The delta between routine sample and actual average compared to delta for double-sampling average and actual average. (a) silicon in hot metal and (b) sulphur in hot metal.

The observation that a changed sampling strategy responds better to the actual composition in hot metal was also found to be true for slag, but in this case the sampling was just changed in time compared to the routine sample. One slag sample was taken 20 minutes after slag start. In Figure 11 the difference between routine sample and new sample time is shown for  $V_2O_5$  in slag.

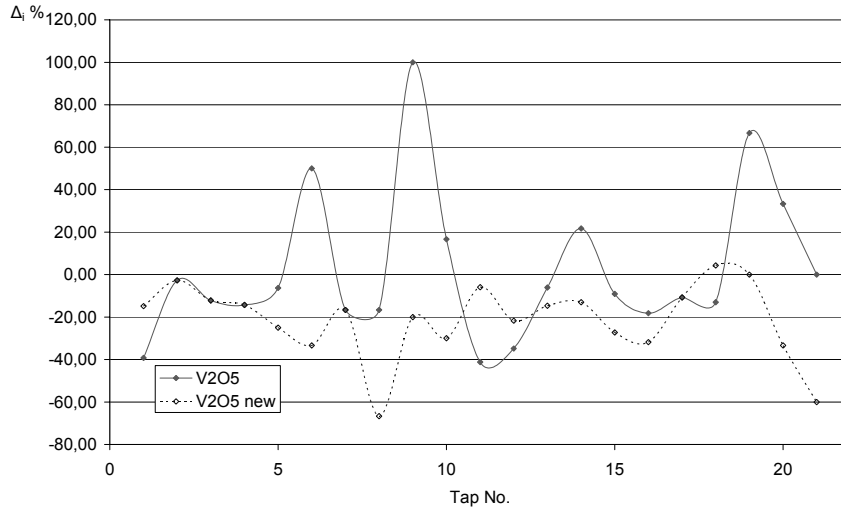


Figure 11 For  $V_2O_5$  in slag the delta between routine sample and actual average compared to the delta for the new time for slag sample and actual average.

### 4.3. Scope of supplement 3

Different operational status such as decreased blast flow, alkali washout or long taps, did not influence the thermodynamic behaviour of the distribution coefficients,  $L_i$ . As can be seen in Figure 12 the trend for the relation between  $L_S$  and  $L_{Mn}$  is the same regarding the operational status, a high  $L_S$  value correlates to a low  $L_{Mn}$  value.

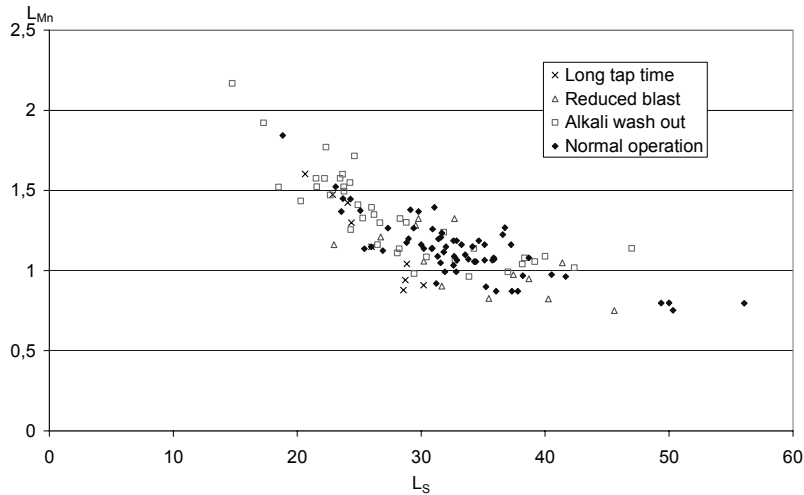


Figure 12 Correlation between  $L_S$  and  $L_{Mn}$  during different operational conditions for 21 taps

The effects of oxygen potential and basicity on the distribution coefficients were studied, and it was concluded that the effect on the  $L_i$  from these two parameters could be explained by slag-metal equilibrium reactions. By dividing the 21 taps in two groups, one with basicity  $\geq 0.956$ , which is the median among the 21 taps, and one group where basicity  $< 0.956$ , the effect of basicity ( $a_{O_2}$ ) could be studied. In Figure 13 the relation between  $L_i$  and carbon in hot metal for the two groups of basicity could be seen, and it is clear that a higher basicity (broken lines) have another effect on the distribution coefficient than the lower basicity (solid lines).

Sulphur and silicon, which have an acid behaviour in the slag, showed an increase in  $L_i$  when the basicity increased. The broken lines are above the solid lines. The effect of basicity on  $L_{Si}$  is vague because basicity is a function of the  $SiO_2$  content in the slag. For manganese and vanadium the opposite could be expected since they have a basic behaviour in the slag. The broken lines are below the solid lines.

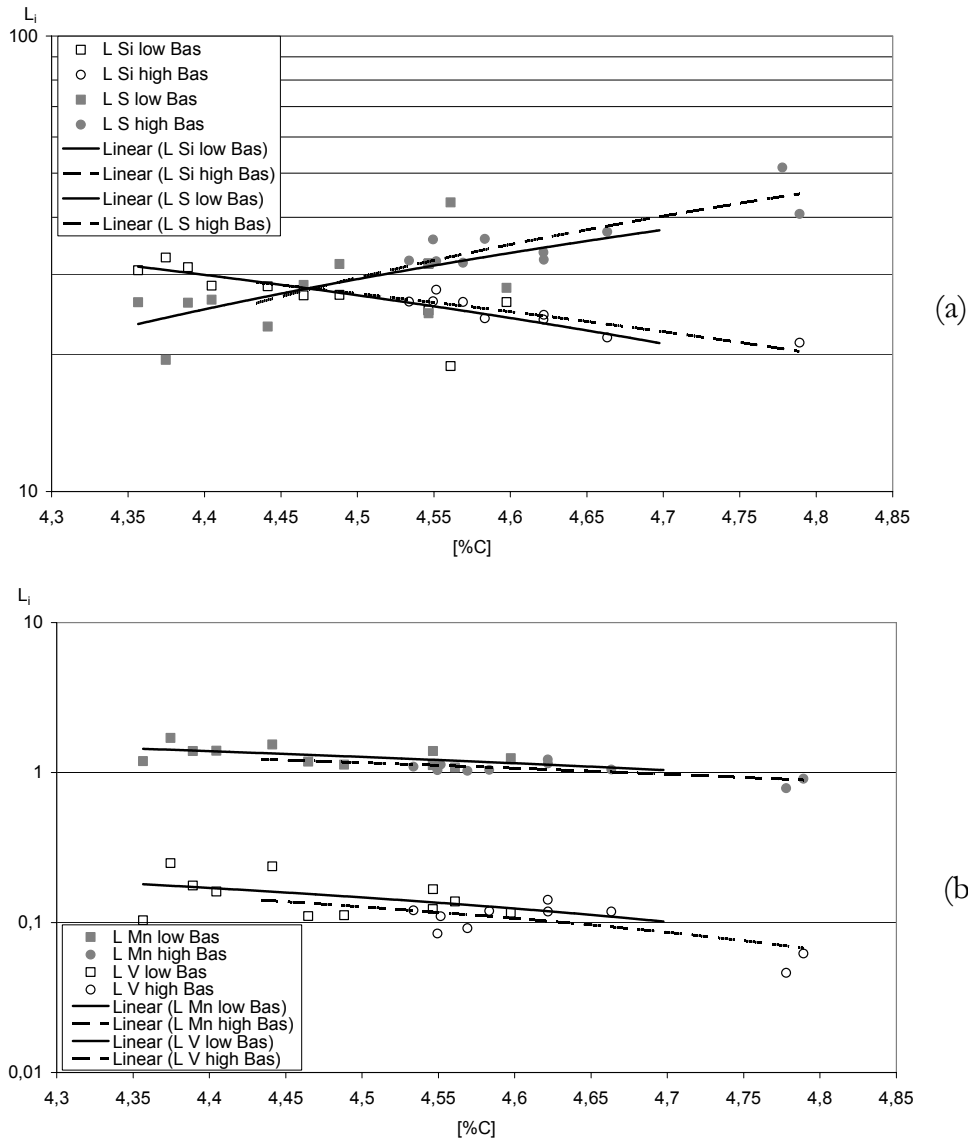


Figure 13 The added effect of basicity and carbon in hot metal on the distribution coefficients  $L_{Si}$ ,  $L_S$ ,  $L_{Mn}$  and  $L_V$ . The basicity was split in two groups, where high basicity  $\geq 0.956$ .

A high carbon content in hot metal indicates that the reducing environment in the furnace is strong, and therefore the partial pressure of oxygen ( $p_{O_2}$ ) should be low, leading to a low activity of oxygen ( $a_O$ ). As can be seen in Figure 13 the distribution coefficients for manganese, vanadium and silicon are lowered when the carbon content in the hot metal increase. For sulphur the opposite could be seen. These behaviours are in accordance with the expected effect of  $p_{O_2}$  on the distribution coefficients for these elements.

#### 4.4. Concluding remarks

The thesis is based on three supplements that are related according to Figure 14.

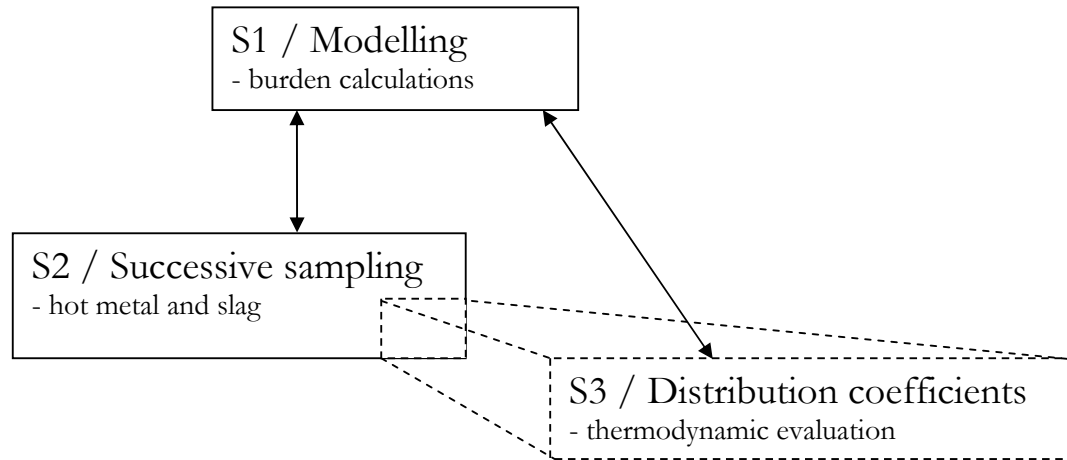


Figure 14 The connections between the three supplements

In supplement one, S1, the optimisation burden calculation for actual production values was used to see how well the model-results agreed with the actual data. In supplement two, S2, the variation in hot-metal and slag composition was studied. From that it was seen that it is of great importance that the samples of hot metal and slag are taken at the right time during tapping for the samples to have the ability to represent the average compositions for the whole tapping in a good way. As can be seen in Table 3 and Table 4 from the discussion about S1, there was a difference in calculated and actual data for hot-metal and slag composition. From the information in S2 it may be surmised that this difference is due to the sampling time of hot metal and slag. This is due to the fact that only routine samples were used in S1, but several samples from one tapping were used in S2.

Supplement three, S3, could be seen as a part of the main subject in S2, since the correlation between distribution coefficients that was studied in S3 is based on the results from the successive sampling of hot metal and slag done in S2. The correlation between different  $L_i$  was obvious and it was also exemplified that this behaviour could be expected when looking at the equilibrium reactions from a thermodynamic viewpoint.

The result from the present thesis suggests the following: For a constant ratio between slag and hot-metal weight (i.e. stable operational conditions as was the case in this study) it was observed that  $L_i$  was a function of carbon



content in hot metal and basicity. Since basicity is a function of carbon content in hot metal, it is most likely that the basicity is controlled by the carbon content in hot metal. High carbon content relates to low  $p_{O_2}$  which leads to a reduction of  $SiO_2$  in the slag, and hence, increased basicity. Therefore it is probable that the carbon content in hot metal ( $p_{O_2}$ ) is the controlling parameter for the  $L_i$ . This conclusion could be useful information for the burden calculation when setting the yield factors for a specific blast furnace.

## 5. Conclusion

The main objective of this study of selected blast furnace phenomena was to gain an increased understanding which could be utilized for an improved blast furnace process control. With an optimisation of the burden calculation the first step towards controlled hot-metal production is taken, since the optimal material mixture for a desired hot-metal composition could easily be found. Due to the fact that the optimisation model uses yield factors, which are easy to calculate from material and hot-metal compositions, these values have to be accurate for a controlled process-control of the furnace. The study of variation in hot-metal and slag compositions during tapping concluded that variations exist. The variations of [Ni], [P], [Cr], [Cu] and [Mo] were so small that they were within the analysis error for that component. On the other hand [C], [Si], [S], [Mn] and [V] show such huge variation during tapping that one single sampling of hot metal was not enough to get a representative value for the composition. The solution was to use a double-sampling practise, where the hot metal was sampled first after tap start and secondly short after slag start, and subsequently an average composition value was calculated. It should be stated that every BF have their own optimal times for sampling, and these times have to be investigated, e.g. with successive sampling of hot metal and slag over a longer period. The variations found for the slag-metal distribution coefficients follow the behaviour that can be expected when looking at the equilibrium reactions from a thermodynamic point of view. The studied slag-metal distributions were also showing strong, trend-like relationships, which was not affected by the operational status of the BF.

The overall conclusion that with a more reliable composition of hot metal and slag from the taps, the distribution coefficients could be calculated with better precision and hence, the yield factors for the optimisation model would be more accurate. This procedure will lead to a more reliable burden optimisation and therefore better and more stable blast furnace control.

## 6. Future work

- ✘ Use the suggested double-sampling times for hot metal and the new time for slag sampling to find hot-metal and slag composition that better match the actual average composition, and use these average values to calculate new yield factors.
- ✘ With new yield factors optimise new burden calculations and see if the fit will increase.
- ✘ Use a thermodynamic approach for extended studies on the equilibrium reactions for relations between distribution coefficients.
- ✘ Repeat this study on another blast furnace in order to see if the concept is general.

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# Supplement 1

The Use of an Optimisation Model for the Burden Calculation  
for the Blast Furnace Process

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# THE USE OF AN OPTIMISATION MODEL FOR THE BURDEN CALCULATION FOR THE BLAST FURNACE PROCESS

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## Abstract

The aim of a burden calculation in the blast furnace process is to compute the amounts of burden materials to be charged for obtaining desired hot-metal and slag composition. Burden calculations are normally based on trial-and-error instead of optimisation. In this study, the use of an optimisation model for a typical blast furnace operation is presented. The yield factors of some components such as, Mn, Si, S, P and V, used in the model have been determined. The more common distribution coefficients have also been studied.

Both the yield factor and distribution coefficient values were generally good and showed stable behaviour for repeated periods under similar operational conditions.

In this study the model was found to be an excellent tool for determining burden material amounts and hot-metal and slag compositions for a blast furnace under steady and normal operation conditions. Using an optimising burden calculation model is time efficient, since it demands only one calculation procedure instead of a couple calculations as in the case with a trial-and-error method.

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## Key words

blast furnace, material balance, iron making, burden calculation, optimisation, distribution coefficient, yield, phosphorus, vanadium, sulphur, silicon, manganese

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# 1. Introduction

The aim of a material balance is normally to compute the inflow and outflow of mass in a process. For the blast furnace process, a simplified material balance, a so-called burden or charge calculation, is commonly used for calculating the amounts of burden materials needed for obtaining a desired quality of hot metal and slag, though the approaches used are quite different for different furnaces. For instance, in Sweden, with three blast furnaces at two different sites and one pilot blast furnace, different calculation procedures are used.

The burden calculations employed for the blast furnaces are generally based on trial and error rather than optimisation. The model used in this study can optimise the amounts of materials between their allowed minimum and maximum values in the burden, with respect to desired quality of hot-metal and slag properties.

The aim of this study has been to determine if a model that optimises the burden from hot-metal and slag properties is as reliable, as common traditional calculation methods [1]. The advantages of such a model are that

- I. it provides information on optimal use of raw materials for attaining desired hot-metal and slag compositions
- II. the impact of the raw material charge is easily spotted when a change in raw material composition occurs
- III. the calculation time needed for determining a suitable charge mixture can be significantly reduced since only one calculation needs to be done in contrast to a series of trial-and-error calculations.

The blast furnace process can be considered to be a continuous process operated in steady state. Thus, there should generally be no accumulation of material within the system. This however is not always true, exemplified by the well-known problem of alkali circulation in the blast furnace. A discussion on accumulation phenomena is not however within the scope of this study.

## **2. Theoretical model**

### **2.1. General**

For a burden calculation, the quantities to be solved are the input amounts of materials, based on the known compositions of the ingoing materials and the desired compositions of the hot metal and slag to be produced in the blast furnace. For the blast furnace, the most commonly used calculation basis is one tonne of hot metal, THM. The burden material flow is schematically illustrated in Figure 1.

The present work was inspired by an undocumented heat and mass balance model, originally designed by Axel Bodén. The model was devised in an Excel spreadsheet and the present authors have analysed and rewritten the equations and made it possible to program the model in JAVA code [2,3]. The present paper is a documentation of the mass-balance part of the new model version (the so-called burden calculation) which today is displayed on the World Wide Web [4] and available to all who have access to the Internet.

The burden calculation always optimises the amount of iron-containing material. The amounts of acid and basic slag former are optimised in order to meet both the desired slag amount and basicity, in case there are both acid and basic slag formers present. The model can also optimise materials that contain a tracer element. Equations for three tracer elements have presently been implemented, namely for manganese, phosphorus and vanadium.

### **2.2. Input data of the model**

#### *2.2.1. Material characteristics*

The materials used in the burden calculation can be divided into two categories: ingoing raw materials (pellets, slag formers, reduction materials etc) and outgoing products (hot metal and slag). The calculation requires chemical composition data on all the ingoing raw materials. Furthermore, the upper and lower limits of the ingoing raw material weights being optimised by the model have to be provided. These limits should



be in a reasonable magnitude, e.g. a material's minimum not less than 0 kg/thm and its maximum not more than about 2000 kg/thm. The weights of the reductants, i.e. coke and pulverized coal or oil, have to be specified before the calculation. By giving the amount of a material a negative sign, the material is defined as an out-going material, but not however, as hot metal or slag. Flue dust could be a typical example of such a material.

The model also needs specific information on the desired product, such as the hot-metal composition, which includes the weight percentage of the main components: silicon, phosphorus, vanadium, manganese and carbon. Information on the, slag requirements, such as amount, iron content and basicity is also necessary.

### 2.2.2. *Distribution coefficients and yield factor*

The blast furnace is assumed to operate at steady state. However, several studies have shown that equilibrium of components between metal and slag could not be reached in the blast furnace [5,6]. Therefore, distribution coefficients, providing information on how much oxide remains in the slag and how much oxide is reduced in the hot metal have often been used. Distribution of element  $i$  between slag and metal can be expressed as

$$L_i = \frac{(\%i)}{[\%i]} \quad (1)$$

where the figure in parentheses indicates oxide in the slag phase and the figure in brackets indicates an element in the metal phase. Although these coefficients can be found in different theoretical and experimental studies [6,7], one potential source of error in using these results is that the systems investigated in these studies were simplified. They normally did not consider a large number of elements that actually existed in the blast furnace. Hence, the use of empirical values is a more realistic way, despite its disadvantage of limitation introduced by using operational data obtained under certain circumstances. Empirical values are therefore only valid for one furnace under basically unchanged operational conditions.

In the present model, the concept of yield factor,  $\eta_i$ , has been introduced instead of using  $L_i$ . The yield factor describes the recovery of elements in the hot metal; its definition can be seen in equation (2), where  $i$  denotes the element.

$$\eta_i = \frac{i_{HM}^{kg}}{i_{Charged}^{kg}} \quad (2)$$

$i_{HM}^{kg}$  is the weight of element  $i$  in the hot metal and  $i_{Charged}^{kg}$  is the total in charged weight of element  $i$  in the blast furnace.

Because the blast furnace seldom reaches equilibrium in a slag-metal reaction, theoretical equilibrium constants are not used. It is also more convenient to use  $\eta$  than  $L$  for the reasons that calculation of  $\eta$  requires material and hot-metal composition data only; the slag weight or composition is not necessary. Obtaining representative samples on the ingoing materials are much easier than for the product and the sampling could very easily be automatized.

### 2.3. Equations

The model contains an equation system with a set of calculations for obtaining the amount of each type of material to be charged. Each equation for calculating a material amount is iterative, and the equation uses the last calculated amount to calculate a new one. The model has a function that calculates start values for each material and each material amount calculation has check gates to control if the calculated amount is within the minimum and maximum set values. The main ingoing material is an iron-containing material in the form of sinter, pellets or lump ore. To gain a smooth operation and desired composition of hot metal, a certain amount of slag with proper properties is necessary. Slag is composed of gangues from iron-containing material, basic and acid slag formers such as limestone and quartzite, and ashes in reductants. The model distinguishes between a basic slag former and an acid slag former. The amounts of reduction materials, including coke, oil and pulverized coal, for providing heat and reduction gas are also needed. These are all assumed to have fixed values and are not optimised by the model.

The calculation of the amount of each ingoing material is based on its main component. For instance, the amount of sinter, pellets or lump ore can be obtained according to its iron content in making a Fe balance, while the amount of fluxes is obtained according to its CaO and SiO<sub>2</sub> contents and the set values of slag amount and basicity. In addition, the balances of some tracer elements, such as Mn, P and V, can also be carried out by the model.

### 2.3.1. Iron balance

The iron balance is the most essential mass balance in the model, since the purpose of the blast furnace is to produce hot metal. Equation (3) has been used to calculate how much iron bearing material has to be charged to produce one tonne of hot metal:

$$(m_{\text{Fe, mtrl}})_n = \frac{\left( (m_{\text{Slag}}^{\text{Fe}})_{n-1} + (m_{\text{HM}}^{\text{Fe}})_{n-1} + (m_{\text{Fe, mtrl}}^{\text{Fe}})_{n-1} - (m_{\text{Charged}}^{\text{Fe}})_{n-1} \right)}{\left( \frac{\% \text{Fe}_{\text{Fe, mtrl}}}{100} \right)} \quad (3)$$

where  $(m_{\text{Fe, mtrl}})_n$  is the new calculation of the amount of iron-containing material,  $(m_{\text{Slag}}^{\text{Fe}})_{n-1}$  is the amount of iron in the slag,  $(m_{\text{HM}}^{\text{Fe}})_{n-1}$  is the amount of iron in the hot metal,  $(m_{\text{Fe, mtrl}}^{\text{Fe}})_{n-1}$  is the amount of iron in the iron-containing material,  $(m_{\text{Charged}}^{\text{Fe}})_{n-1}$  is the amount of iron totally charged, (n-1) is the term calculated with the results from the previous calculation and  $\% \text{Fe}_{\text{Fe, mtrl}}$  the weight percentage of iron in iron-containing material.

If there are two or more types of materials that are classified as iron-containing, the share of these materials has to be specified. These types of materials will be calculated as one material, with a mean value of analysis, in proportion to their portions in the mixture before the start of the calculation. When the calculation is finished the amounts of different types of original iron-containing materials will be recalculated based on the proportions of each material at the start of the calculation.

### 2.3.2. Tracer element balance

The burden materials charged, especially the recycled waste materials, often contain a certain amount of tracer elements (e.g. phosphorus, vanadium and manganese) that must be controlled to avoid overcharging in consideration to the quality of the hot metal to be produced. The amounts of the charged materials can be obtained by the model based on the balances of these elements using equation (4):

$$(m_i)_n = \frac{\left( \left( \frac{\%i_{HM}^{Estimated}}{\eta_i} \cdot 10 \right) + (m_i)_{n-1} - (m_{Charged}^i)_{n-1} \right)}{\left( \frac{\%i_i}{100} \right)} \quad (4)$$

where  $(m_i)_n$  is the new calculated amount of material for controlling the amount of element  $i$  (in this model  $i = P, V$  or  $Mn$ )  $\%i_{HM}^{Estimated}$  the desired weight percentage of element  $i$  in the hot metal,  $\eta_i$  the yield factor of element  $i$  between the hot metal and total charge (see equation (2)),  $(m_i)_{n-1}$  the amount of element  $i$  in the  $i$  material,  $(m_{Charged}^i)_{n-1}$  the amount of total charged element  $i$ .  $(n-1)$  indicates that the term is calculated based on the last iteration and finally  $\%i_i$  denotes the weight percentage of element  $i$  in the  $i$  containing material.

### 2.3.3. Slag balance

In order to attain favourable operational conditions, the slag composition and slag amount should be controlled. Slag mainly consists of basic and acid oxides. In the model the basic oxide, calcium oxide (CaO) and the acidic oxide, silica (SiO<sub>2</sub>) are used when making the material balance. Using two components instead of one makes it possible to control both the slag amount and slag basicity. The basicity,  $B_2$ , is defined as follows:

$$B_2 = \frac{(\%CaO)}{(\%SiO_2)} = \frac{m_{Slag}^{CaO}}{m_{Slag}^{SiO_2}} \quad (5)$$

where  $(\%CaO)$  and  $(\%SiO_2)$  are the weight percentages of calcium oxide and silica in the slag and  $m_{Slag}^{CaO}$  and  $m_{Slag}^{SiO_2}$  the mass of calcium oxide and silica in the slag. The lime or silica balance can be written as:

$$m_{Slag}^i = m_{Slag,0}^i + m_{Bas}^i + m_{Acid}^i \quad (6)$$

where  $i$  denotes CaO or SiO<sub>2</sub>,  $m_{Slag}^i$  is the amount of  $i$  in the slag,  $m_{Slag,0}^i$  is the amount of  $i$  in the materials charged except basic or acid slag formers, and  $m_{Bas}^i$  and  $m_{Acid}^i$  are the amounts of  $i$  charged in basic and acid slag formers, respectively. The amount of slag rendered from basic and acid slag formers,  $D$ , is obtained by the following equation:

$$D = m_{\text{Slag}}^{\text{Estimated}} - m_{\text{Slag}}^{n-1} + m_{\text{Acid}} + m_{\text{Bas}} \quad (7)$$

where  $m_{\text{Slag}}^{\text{Estimated}}$  is the desired slag amount and  $m_{\text{Slag}}^{n-1}$  is the previously calculated slag amount, and  $m_{\text{Acid}}$  and  $m_{\text{Bas}}$  are the latest calculated amounts of acid and basic slag formers, respectively. When the term  $(m_{\text{Slag}}^{\text{Estimated}} - m_{\text{Slag}}^{n-1})$  approaches zero, equation (8) is used to calculate the amount of acid slag former necessary to reach a desired  $B_2$  and slag amount.

$$m_{\text{Acid}} = \frac{k_3 - k_1 \cdot D}{k_2 - k_1} \quad (8)$$

Three variables ( $k_1$ ,  $k_2$ , and  $k_3$ ) were introduced, which are separate ways to explain the variance in added amounts of CaO and SiO<sub>2</sub> from different materials.

$$k_1 = \frac{(\% \text{CaO})_{\text{Bas}}}{100} - B_2 \cdot \frac{(\% \text{SiO}_2)_{\text{Bas}}}{100} \quad (9)$$

The variable  $k_1$  is the content of CaO that is not compensated with SiO<sub>2</sub> contained in the basic slag former to create the desired basicity  $B_2$ .  $(\% \text{CaO})_{\text{Bas}}$  and  $(\% \text{SiO}_2)_{\text{Bas}}$  are the weight percentages of CaO and SiO<sub>2</sub> in the basic slag former.

$$k_2 = \frac{(\% \text{CaO})_{\text{Acid}}}{100} - B_2 \cdot \frac{(\% \text{SiO}_2)_{\text{Acid}}}{100} \quad (10)$$

The variable  $k_2$  is the share of CaO that is not compensated with SiO<sub>2</sub> contained in the acid slag former to create the desired basicity  $B_2$ .  $(\% \text{CaO})_{\text{Acid}}$  and  $(\% \text{SiO}_2)_{\text{Acid}}$ , the weight percentage of CaO and SiO<sub>2</sub> in the acid slag former.  $k_2$  normally has a negative value because of the high content of SiO<sub>2</sub> in acid slag formers.

$$k_3 = m_{\text{Slag},0}^{\text{SiO}_2} \cdot B_2 - m_{\text{Slag},0}^{\text{CaO}} \quad (11)$$

The variable  $k_3$  is the amount of CaO or SiO<sub>2</sub> contained in the burden materials excluding slag formers, where a positive  $k_3$  denotes an excess of SiO<sub>2</sub> and a negative  $k_3$  denotes an excess of CaO.

From equations (7) and (8) the amount of basic slag former,  $m_{\text{Bas}}$ , can be calculated as

$$m_{\text{Bas}} = D - m_{\text{Acid}} \quad (12)$$

This is an iterative approach in the calculations which gives a calculated amount that is used in the next iteration.

## 2.4. Optimisation procedure

The model uses a series of equations to calculate the optimal amounts of burden materials for producing the desired hot-metal and slag compositions. The calculation procedure is schematically outlined in Figure 2 and Figure 3. As can be seen, the calculation is iterative and uses the latest calculated amounts to get new ones. The start values are the average values of the minimum and maximum amounts allowed for each material, i.e.  $m_i^{\min}$  and  $m_i^{\max}$  respectively, where  $m$  is the amount of either tracer material or slag former and  $i$  denotes the element (P, V, Mn, Bas or Acid). The amount of iron-containing material optimised has a start value of 1200 kg/thm, which is taken from experience.

This model always optimises the amount of iron-containing material,  $m_{\text{Fe, mtrl}}$  (equation (3)). The slag is optimised both regarding amount and basicity if there are both an acid and a basic slag former present (equation (8) and (12)). If one kind of slag former is excluded, the model can not optimise towards both the desired set values of slag amount and basicity. The model can also optimise three different materials (equation (4)) that contain manganese, phosphorus or vanadium so that the hot metal will contain these elements up to set values. Manganese can be within minimum and maximum set values in the hot metal, but for phosphorus or vanadium there are only maximum set values for their content in the hot metal. Furthermore, the model is able to optimise a material that contains both phosphorus and vanadium; the model determines out which of these elements first reaches its maximum allowed content in the hot metal.

The calculation stops when results from the two previous calculations do not differ by more than 0.1%. The difference between the “sum in” of an element and the “sum out” of the element were less than 0.3%, and this difference was due to rounding error in the JAVA-language.

## 2.5. Output data of the model

Calculations with the model give the following results as its output data; the amount of various types of materials to be charged, hot-metal and slag compositions. The first output data are the hot-metal and slag compositions, calculated based on the materials charged and yield factors given. The slag is mainly composed of CaO, Al<sub>2</sub>O<sub>3</sub>, MgO and SiO<sub>2</sub>. The first three components contained in the burden materials almost completely end up in the slag, while only about 70% of the fourth one, SiO<sub>2</sub>.

The second output data is the calculated amount, in kg/thm, of the mixture of Fe-bearing materials, slag formers, tracer materials and materials given fixed values that are required to produce one tonne of hot metal with a certain amount of slag with a specific basicity. It is important to note that the optimal mixture of burden for a desired hot-metal and slag composition can only be obtained when the initial values of materials have been specified by minimum and maximum values. If the material amounts are set constant for all materials, a calculation is done and the hot-metal and slag compositions are calculated. This procedure will probably not result in the desired product composition, and is more like a trial-and-error calculation.

These two sets of output data, burden mixture and product composition are linked closely together. It is important to evaluate these sets side by side and not independently, since the mix of material determines the composition, which is very dependent on the yield factors provided as input data.

## 3. Method

### 3.1. Blast furnace information

The present study is based on operational data from blast furnace No. 2 at SSAB Oxelösund. The No. 2 furnace has an annual production of ~550 ktonnes, a capacity of 2000 tonne/24h, a hearth diameter of 6.9 m and a working volume of 760m<sup>3</sup>. The last relining was done in 1996 and the furnace has been equipped with a rotating chute since then. During 2002, i.e. the period studied, the blast flow was 77 kNm<sup>3</sup>/h with a pressure of 1.8 bar (abs), and a blast temperature around 1000°C. The oxygen enrichment was

about 3% and the added moisture around 9 g/Nm<sup>3</sup>. For more production data during the study, see Table 1.

The furnace was operated with a 100% pellet burden. The amount of reduction material was about 470-480 kg/thm, of which ~90kg/thm coal powder injection (PCI). The slag volume was about 160 kg/thm and the slag former materials were mainly limestone and spent BOF slag. Manganese was added to the blast furnace through briquettes made from a waste material doped with manganese slag. The detailed information concerning the mixture of materials charged for the six periods can be seen in Table 2. The variation in composition of these raw materials in the study can be seen in Table 3.

### **3.2. Yield factors**

Since the yield factors are the constants that have the greatest effect on the result, empirical yield factors were determined for the No. 2 furnace during regular operation and used in the model calculations. During the six periods the furnace was under stable conditions; no significant changes in amounts of charged material, blast flow or PCI amount were made. The selection of the periods was made based on logged process operation journals and the experience of the blast furnace operators.

From the amounts of materials charged and the composition of raw materials and hot metal, yield factors ( $\eta_i$ ) for five elements ( $i = \text{Mn, Si, S, P and V}$ ) were obtained. This resulted in six yield factors for each element corresponding to each period.

### **3.3. Actual distribution coefficients**

Although the yield factor was used in the model, it was of interest to look into the actual distribution coefficients during the six periods. The actual hot-metal and slag compositions were used to calculate the actual distribution coefficients for Mn, Si, S and V. However, a distribution coefficient for phosphorus could not be obtained, because the amount of P<sub>2</sub>O<sub>5</sub> in the slag was too low to be determined accurately at SSAB Oxelösund. This is due to the poor ability of XRF to measure elements with an atomic number lower than 23 (vanadium) [8].



### 3.4. Comparing model results with actual data

The model was tested with actual data to compare the calculated results with data from a production furnace. Two different types of calculations were made.

- I. Given the actual charge of material, the model calculated the hot-metal and slag compositions for the six periods.
- II. Given the actual hot-metal composition, slag amount and basicity, an optimal burden mixture to fit the hot-metal and slag properties was calculated. This was also done for the six periods.

Both types of calculations were based on the actual average yield factors presented in Table 4. In this way model results could easily be compared with actual data obtained from the blast furnace. This could also show whether or not an optimised burden calculation could provide hot-metal and slag composition data that is in agreement with actual average plant data over periods that vary from 3-15 days.

## 4. Results and discussion

### 4.1. Yield factors and distribution coefficients

For each element (Mn, Si, S, P and V) there are six values of  $\eta_i$ , one from each period, from which an average value and a Relative Standard Deviation (RSD) were calculated, (Table 4).

Distribution coefficients were calculated for all elements, except phosphorus, from actual data for all six periods. The graphs in Figure 4 illustrate that all coefficients were very stable for the six periods that are separated in time. The periods were of different length, 3-15 days, but with similar amounts of burden and operation conditions.

#### 4.1.1. Manganese

When studying literature values for the yield of manganese in hot metal, a theoretical recovery of about 85-90% can be expected at equilibrium [6]. The actual average recovery in the present work was 74 % (Table 4) indicating that equilibrium was in fact not reached in the operating blast furnace. The distribution coefficient was close to 1.5,

which was higher than those given in literature references where values of about 0.5-1.4 were found [9,10].

#### 4.1.2. Silicon

Silicon is picked up mainly by the hot metal from gaseous SiO that is reduced from silica in slag with carbon or carbon monoxide as expressed by equations (13) - (15) [11].



Absorption of silicon by iron-containing carbon occurs according to:



Since silica reduction involves three phases (slag, metal and gas) as well as simultaneous reactions with manganese and sulphur, it is unlikely that the reaction will approach equilibrium in the blast furnace [5]. The yield factor for silicon in the present work was 0.18 (Table 4). The actual distribution coefficient for the six normal operation periods was nearly 30 as shown in Figure 4. The actual distribution coefficient was between what could be found in literature, where values of 15-35 for a sinter blast furnace [12] and 30-60 [10] for a mixed sinter pellet furnace were observed.

#### 4.1.3. Sulphur

Depending on the sulphur load, the amount and basicity of the slag, the slag can carry as much as 80-90% of the total load [6]. In contrast to other elements, which are distributed mainly in the slag and hot metal, sulphur can also, to a certain extent spread to the gas phase. According to the literature, it is possible that as much as 10-15 % of the total sulphur load leaves the furnace with the top gas and the flue dust [6]. In Figure 6 there is a difference of about 10% between the calculated and actual sulphur content in the slag. The difference could easily be explained by a loss through top gas and flue dust since the model assumes that the sulphur is only distributed within the slag and hot metal.

On the equilibrium of sulphur, once again the sulphur reactions involve the slag, metal and gas phases, which in ironmaking results in a sulphur distribution coefficient that can fluctuate from 20-120 [5]. The equilibrium of sulphur is also strongly influenced by operational conditions. In this study the sulphur distribution was about 20 (Figure 4). In a study by Volvik [13], values for  $L_S$  varied from 5 to 25 at a  $B_2$  around 0.9.

#### 4.1.4. *Phosphorus and vanadium*

According to the literature, the reduction of phosphorus and vanadium oxides should be nearly completed in the blast furnace, and small amounts of phosphorus and vanadium can be found in either the slag or the flue dust or can be absorbed by the refractory lining [6]. This was also the case for the furnace in the present study and in Table 4 it can be observed that the phosphorus and vanadium recovery in the hot metal was more than 100%. When calculating the yield for phosphorus and vanadium one should keep in mind that the levels of these elements in the material usually are very low and the charge amount of material is high. Very small differences in the weighing system and chemical analysis errors can influence the results. All these factors could affect the levels of recovery and explain why they exceed 100%.

## 4.2. Comparing model results with actual data

### 4.2.1. *Hot metal*

The agreement between the calculated hot-metal component contents with actual composition data from analyses for the six periods was good, as can be seen in Figure 5. The agreement between actual and calculated values suggests that the model predictions are reliable as well as indicate that the analysis results of the hot-metal composition is reliable. For period No. 5 a higher calculated value for sulphur in the hot-metal was probably a consequence of a higher sulphur load, due to the input of 10kg/thm of blast furnace slag in this period (Table 2).

The peak value of silicon for period No. 5 was probably caused by a higher load of silica than for the other periods. The source was the same as for the higher sulphur load, the 10 kg/thm extra of blast furnace slag.

### 4.2.2. *Slag*

Element standard deviations pertaining to the slag analyses [14] were more than ten times those of the hot metal. For the four main oxides in the slag the standard deviation can be seen in Table 5. The larger uncertainty regarding slag composition analysis data causes a greater difference between actual and calculated values for the slag than for the

hot metal. However, it should be noted that the calculated composition method error does not include a possible variation in the slag composition over time, i.e. during tapping.

In the present study CaO and SiO<sub>2</sub> were the two oxides used to define the basicity. Figure 6a shows that the calculated contents in the slag for the two oxides follow the trend of actual values quite well. Two high values for the calculated CaO content in the slag for periods No. 1 and 2 are mainly due to a significantly higher load of CaO compared with the four other periods. The high calculated contents of SiO<sub>2</sub> in the slag for periods No. 3 and 5 are probably a consequence of a higher load of silica. The high calculated SiO<sub>2</sub> content for period No. 4 can be attributed to the low charge of CaO, resulting in a low slag amount.

Figure 6a and Figure 6c illustrate fluctuation of the basicity, B<sub>2</sub>, which is a consequence of the variation of CaO and SiO<sub>2</sub> levels in the slag.

As for the two oxides Al<sub>2</sub>O<sub>3</sub> and MgO in the slag, Figure 6b shows very good agreement between the trends for calculated and actual values. In fact these two oxides are completely transferred to the slag phase.

#### 4.2.3. Pellet charge

The model always optimises the pellet charge. The six periods in the study always had a pellet share of 60% Pellet A and 40% Pellet B and this share was given as input data. Based on the share of pellet A and B the model calculates how much pellets that totally is needed as well as the separate amounts of Pellet A and Pellet B in kg that are needed to produce one tonne of hot metal. A difference between actual and calculated values was observed, which could be due to the loss of iron through flue dust. Since there was little control over how much flue dust was lost and its composition, the calculated values were compensated with an average loss of iron through the flue dust. The results are presented in Figure 7. The downward trend after the first two periods was due to the higher briquette charge for periods 3-6 (Table 2). The upward trend for period six can be attributed to the lower charge of scrap, 10 kg/thm instead of 20 kg/thm.

#### 4.2.4. *Comparing actual and calculated charge values based on actual hot-metal and slag composition data*

Actual hot-metal and slag analysis data were used as set values for an optimisation calculation for each of the six periods. The resultant optimal charge mixture is presented in Figure 8 for each of the six periods. Variation in calculated values can be seen in the pellet and briquette charges, which was due to the consideration of manganese in the hot metal. The manganese-rich briquettes are used to optimize the manganese content in the hot metal, and since the level of Mn in the briquettes varied, the calculated charge values also varied. These fluctuations influenced the pellet charge since the briquettes were also rich in Fe.

The calculated peak in the briquette charge for period No. 5 was a consequence of the low Mn content in the briquettes during this period (Table 3). The low calculated charge of limestone in period No. 5 was due to the extra charge of 10kg/thm of BF slag.

This proves that data calculated from the optimised burden calculation model can give results that agree well with operational data, when the comparison is made over a time period consisting of 3-15 days of stable furnace operation.

## **5. Conclusions**

The model showed itself to be an excellent tool for calculating suitable charge mixture and hot-metal and slag composition for a blast furnace under steady and normal operation conditions when using actual yield factors. The results showed good agreement with actual plant data from SSAB Oxelösunds No. 2 furnace. The difference observed between calculated and actual values could be explained by errors in analysing and the lack of control of the flue dust and top gas.

By using an optimising burden calculation, the time to find a suitable charge mixture is greatly reduced, since only one calculation has to be done. Letting the model optimise the charge mixture based on desired hot-metal and slag compositions, only one calculation has to be done to find the optimal result instead of making several trial-and-error calculations to find the most fitting result. So when a material composition or the amount

of a reduction material needs be adjusted, or if the slag basicity is not as expected, the operator can easily determine the new optimal burden mixture with the optimisation model.

Both the yield factors and the distribution coefficients were stable under steady operation conditions. The yield factors and distribution coefficients also had the same values at different periods but under the same operation conditions.

What this study also has shown is that the use of yield factors can be one suitable way to handle the uncertainty of the equilibrium in metal-slag reactions. For all elements (Mn, Si, P and V) except S, the yield factor could be used with no problem in the mass balance for steady operational conditions. For the case of sulphur, one needs to consider the gas phase also. This could be done using a heat balance or possibly with some sort of factor in the ordinary mass balance, e.g. a loss in the soot stream.

The yield factors and distribution coefficients should further be studied under different operational conditions, to determine trends coupled to changes in operational conditions of the furnace. In what time span the distribution coefficients are stable is also of interest. In this study the shortest period was 3 days, and it would be of interest to examine periods not longer than a day or even just during one tapping.

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I would like to thank the Stockholm Foundation of Technology Transfer, TBSS, for their financial support and Bo Sundelin, Kim Kärström, Ann-Kristin Lidar and Claus Røyem at SSAB Oxelösund for providing data and fruitful discussions. I would also like to express my appreciation to Prof. Emeritus Jitang Ma for critically reviewing the manuscript. Thanks are also due to Per Schögarne and Jan Bergstrand at Kobilde & Partners AB for their assistance during the models development.

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**Table 1 Production data from blast furnace No. 2 during 2002**

	Amount	
Blast volume	77400	Nm <sup>3</sup> /h
Blast temperature	1010	°C
Steam	9	g/Nm <sup>3</sup>
Oxygen	3	%
Production	1840	metric ton/24h
Calculated slag	183	kg/thm
B <sub>2</sub>	0.92	
Hot metal		
C	4.5	%
Mn	0.31	%
Si	0.55	%
S	0.069	%
P	0.039	%
V	0.27	%



**Table 2 The actual charge, kg/thm, of material for the six periods.**  
BF = blast furnace

Period	Pellet A	Pellet B	Mn briquettes	BOF slag	Limestone	Coke	Coal	BF slag	Scrap
1	791	528	67	53	26	384,0	90		20
2	791	528	67	53	24	381,5	90		20
3	788	520	80	53	18	383,0	95		20
4	788	520	80	53	15	379,2	95		20
5	788	520	80	53	15	387,0	95	10	20
6	792	527	80	55	24	385,0	95		10

**Table 3 Composition of materials used in the study, [wt-%]**

BF = blast furnace

Material	Pellet A	Pellet B	Mn briquettes	BOF slag	Limestone	Quartzite	Coke	Coal	BF slag	Scrap	Small pellets
Balancing element	Fe	Fe	Mn	PV	CaO	SiO <sub>2</sub>	Constant	Constant	Constant	Constant	Constant
Al <sub>2</sub> O <sub>3</sub>	0.330	0.250	1.130	1.200	0.300	0.400	3.329	1.420	11.300	1.100	0.500
C			1.300				87.067	77.000	0.000	2.000	0.000
CaO	0.350	0.470	9.350 - 11.30	41.65 - 43.55	54.80 - 55.45	1.000	0.000	0.440	32.600	6.800	0.400
Fe	66.800	66.740	55.610	19.500	0.220	0.700	0.400	0.390	0.300	81.000	65.900
K <sub>2</sub> O	0.017	0.035	0.090	0.020	0.020	0.080	0.138	0.120	0.590	0.100	0.030
MgO	1.540	1.450	2.290	8.70 - 9.65	0.85 - 1.0	0.400	0.000	0.190	15.700	1.300	1.570
Mn	0.050	0.085	2.014 - 2.865	2.556 - 2.827	0.080	0.010	0.010	0.004	0.390	0.500	0.070
Na <sub>2</sub> O	0.039	0.041	0.110	0.040	0.040	0.070	0.054	0.033	0.590	0.050	0.040
P	0.008	0.021	0.016 - 0.020	0.240 - 0.253	0.004	0.017	0.011	0.004	0.004	0.018	0.014
S	0.0004	0.0005	0.350	0.080	0.030	0.020	0.566	0.720	1.300	0.003	0.001
SiO <sub>2</sub>	1.700	2.000	5.50 - 6.60	10.4 - 11.6	0.70 - 1.10	98.000	6.469	4.190	34.000	4.600	1.900
TiO <sub>2</sub>	0.360	0.195	0.550	1.170	0.020	0.010		0.060	1.750	0.150	0.290
V <sub>2</sub> O <sub>5</sub>	0.240	0.210	0.26 - 0.30	2.90 - 3.10	0.010	0.010			0.100	0.010	0.220

**Table 4 The average yield factor, calculated for five elements at normal operation for No. 2 blast furnace at SSAB Oxelösund**

Element, i	Average $\eta_i$	Standard deviation	RSD* [%]
Mn	0.74	0.042	5.68
Si	0.18	0.004	2.44
P	1.04	0.034	3.30
V	1.00	0.025	2.47
S	0.21	0.012	5.81

$$* \text{ RSD} = \frac{i : \text{ Standard deviation for the six reference cases}}{i : \text{ Average yield factor for reference case no.1 to no.6}} \cdot 100$$

**Table 5 Standard deviation for slag composition data**

Element	Std error *
CaO	0.739
SiO <sub>2</sub>	0.517
Al <sub>2</sub> O <sub>3</sub>	0.274
MgO	0.497

$$* \zeta_{slag}^i = \sqrt{\left(\sqrt{\%w^i} \cdot K_{cal}^i\right)^2 + \left(\zeta_{samp}^i\right)^2 + \left(K_{samp}^i\right)^2 + \left(\gamma^i\right)^2}$$

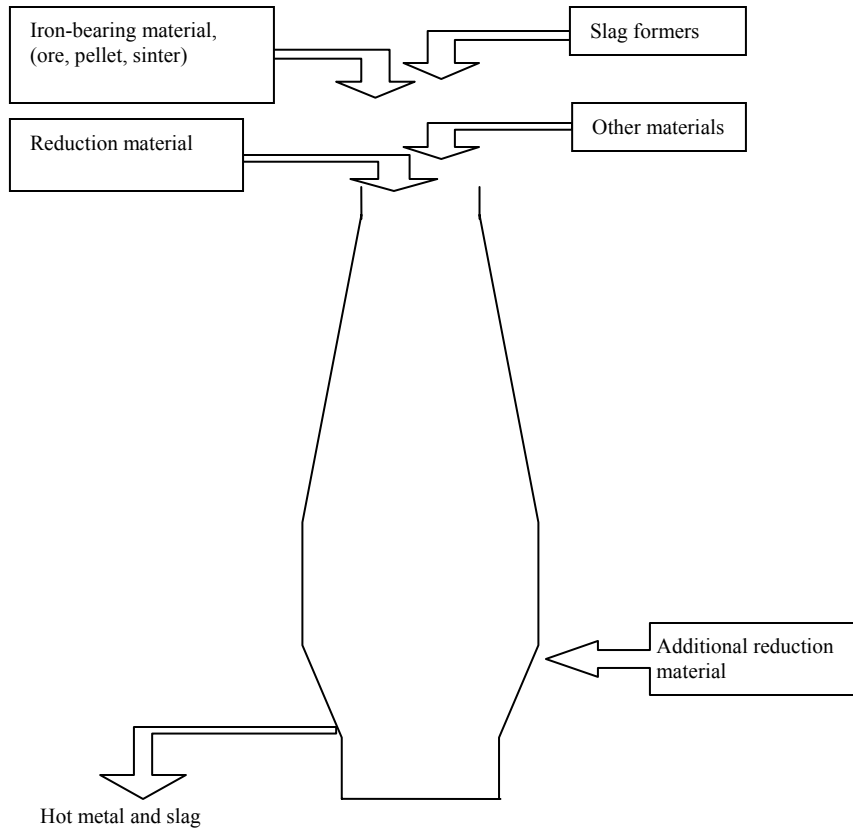
$\zeta_{slag}^i$  = total error for XRF determination of amount  $i$  in slag

$\zeta_{samp}^i$  = standard deviation for sampling error

$\gamma^i$  = standard deviation for control sample

$K_{samp}^i$  = sample preparation error

$K_{cal}^i$  = calibration error factor and  $\%w^i$  = weight percentage of element  $i$  calibration error, standard deviation



**Figure 1. The flow of material in the blast furnace.**

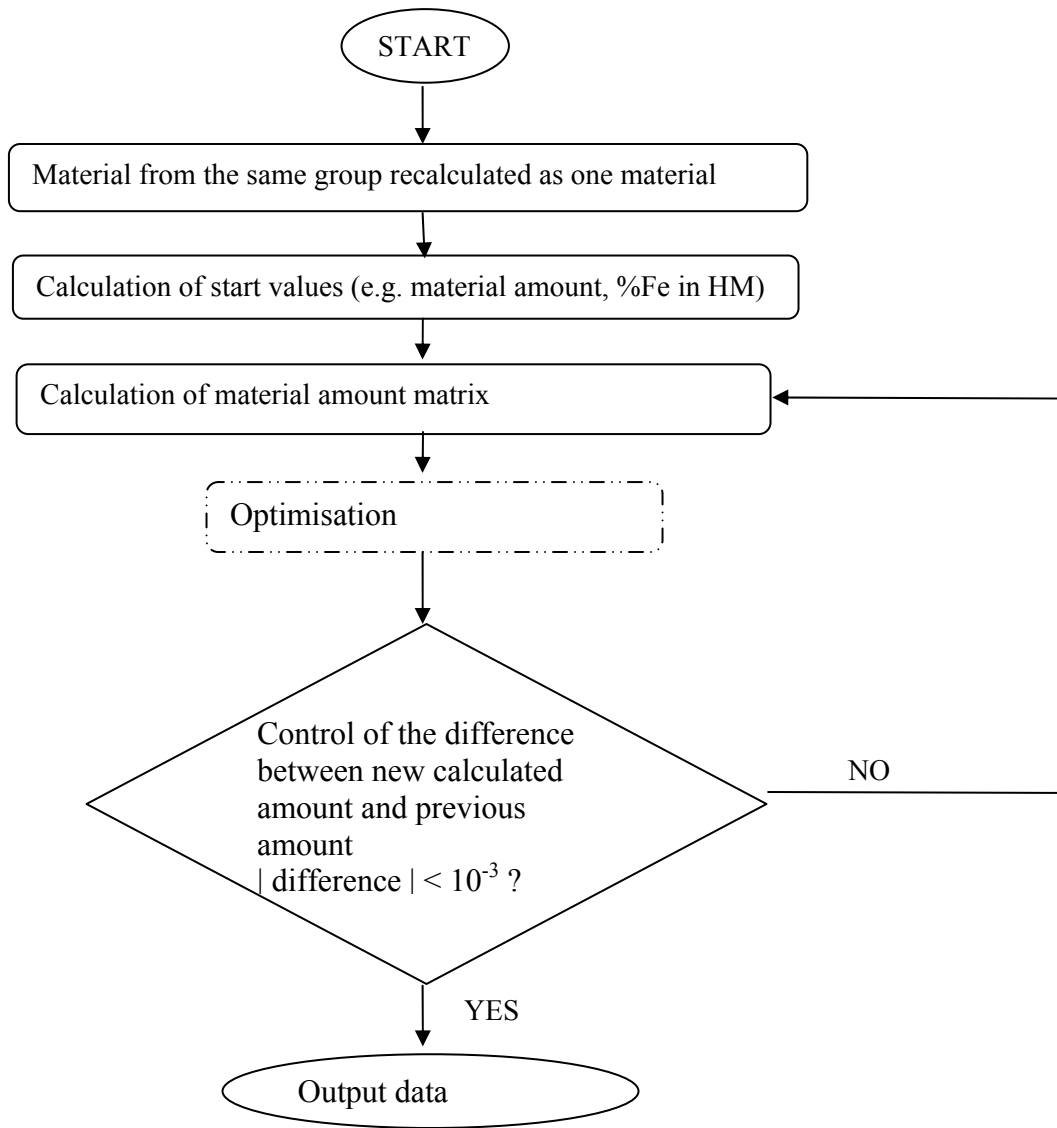
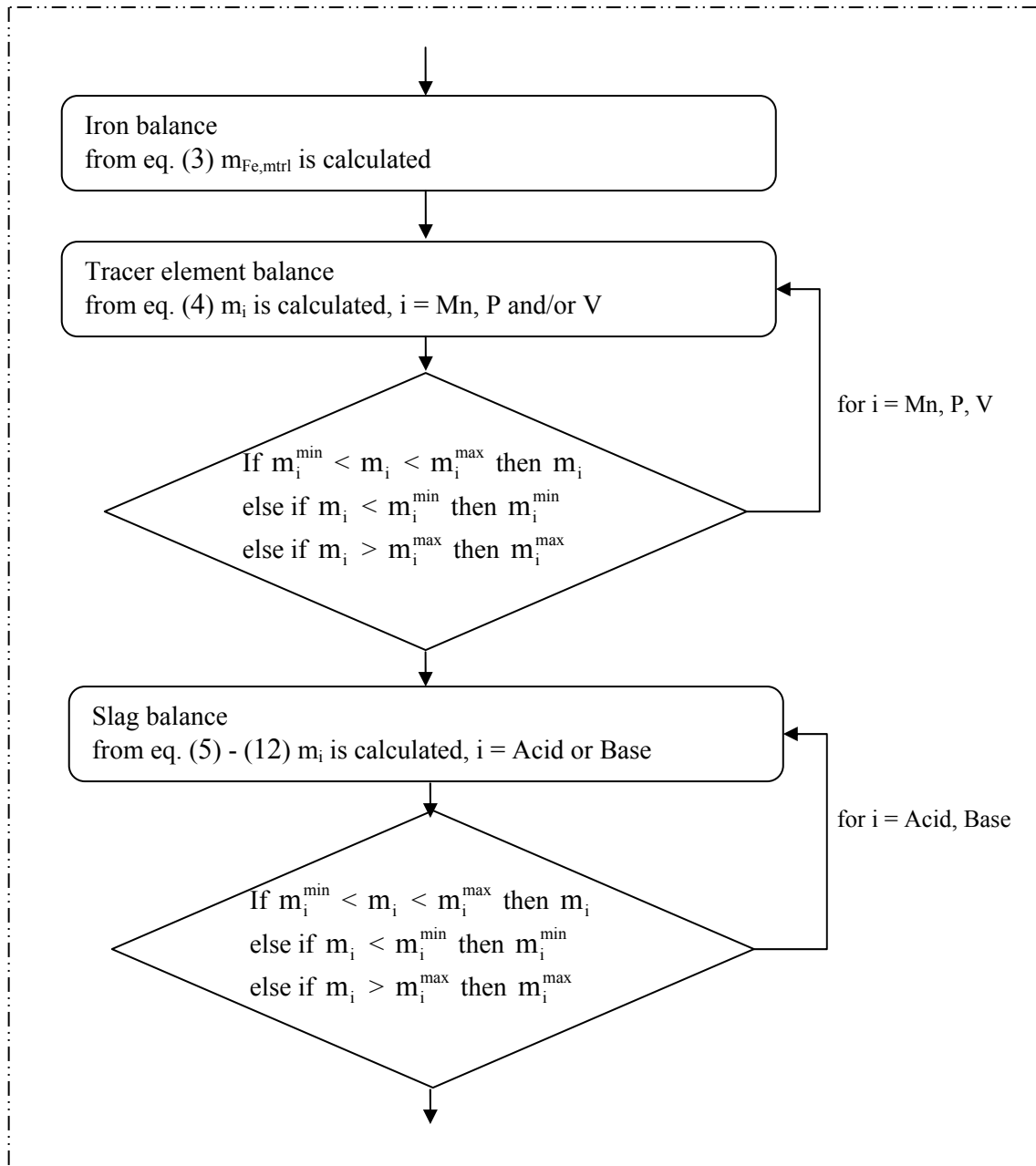
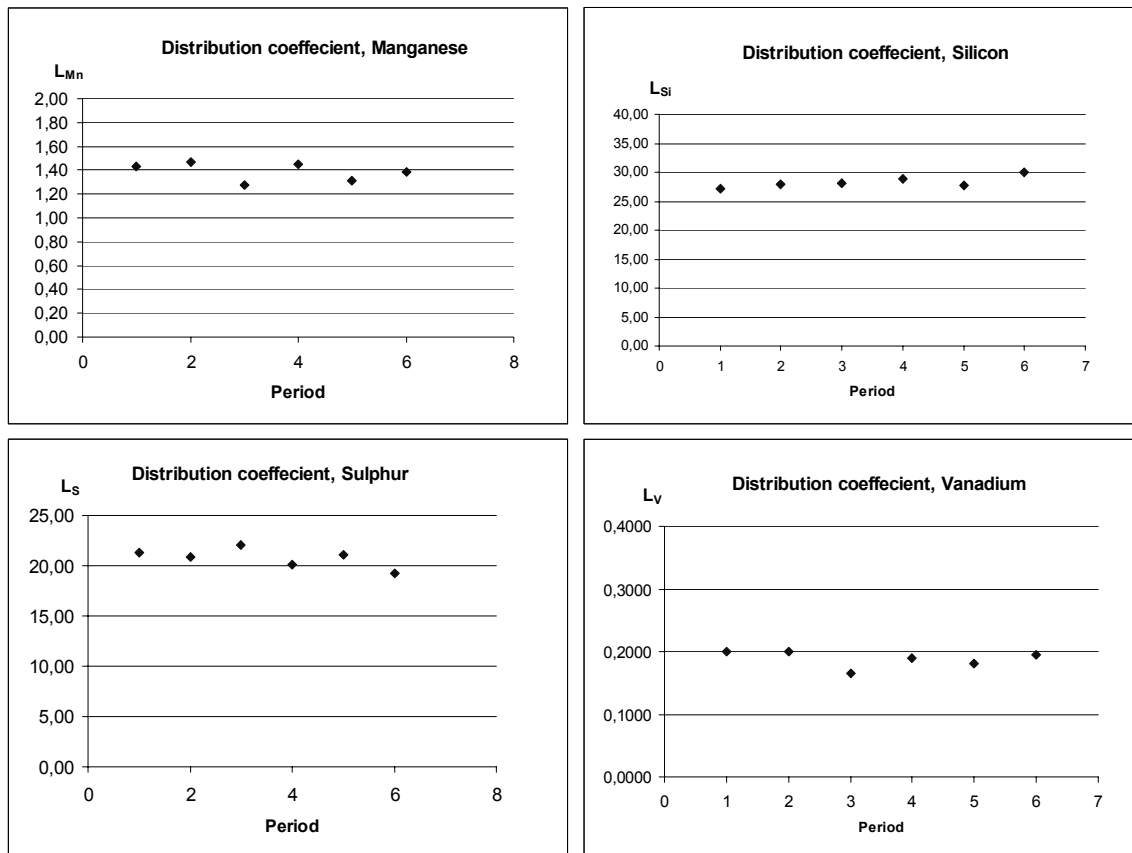


Figure 2 Flowsheet of the burden calculation.



**Figure 3** Details of the optimisation function of the model



**Figure 4** Distribution coefficients for manganese, silicon, sulphur and vanadium calculated for six periods of normal operation of blast furnace No. 2 SSAB Oxelösund, 2002



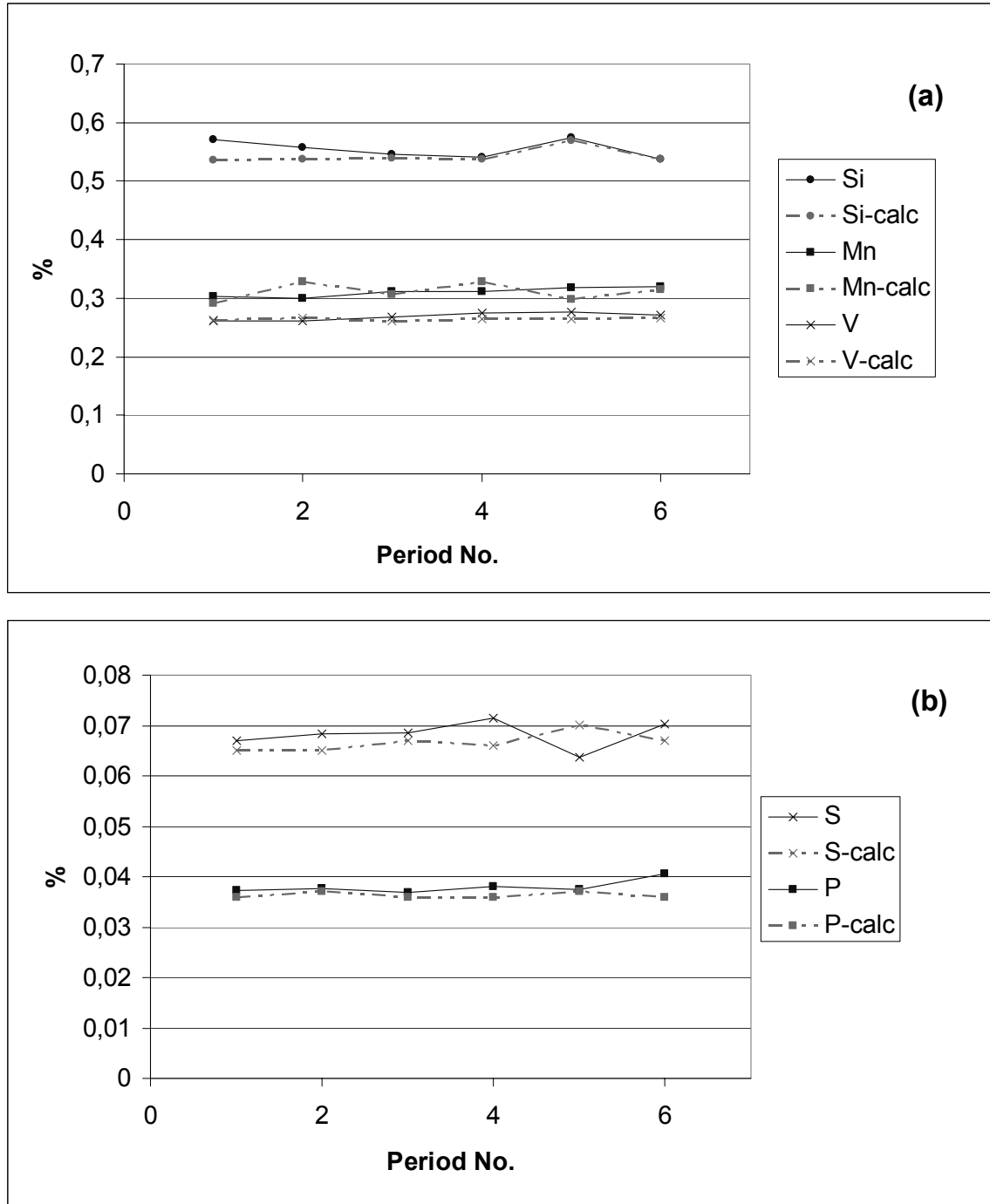


Figure 5 Comparison of actual production values with calculated hot-metal composition data:  
 fig. a) Silicon, Manganese and Vanadium  
 fig. b) Sulphur and Phosphorus

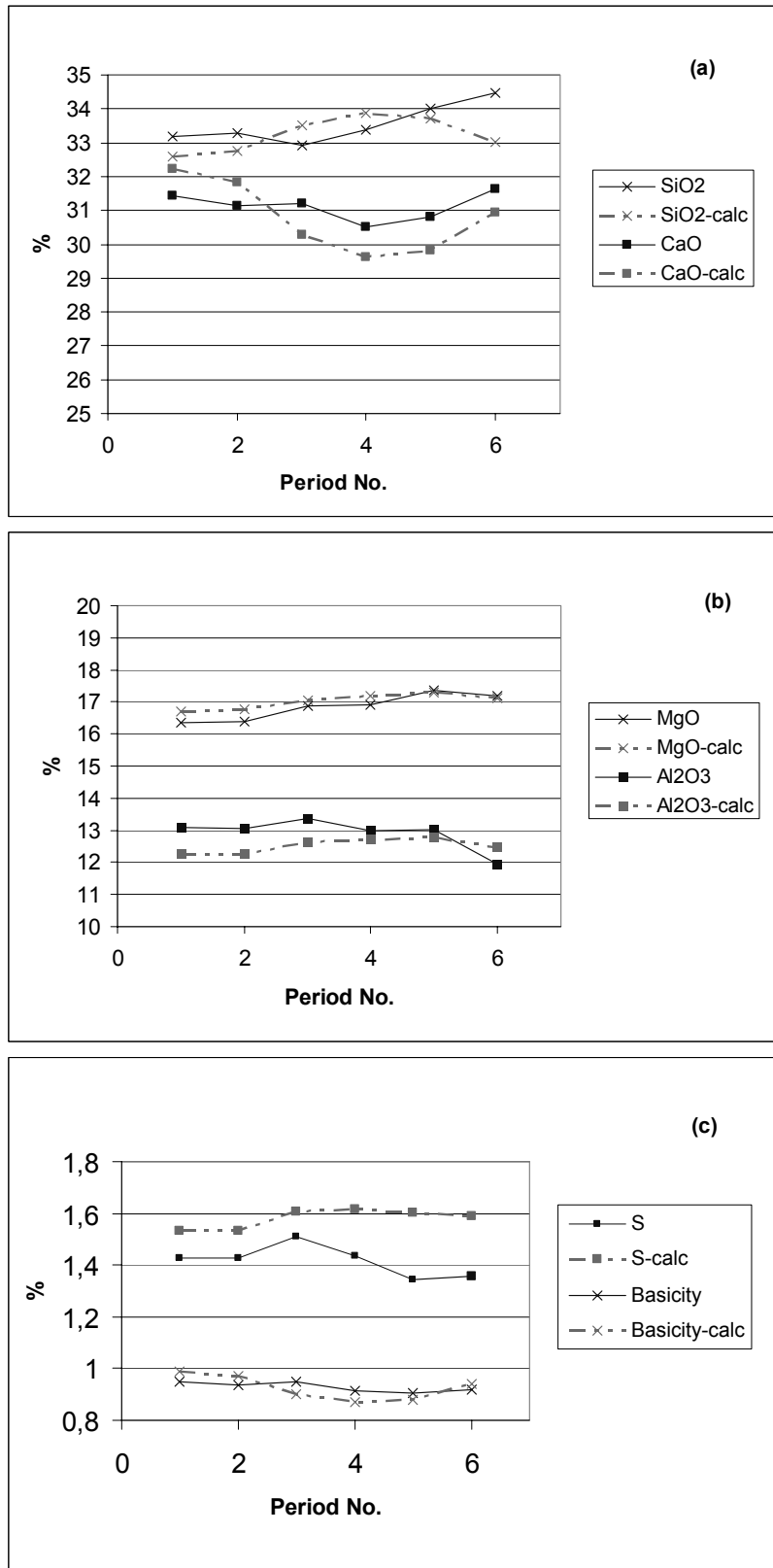


Figure 6 Comparison of actual production values with calculated slag composition data  
fig. a) SiO<sub>2</sub> and CaO, fig. b) MgO and Al<sub>2</sub>O<sub>3</sub> and fig. c) S and Basicity

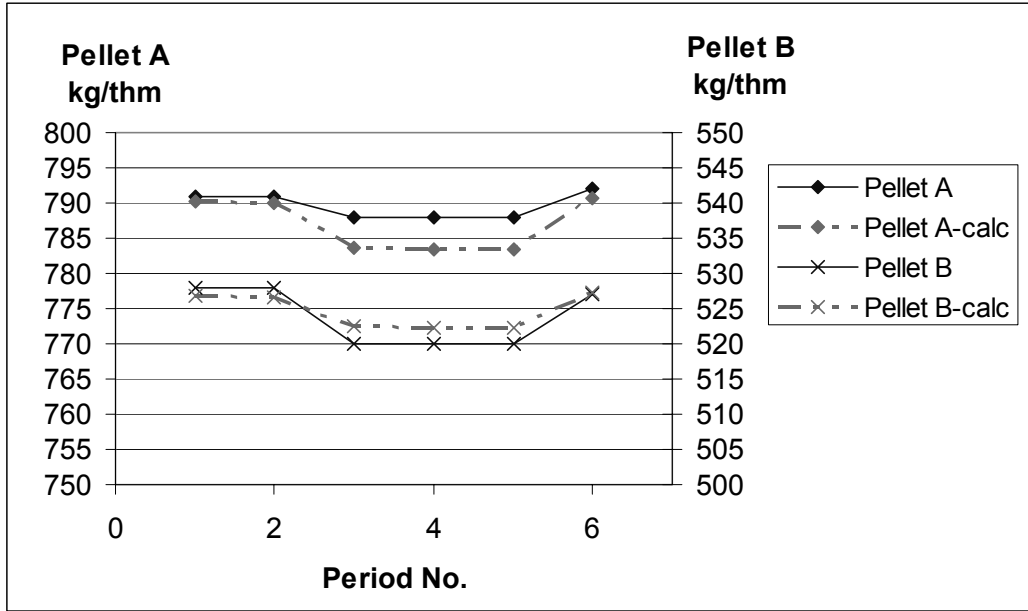


Figure 7 Comparison of actual production values with calculated pellet charge combinations

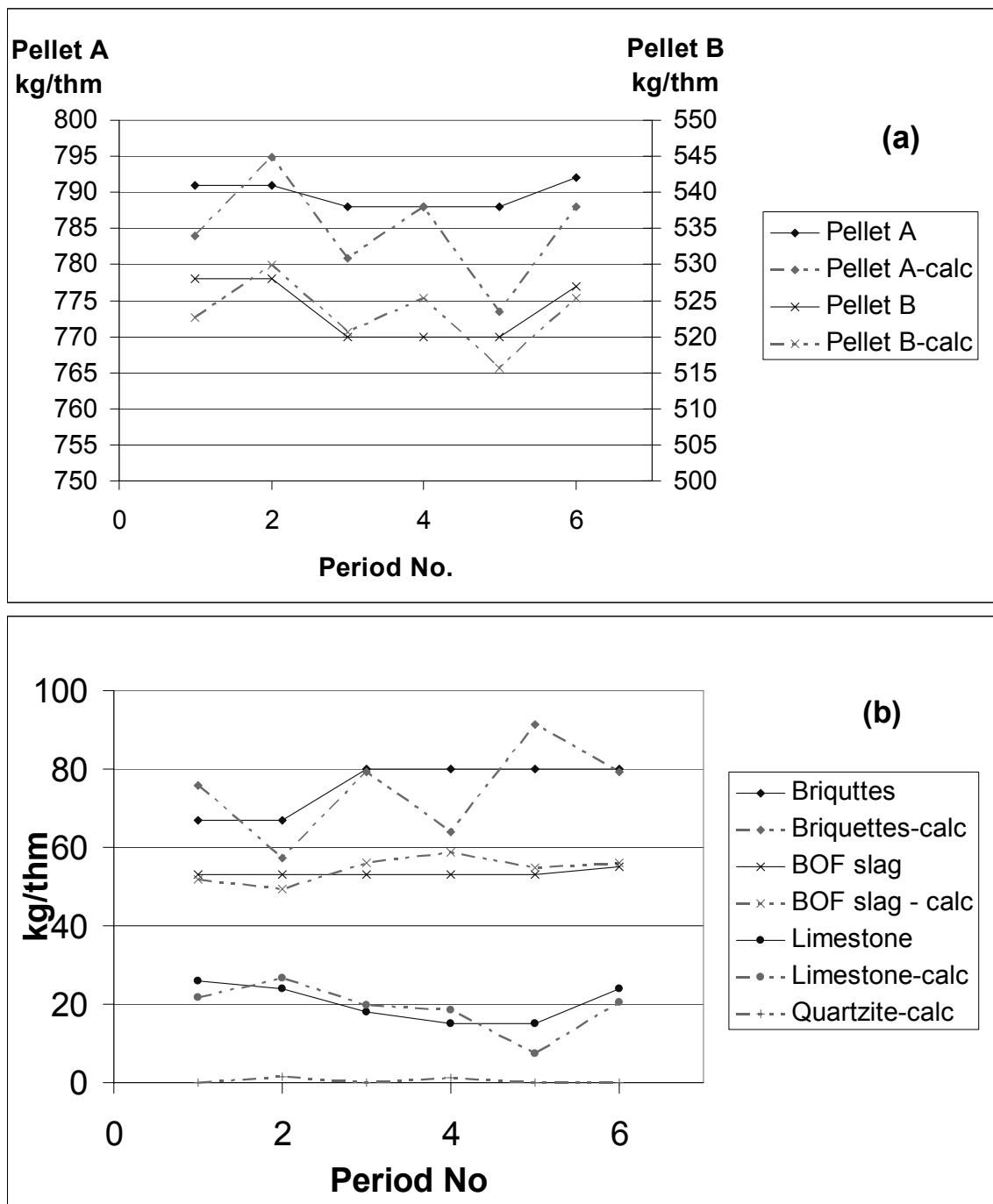


Figure 8 Comparison of actual production values with calculated charged material amounts: fig. (a) Pellet charge, fig. (b) Briquette, BOF slag and limestone charge

## **Supplement 2**

Variations in Hot-Metal and Slag Composition  
During Tapping of the Blast furnace

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ISRN KTH/MSE--03/58--SE+APRMETU/ART

*Submitted to Ironmaking and Steelmaking*

# VARIATION IN HOT-METAL AND SLAG COMPOSITION DURING TAPPING OF THE BLAST FURNACE

## Abstract

In order to determine the quality of the hot metal and the thermal conditions inside the blast furnace, the composition of the hot metal and slag must be known. Obtaining representative metal and slag samples during tapping is thus highly important to blast furnace operation. The study covered in this report has focused on hot-metal and slag composition variation during tapping from a commercial blast furnace. From the results, optimal sampling time points for obtaining elemental concentrations that can be taken as representative for the whole tapping sequence were identified. It was furthermore concluded that the reliability of hot-metal composition data is significantly improved by averaging elemental concentrations determined from two samples, each taken at a particular time point. One sampling, however, was found to be adequate for slag. Results from the study also showed a fairly strong correlation between amounts of silicon and carbon, sulphur and carbon and silicon and sulphur in the hot metal, while a weaker correlation between hot-metal temperature and each of these elements was observed.

**Key words:** hot metal, slag, composition, tapping and blast furnace.

# 1. Introduction

The blast furnace (BF) is a complex non-isothermal high-temperature multiphase reactor which transforms iron ore to liquid hot metal. A variety of reactions and phase transformations occur at different places at different temperatures simultaneously in the furnace. Despite the fact that a large number of advanced instruments have been used for monitoring phenomena and measuring operational data, the blast furnace is still considered a “black box”. The quality of the product as well as the thermal conditions inside the furnace can only be clearly known when the actual composition of the hot metal, as well as the slag, is known. In addition, some components of the hot metal, (especially silicon, carbon and sulphur contents) as well as the temperature of the hot metal, have commonly been used as main indicators of the thermal conditions in the furnace.<sup>1,2</sup> The operators always closely monitor changes in these parameters in daily practice in order to maintain a smooth operation. Consequently, metal and slag sampling during tapping is a significant part of furnace operation as well as control of the quality of the hot metal produced. However, only a few samples of hot metal and slag are normally taken for each tap. This is perhaps based on the assumption that the hot metal and slag in the blast furnace are almost homogenous, or that the compositions of the hot metal and slag are considered to be practically the same during the entire tapping sequence.

The purpose of this study was to investigate variation in the composition of hot metal and slag as well as in the temperature of the hot metal during tapping from a commercial blast furnace. To the authors' knowledge only one previous investigation has studied the change in slag and hot-metal composition during tapping.<sup>3</sup> Naidenov et al.<sup>3</sup> took metal samples every 10 minutes and slag samples every 5 minutes. They presented their data as the ratio of the content at a given sampling time over the average value for a tap. Special attention was paid to the behavior of lead during tapping. Since this study was conducted 25 ago, it cannot fully represent current BF operation conditions. Furthermore, the investigation was based on a sinter burden, while this study has focused on a pellet burden.

Process control of the No.4 blast furnace at SSAB, the furnace used in our study, is to a great extent based on the hot-metal and slag composition determined from a routine sample taken only once every tap, even though a tap can be 2 to 4 hours long. This means that a

very small sample of metal (and slag) is taken as representative for the average composition of a large production amount. Decisions regarding changes in charged materials or process parameters are then based on the results of this sampling. Thus, it is of great importance that the sample reliably represents the entire tap.

The present study has focused on hot-metal and slag composition behaviour during tapping. Results include determination of the best possible time point for sampling in order to obtain composition data representative of the hot metal and slag for the whole tapping sequence for the No. 4 blast furnace at SSAB Oxelösund.

## **2. Method**

### **2.1. Plant trial**

A trial was set up using BF No.4 at SSAB Oxelösund, Sweden in June 2003. The total trial period lasted nearly 3 days (68 hours) and during that time samples of hot metal and slag, as well as temperature measurements of the hot metal, were taken at intervals of 10 minutes. The location of the hot-metal sampling and temperature determination was the area directly following the skimmer. The slag sampling was performed in the first part of the slag runner. The process was running on an ordinary burden mixture and under normal operational conditions. One exception was that an excess of hot metal in the steel shop caused a minor decrease in the blast of 15% for 6 hours towards the end of the trial. The production data for the trial can be seen in Table 1.

### **2.2. Blast furnace information**

#### *2.2.1. General*

Production data from June 2003 for blast furnace No. 4 at SSAB Oxelösund have been used. The No.4 furnace annually produces approximately 1000 ktonnes and it has a capacity of 3000 tonne/24h, a hearth diameter of 8.6 m, and a working volume of 1339 m<sup>3</sup>. The furnace is equipped with a rotating chute and the last relining was done in 1996. During the trial the furnace operated on a 100% pellet burden and had PCI (Pulverized Coal Injection) as a complement reduction material. Slag fluxes (BOF slag, limestone) and manganese (in the form of briquettes) were also added.



The targeted hot-metal composition for the studied blast furnace was: C > 4.25%, Si 0.32-0.72%, S < 0.090%, Mn 0.25-0.35% and V < 0.28%. For the slag, component concentrations of S < 1.8%, MgO < 18% and a basicity > 0.88 were targeted.

### 2.2.2. Routine sampling of hot metal and slag

Inside the blast furnace, the slag with its lower density stays on top of the denser hot metal. So when the furnace opens, the hot metal flows out first, and when the level inside the furnace has decreased, the slag comes. During a routine furnace tapping, one sample of hot metal and slag are taken. These samples are taken at the same location as the trial samples were taken. These two samples are taken after the slag has come, and more specifically, after about half a pot of slag has been tapped. The hot metal is sampled using a lollipop sampler and a scoop is used to sample the slag. About a handful of slag is sampled and poured out on a slag shovel. After the samples have cooled down, the slag is also crushed before it and the hot metal are analysed. Within about 10 minutes the analysis results are sent back to the tapping personnel. The hot-metal sample elemental concentrations, except for carbon, are determined with one of two automatic XRF (X-ray fluorescence) spectrometers, one ARL8680 and one Philips W2400. The carbon concentration is determined using high-temperature decomposition, which converts the carbon to gaseous carbon. The instrument employed is a CS444 from LECO. The slag samples are analysed with the same instrument used for the hot metal.

### 2.2.3. Slag mass calculation

It was deemed of interest to this study to determine the change in slag mass between taps and this was done by calculation after estimating the slag volume and density. First the slag volume in the total number of pots for a tap was measured. At SSAB Oxelösund, the smallest reported unit is a quarter of a slag pot and the total volume of a slag pot is 10 m<sup>3</sup>. The slag density was calculated from Mills' equation based on slag composition:<sup>4</sup>

$$\rho = \frac{M_1x_1 + M_2x_2 + M_3x_3 + \dots}{x_1\bar{V}_1 + x_2\bar{V}_2 + x_3\bar{V}_3 + \dots} \quad (1)$$

where  $M$ ,  $x$  and  $\bar{V}$  are the molecular weight, mole fraction and the partial molar volume, respectively, and the subscripts 1, 2 and 3 denote the various oxide constituents of the slag.

The calculated slag density was multiplied by the volume of slag in the pots and an estimated value of the slag amount for each tap was obtained. This procedure of estimating the slag volume of course leaves room for error in the calculated slag amounts, estimated to be up to a maximum of 12% for the plant trial.

### **3. Results and discussion**

#### **3.1. Main components for BF process control**

The BF process is to a great extent controlled using the hot-metal and slag composition data. Thus, it is very important that the information upon which control decisions are based be reliable. The standard deviation for the elements in the hot metal, denoted by [Me], and components in slag, denoted by (MeO), was calculated for each tap. All temperature measurements (except for the first which was excluded) and samples taken throughout each tap were used. The total accuracy in determination of elemental/component concentrations in the hot metal or slag was calculated using the equations given in Table 2.<sup>5</sup>

If the standard deviation for an elemental concentration was of the same magnitude or less than the analysis error, the determination of that element was done with inadequate accuracy. The standard deviation has to be greater than the analysis error, otherwise the variation in the particular element or component amount is too small to be of any significant use in the process control of the blast furnace. From this trial, Table 3 presents data on the analysis error for the element concentration in the hot metal, minimum and maximum values determined, the intervals of the standard deviations for individual taps and the standard deviation based on the average composition for all taps. As could be seen, only four of the elements, namely [C], [Si], [S] and [Ti], had a standard deviation variation that was greater than their corresponding analysis error, which means that these elements showed significant variation during the trial. Thus, these elements could be looked upon as reliable indicators for BF process control during the studied production period. For manganese and vanadium, the standard deviations were at the same level as the analysis error, which made [Mn] and [V] less useful for process control during the studied production period. Furthermore, [Ni], [P], [Cr], [Cu] and [Mo] were taken as poor process control indicators during the same period.

However, since manganese in hot metal is a very important element for the steel shop in Oxelösund and vanadium for control of the raw material, these elements have been taken into account in this study. Titanium though, is not commonly used for BF process control and was not considered in this study.

In Table 4 the corresponding slag-component data are presented. It was observed that ( $\text{Al}_2\text{O}_3$ ), ( $\text{MnO}$ ), ( $\text{V}_2\text{O}_5$ ), ( $\text{TiO}_2$ ), ( $\text{K}_2\text{O}$ ) and ( $\text{S}$ ) showed significant variation during tapping, whereas ( $\text{CaO}$ ), ( $\text{SiO}_2$ ), ( $\text{MgO}$ ) and ( $\text{FeO}$ ) showed less considerable concentration variation. Thus, the latter were considered to be less appropriate for BF process control during the studied production period.

### **3.2. Changes in hot-metal composition during tapping**

The BF process is often not considered as one that responds swiftly to changes. However, this study showed that there was a continuous variation in hot-metal and slag compositions during tapping. The variation during the 68-hour trial in carbon, silicon and sulphur contents in the hot metal can be seen in Fig. 1. It was found that the composition changed during tapping, but showed a connection to the previous tap. The last sample composition from a tap was at the same level as the first samples in the next tap. This behaviour was most obvious for silicon and sulphur. Examples of more detailed variation within three different taps can be seen in Fig. 2. Fig. 2a illustrates a tap of stable behaviour, while the tap in Fig. 2b illustrates one of larger variation in composition. More specifically, the latter shows a significant drop in silicon and carbon just before the slag arrives and an increase in sulphur at the same time. In Fig. 2c, the tap starts with a rising trend in the amounts of silicon and carbon, whereas the sulphur amount decreases, and before the slag arrives, the composition becomes more varied for all three elements.

#### *3.2.1. Hot-metal temperature*

Generally the temperature of the hot metal had the most obvious trend of all parameters investigated during the different parts of tapping. In Fig. 3 all measured temperatures during tapping were within the marked interval; this has also been observed in the literature.<sup>6,7</sup> The hot-metal temperature increased about  $10^\circ\text{C}$  to  $70^\circ\text{C}$  during the first part of tapping. After this increase, the temperature levelled off until the end, where a small increase of about  $15^\circ\text{C}$  occurred. The first increase could be due to the loss of heat to the

surroundings such as the runners. This argument is supported by the results by Oya and Hayasaki<sup>7</sup>, where it was found that the actual hot-metal temperature directly after the start of tapping was much higher than the temperature measured after the skimmer. The second temperature increase could be due to the slag arrival, where the slag forms a “lid” that isolates the hot metal in the main runner. This, in turn, reduces heat radiation to the surroundings from the hot metal. It should also be noted that none of the elements in the hot metal showed the same unmistakable behaviour during tapping as was observed for the hot-metal temperature.

### 3.3. Variation in slag composition during tapping

#### 3.3.1. Basicity and sulphur

A variation in the slag composition during taps was observed. Fig. 4 presents the variation in the slag sulphur content and basicity, defined in equation (2), for the whole trial.

$$\text{basicity} = \frac{(w\% - CaO)}{(w\% - SiO_2)} \quad (2)$$

The observed changes in sulphur content during tapping were considerable. In tap No. 21 (afternoon the 6<sup>th</sup> of June), the relative decrease was 19% from 1.6 to 1.3 wt%. The basicity data did not show a general upward or downward trend and the highest relative increase was 7% (0.92 to 0.99).

In the three graphs in Fig. 5, the changes over three specific taps can be seen. Fig. 5a shows very high values of sulphur and basicity, whereas Fig. 5b shows very low values and in Fig. 5c, a more stable trend can be identified.

A correlation between slag sulphur content and basicity was found by looking at more than one single tap, as in Fig. 4, where a decrease in basicity could be correlated to a decrease in sulphur content. However, when studying one single tap, this correlation could not be observed. This is exemplified in Fig. 5a where the basicity could have an increasing or decreasing trend, but the sulphur always had a decreasing trend. High basicity promotes sulphur removal in the hot metal and therefore the results illustrated in Fig. 4 could be expected.<sup>8</sup>

The amount of BF slag at SSAB has actively been decreased during the last 15 years to levels that are well below the EU average (approx. 250 kg/thm), and sometimes as low as

150 kg/thm.<sup>9</sup> Fig. 6 presents the calculated slag amounts for the trial. It can be seen that the slag volume fluctuates, which can be due to changes in the process status during the trial.

### 3.3.2. *An alkali washout*

A washout of alkali occurred during the trial (illustrated in Fig. 7) which led to a change in slag composition (average values from each tap) in the form of an increase in K<sub>2</sub>O. For the hot metal, a decrease in carbon, silicon and manganese, and an increase in sulphur was observed. The alkali washout is not just notable by a higher K<sub>2</sub>O content in the slag, but as seen in Fig. 4, both the sulphur content and basicity decreased dramatically on the morning the 5<sup>th</sup> of June, when the alkali washout started. A low basicity promotes alkali washout.<sup>8</sup> A decrease in the basicity would mean that the silica content in the slag increased. If it is assumed that the silicon content in the furnace is constant, this should lead to decreased silicon content in the hot metal, and with a low basicity, sulphur removal should decrease and the sulphur content in the hot metal should increase. The low silicon level could also be a sign of a weaker reducing environment and it is not unlikely that the carbon content in the hot metal could be decreased under these circumstances. Since the heat loss increased just before the alkali washout, a further explanation could be that the alkali skull with a mix of oxides (e.g. FeO, K<sub>2</sub>O) was released from the furnace wall. These oxides would react with carbon and silicon in the hot metal and be reduced, causing a drop in [C] and an increase in SiO<sub>2</sub> in the slag according to the following equations:



Thus, the slag basicity would decrease and the sulphur removal would be impeded or even reversed, explaining the increase in [S].

It should be noted that the alkali washout did not influence the standard variation in hot-metal and slag composition during tapping. However, the slag amount was slightly influenced by the alkali washout that began on the morning June 5<sup>th</sup>. The calculated slag amount in Fig. 6 peaked during the alkali washout, which could be explained by the above-mentioned release of oxide skulls from the wall.

### 3.4. Correlation of hot-metal elements

As pointed out before, temperatures taken upon tapping are often used as indicators of the furnace internal thermal state. During this trial the hot-metal temperature was measured at the same time as the hot-metal samples were taken. Since the temperature had a more or less constant increase during tapping (Fig. 3), it was difficult to find a typical point of time where the temperature value could represent the entire tap. Temperatures measured 30 minutes after the start of tapping (normalised time between 0.13-0.38, see Fig. 3) were taken as representative values. These temperatures were plotted versus the average content of carbon, silicon and sulphur in the hot metal for each tapping (Fig. 8). It was clear that the hot-metal temperature showed only a weak correlation with the other elements in the hot metal. Therefore, the use of hot-metal temperature as the only indicator of the furnace thermal state should be used with care. Under the conditions during this trial, Fig. 8 clearly showed that the temperature was not a parameter that could clearly predict the thermal conditions in the SSAB Oxelösund No.4 furnace.

The correlation between elements in the hot metal was on the other hand strong. In Fig. 9 the correlation between carbon, silicon and sulphur can be seen. The strongest correlation could be found between silicon and carbon. The silicon-sulphur correlation indicated a close connection between these elements, whereas the sulphur-carbon correlation was more modest.

The reason for the above-observed relationships could be that high contents of carbon and silicon in the hot metal result from the furnace operating under strong reducing conditions (*i.e.* low oxygen activity). This would be beneficial for sulphur refining of the hot metal, which can be concluded from the expression of the equilibrium sulphur-distribution ratio in equation (5)<sup>10</sup>:

$$\frac{(\%S)}{[\%S]} = K \cdot \frac{f_S \cdot C_S}{a_O} \quad (5)$$

where (%S) and [%S] is the sulphur content in slag and hot metal, respectively. The parameter  $C_S$  is the sulphide capacity of the slag (*i.e.* the ability of the slag to absorb sulphur),  $f_S$  is the activity coefficient of sulphur in the hot metal, and  $a_O$  is the activity of oxygen in the hot metal. The equilibrium constant  $K$  in equation (5) represents the reaction:



and can be written as<sup>10</sup>

$$\log K = -\frac{935}{T} + 1.375 \quad (7)$$

Furthermore, if it is assumed that Wagner's equation can be applied, the activity coefficient  $f_S$  can be expressed by:

$$\log f_S = \sum_i (e_S^i \cdot [\%i]) \quad (8)$$

where  $e_S^i$  denotes the interaction parameters for sulphur in liquid iron and [%i] dissolved elements in the liquid iron (carbon, silicon, etc.). Carbon and silicon show positive interaction on sulphur, which can be seen from their interaction parameters  $e_S^C = 0.11$  and  $e_S^{Si} = 0.063$ .<sup>11</sup> Thus, higher contents of carbon and silicon in the hot metal increase the value of  $f_S$  (and the activity of sulphur) and benefit sulphur refining. This could be one of the reasons why high carbon and silicon contents were observed in correlation with lower sulphur contents in the hot metal.

### 3.5. Optimum sampling time

#### 3.5.1. Single sampling of hot metal and slag

Differences were revealed in comparing the routine sample composition with the average composition from the taps from blast furnace No.4 at SSAB Oxelösund. In order to compare the average composition values from the trial with the routine samples taken by the furnace operators, a relative difference,  $\Delta_i$ , was calculated

$$\Delta_i = \frac{\%i_{routine} - \%i_{average\ trial}}{\%i_{average\ trial}} \cdot 100 \quad (9)$$

where  $i$  represents the element or component in the hot metal or slag.

Differences of up to 15% were easily found for the hot metal, and for the slag the cases of discrepancy were even greater, sometimes more than 50%. The calculated relative difference (see equation (9)) for some of the hot metal elements and slag components can be seen in Fig. 10 and Fig. 11. Taps 1-9 could be regarded as normal taps. In the No.10 tap, the alkali washout started, but that could not be noticed in the relative difference  $\Delta_i$ . Tap No.18 showed a very different  $\Delta_i$ , and this was probably due to the fact that the routine sample was taken when the tapping had a huge fluctuation. The smallest discrepancy in

hot-metal composition was found for carbon, where the routine samples were around 0-5% lower than the actual carbon average for the tapping. In the slag, CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgO all had a relative difference  $\Delta_i$  of less than 4%, whereas the other slag components showed considerably higher discrepancies. These observations indicate that a routine sample would be valid only for five components; carbon in hot metal and CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgO in slag, and therefore, the routine sampling strategy should be changed in order to obtain more reliable representative values for the other elements.

### 3.5.2. *Probability evaluation of sampling time*

In order to determine the optimum sampling time during the tapping of BF No.4, average elemental concentrations for the hot metal and slag were calculated for each entire tap from analysis results of the samples taken at 10-minute intervals throughout tapping. Thereafter, the variation in C, V, S, Si and Mn in the hot metal and S, CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, MnO, V<sub>2</sub>O<sub>5</sub> in the slag and slag basicity were studied to determine which time point best corresponded to the average element or component concentration.

The average value could occur at one or more times during the tapping and the search for an average composition value for the hot metal was divided into two general time spans. The first time span was defined as being after the start of the tapping, but before the start of the slag flow (Fig. 12), while the second time span was defined as being after the start of the slag flow up until the end of tapping (Fig. 13). In general, the average concentrations of the studied elements pertaining to the first time span (Fig. 12) were identified with one of the three following periods: within 20 minutes after the tap startup, 20-30 minutes after tap startup and 30-50 minutes after tap startup. The second time span (Fig. 13) was divided into the following four time periods: at slag arrival, and within 20 minutes, 20-30 minutes after, and more than 30 minutes after the start of slag flow.

In studying Fig. 12 in detail, we can see that the results indicate a likelihood of roughly 28% for obtaining a sample which was representative for the average carbon concentration of the whole tap within 20 minutes after the startup of tapping. For the time period of 20-30 minutes after tap start, the probability increases to 44% and 30-50 minutes after tap start it is 28%. Looking at the second time span, illustrated in Fig. 13, the probability of taking a sample of representative carbon content was 35% within 20 minutes after the start of the slag flow.



The corresponding results for the slag components are shown in Fig. 14. The average concentration of the studied slag components was obtained in the trial during one of the four following periods: within 20 minutes of the start of slag flow, 20-30 minutes after, 30-50 minutes after and more than 50 minutes after the start of slag flow.

Determining one single common time period that had the highest probability of returning a representative tap sample for the average content of all the studied hot-metal elements was impractical. For example, after tap startup the highest probability of obtaining an average concentration value for [C], [S], [Si] and [Mn] was during the short time period of 20-30 minutes after tap startup, but for [V] the best time period was within 20 minutes of tap startup. The time span defined as being after the start of the slag flow showed even greater discrepancies in the studied elements. The best time, for example, for obtaining a sample containing average [V] and [S] amounts for a tap was within 20 minutes after the start of slag flow, but the corresponding period for [Si] and especially [Mn] was just at the start of the slag flow. For [C], results showed sampling within 20 minutes after start of the slag flow to have a slightly higher probability of obtaining an average C concentration value compared to other time periods. These observations clearly show that obtaining only a single sample which reflects the average hot-metal composition by containing representative average concentrations of all of the elements for a tap was practically impossible.

### 3.5.3. *Double sampling of hot metal*

Since it was found to be impractical to use only one sample to represent the composition of the hot metal during tapping of the SSAB No.4 furnace, it was decided that the hot-metal sampling should be extended to two samples per tapping to explore the possibility of increasing the reliability of the results. The results in Fig. 12 suggest that for the hot metal, the average elemental concentration can be found with 70% accumulated probability within 30 minutes after the start-up of tapping. Within 20 minutes after the slag starts to flow, there is a 55% accumulated probability of obtaining a sample that represents the average hot-metal composition, as seen in Fig. 13.

Based on these observations, two hot-metal sampling times for each tap were selected: (i) one taken 30 minutes after the start of the tapping and (ii) one taken 20 minutes after the slag had started to flow. Thereafter, a double-sample average for the hot-metal composition

was calculated for each tap. The double-sample averages for hot-metal concentrations were then compared with the corresponding values averaged from all tap samples by using equation (10).

$$\Delta_i^{\text{dbl}} = \frac{\%i_{\text{double-sample average}} - \%i_{\text{average trial}}}{\%i_{\text{average trial}}} \cdot 100 \quad (10)$$

The results are shown in Fig. 15, where it can be seen that the absolute values of  $\Delta_i^{\text{dbl}}$  for  $i = [\text{C}], [\text{Si}], [\text{Mn}]$  and  $[\text{V}]$  are less than 6%. This is a significant change compared to Fig. 10, where the relative difference  $\Delta_i$  values could be more than 15%. The  $\Delta_S^{\text{dbl}}$  value for  $[\text{S}]$  is also reduced compared to Fig. 10a. It can also be seen that the variation in the  $\Delta_S^{\text{dbl}}$  value decreased and that it generally became less than zero with the double-sample average. For carbon, the  $\Delta_C^{\text{dbl}}$  value was greater than zero with double-sample average, meaning that the double-sample average elemental concentration is greater than the tap average. For  $i = [\text{Mn}]$  and  $[\text{V}]$ , the  $\Delta_i^{\text{dbl}}$  values in Figure 15b show less variation compared to Fig. 10b, and for  $[\text{V}]$  the  $\Delta_V^{\text{dbl}}$  value generally shifted to values greater than zero. The last tap (No. 21) was exceptionally long, almost 4 hours. This circumstance could have led to less reliable  $\Delta_i^{\text{dbl}}$  values for the hot-metal elements plotted in Fig. 15b for that particular tap.

The overall result is that if two samplings of hot metal are introduced, values that better represent the average hot-metal elemental concentrations for a tap can be obtained. Since only a few elements were considered to be reliable for BF process control in this study, it is unnecessary to carry out a complete elemental analysis for both hot-metal samples. One of the two samples could be analysed for carbon, silicon, sulphur, vanadium and manganese concentrations only, which would be enough to get a representative average.

#### 3.5.4. Slag sampling

For the slag, it was suggested that one sample should be adequate to get a representative composition. One reason for this choice was that the time span for the slag flow is usually much shorter compared to the total time span for the hot-metal flow. However, in regards to the procedure applied at the plant today, the point of time for slag sampling should be changed. Fig. 14 shows that the accumulated probability of obtaining the average concentration for any of the studied slag components was more than 50% if the sample was

taken within thirty minutes after the slag started to flow. Since the probability of obtaining an average concentration value for almost all of the slag components was highest for sampling within 20 minutes after the start of slag flow (and the suggested second hot-metal sample being at 20 minutes after the start of slag flow), the new slag sample time was set to 20 minutes after the slag arrival.

Fig. 16 shows the difference, expressed as a  $\Delta_i^{\text{dbl}}$  value from equation (10), between slag component concentrations in the samples taken 20 minutes after the start of slag flow and the tap average concentrations. In studying Fig. 16 and Fig. 11, it can be observed that the values determined from samples taken 20 minutes after the start of the slag flow are closer to the tap average concentrations compared to those corresponding to slag samples taken in accordance with the regular plant procedure. It can also be seen that the variation is significantly decreased. The advantage of taking a slag sample at 20 minutes after start of the slag flow compared to a routine sampling is thus readily apparent.

## 4. Conclusions

The hot metal and slag tapped from the blast furnace showed continuous variation in composition during tapping. For the hot metal there was an obvious change in composition at the point when the slag starts to flow. It is therefore impossible for a single sample to reflect the average hot-metal composition. With two hot-metal samples, more accurate average elemental concentrations were calculated, which could more reliably be used to represent the average hot-metal composition for the whole tap. By introducing more than one sampling, the natural variation in the composition of the hot metal (and slag) during tapping of the BF over longer time periods and under different operational conditions could be examined, thus helping to improve BF process control. For blast furnace No.4 at SSAB Oxelösund, this study's findings suggest that two samples of hot metal should be taken, one 30 minutes after the start-up of tapping and one 20 minutes after the start of slag flow.

In general, decisions on changes in BF process control should be made based on elements and components in hot metal and slag that have a concentration with a standard variation higher than the corresponding analysis error. In the present study, carbon, silicon, sulphur and vanadium in hot metal met this requirement and were therefore considered

suitable parameters for process control. For the slag,  $\text{Al}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{TiO}_2$ ,  $\text{K}_2\text{O}$ ,  $\text{V}_2\text{O}_5$  and S were deemed suitable for process control during the trial period.

Another finding of this study was a strong correlation between amounts of silicon and carbon, sulphur and carbon and silicon and sulphur in the hot metal, and a weaker correlation between hot-metal temperature and each of these elements. It is often suggested that there is a clear correlation between temperature and silicon, but the present study did not find evidence to support this.<sup>1,2,8</sup> No reasonable explanation could be found as to why this was the case in this study and the authors feel that it is worthwhile to investigate the correlation between temperature and silicon in the future.

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**Table 1 Production data from BF No.4 at SSAB Oxelösund for the trial period in June 2003**

	Amount	
Blast volume	114700	Nm <sup>3</sup> /h
Blast temperature	1033	°C
Steam	7.5	g/Nm <sup>3</sup>
Oxygen	4.8	%
Production	2858	metric ton/24h
Cooling effect	22796	MJ/h
Material charged		
Pellet	1427	kg/thm
Slag fluxes (BOF-slag and limestone)	~70	kg/thm
Mn briquettes	65	kg/thm
Coke	~360	kg/thm
PCI	~100	kg/thm

**Table 2 Equations and terms used in calculating the analysis error [5]**

$$\zeta_{HM}^i = \sqrt{(\zeta_{cal}^i)^2 + (\zeta_{samp}^i)^2 + (\gamma^i)^2}$$

$$\zeta_{slag}^i = \sqrt{(\zeta_{cal}^i)^2 + (\zeta_{samp}^i)^2 + (K_{samp}^i)^2 + (\gamma^i)^2}$$

$$\zeta_{cal}^i = \sqrt{\%w^i} \cdot K_{cal}^i$$

Term	Description
$\zeta_{HM}^i$	total analysis error for XRF determination of i in hot metal
$\zeta_{slag}^i$	total analysis error for XRF determination of i in slag
$\zeta_{cal}^i$	calibration error, standard deviation
$\zeta_{samp}^i$	standard deviation for sampling error
$\gamma^i$	standard deviation for control sample
$K_{cal}^i$	calibration error factor
$K_{samp}^i$	sample preparation error
$\zeta_{HM}^i$	total analysis error for XRF determination of i in hot metal
$\%w^i$	weight percentage of element i

**Table 3 Variation and standard deviation in hot-metal elemental concentrations [w-%]**

	Standard deviation for the trial period	Standard deviation intervals for individual taps	Minimum value determined	Maximum value determined	Analysis error $\zeta_{HM}^i$	Representative for BF process control
Hot-metal temperature	5.5°	6° – 18°	1441°	1518°	3° *	Yes
C	0.12	0.07 - 0.19	4.08	4.95	0.07 *	Yes
Si	0.08	0.03 - 0.12	0.41	0.93	0.05	Yes
S	0.008	0.003 - 0.01	0.03	0.08	0.004	Yes
V	0.006	0.006 - 0.016	0.25	0.32	0.006	Yes / No
Ti	0.021	0.014 - 0.044	0.092	0.26	0.007	Yes
Fe	0.14	0.06 - 0.21	93.47	94.36	--	Yes
Mn	0.01	0.01 - 0.03	0.24	0.36	0.01	Yes / No
Ni	0.002	0.001 - 0.007	0.017	0.037	0.008	No
P	0.001	0.001 - 0.002	0.034	0.044	0.004	No
Cr	0.000	< 0.001	0.036	0.041	0.006	No
Cu	0.001	< 0.001	0.003	0.022	0.002	No
Mo	0.000	< 0.000	0.000	0.002	0.004	No

\* Not from equations in Table 2<sup>5</sup>

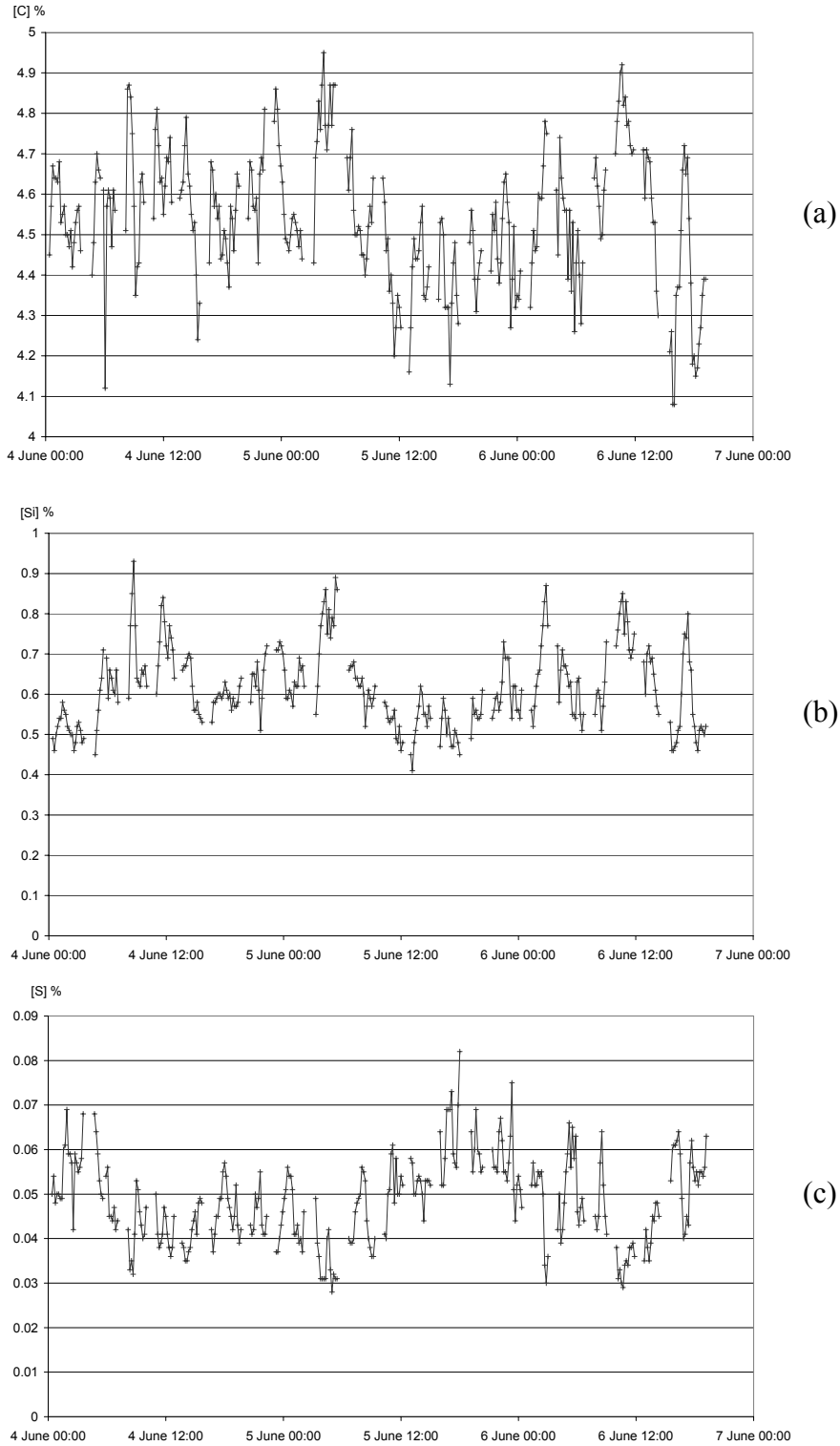


**Table 4 Variation and standard deviation in slag component concentrations [w-%]**

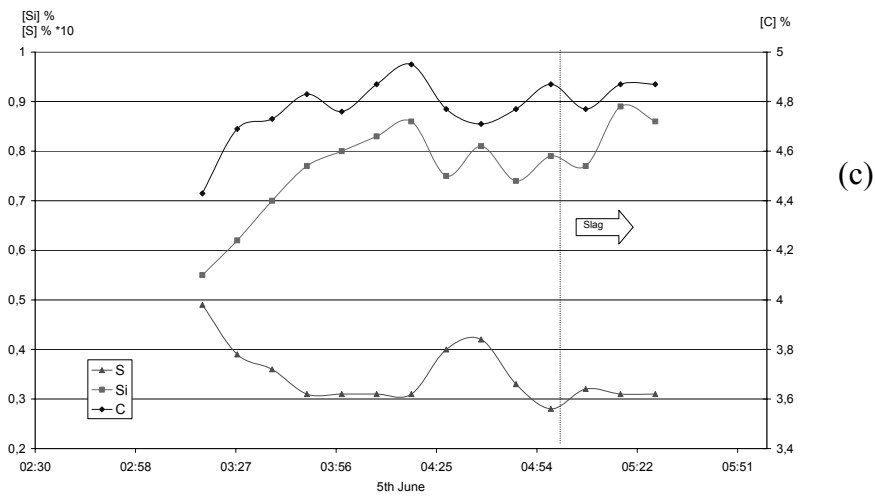
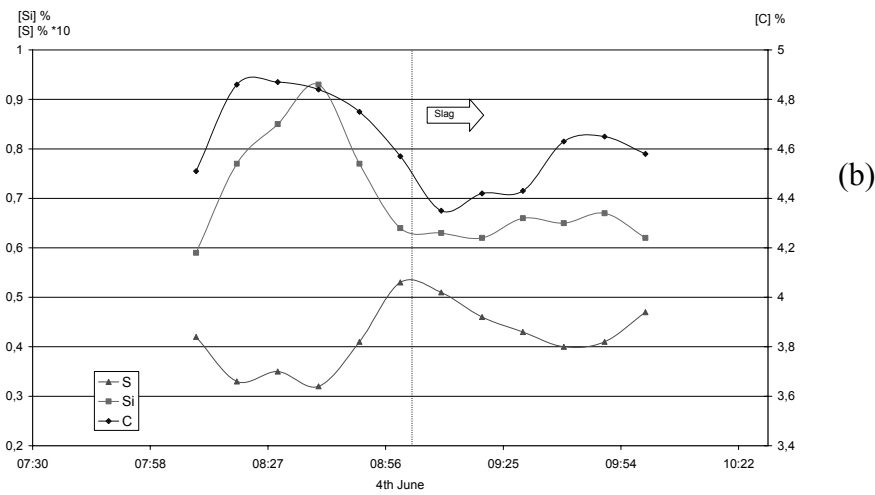
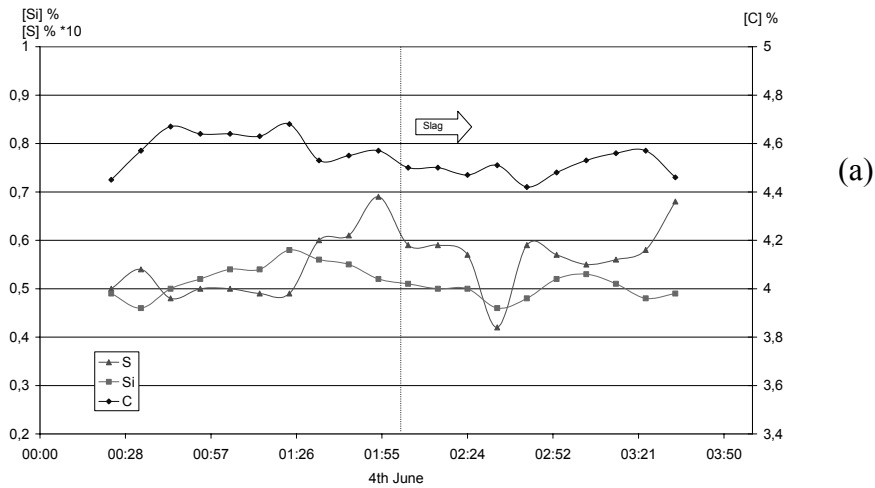
	Standard deviation for trial period	Standard deviation intervals for individual taps	Minimum value determined	Maximum value determined	Analysis error $\zeta_{slag}^i$	Representative for BF process control
CaO	0.47	0.05 - 0.68	30.10	32.90	0.74	Yes/No
SiO <sub>2</sub>	0.39	0.08 - 0.67	31.50	34.30	0.52	Yes/No
Al <sub>2</sub> O <sub>3</sub>	0.27	0.05 - 0.45	12.20	13.60	0.27	Yes
MgO	0.15	0.04 - 0.27	17.70	18.70	0.51	Yes/No
FeO	0.06	0.02 - 0.21	0.19	0.62	0.28	Yes/No
MnO	0.06	0.02 - 0.11	0.31	0.70	0.039	Yes
V <sub>2</sub> O <sub>5</sub>	0.02	0.01 - 0.05	0.01	0.19	0.007	Yes
TiO <sub>2</sub>	0.21	0.01 - 0.21	1.69	2.78	0.026	Yes
K <sub>2</sub> O	0.12	0.01 - 0.15	0.28	0.78	0.012	Yes
S	0.07	0.01 - 0.14	1.21	1.60	0.015	Yes
Basicity	0.025	< 0.03	0.89	1.04	--	--

## FIGURE CAPTIONS:

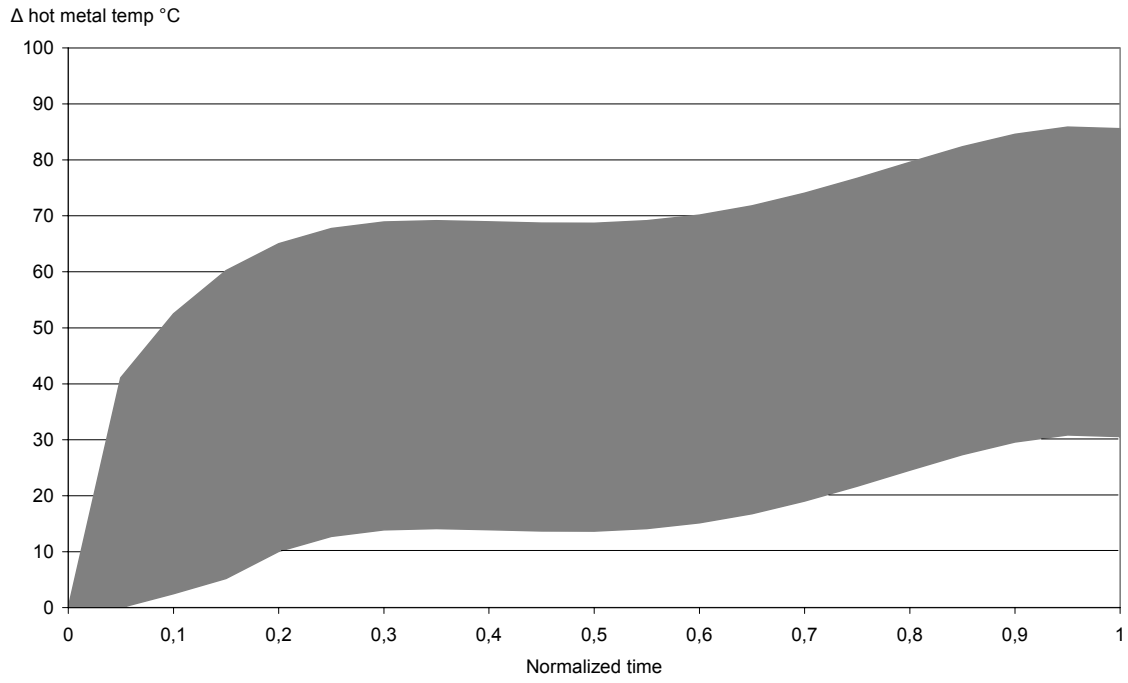
- Fig. 1 Variation in carbon, silicon and sulphur content in hot metal during tapping for a period of 68 hours
- Fig. 2 Variation in hot-metal composition for three different taps
- Fig. 3 Temperature increase in hot metal during tapping for a period of 68 hours
- Fig. 4 Variation in slag sulphur content and basicity during tapping for a period of 68 hours
- Fig. 5 Variation in slag sulphur content and basicity for 3 different taps
- Fig. 6 Calculated slag amounts for the 21 taps
- Fig. 7 Some hot-metal and slag average elemental/component concentrations from 21 taps, illustrating the alkali washout.
- Fig. 8 Hot-metal temperature versus [C], [Si] and [S] concentration
- Fig. 9 Correlation between [C] and [Si], [C] and [S], and [Si] and [S] for 21 taps
- Fig. 10 Difference between routine sample concentration and tap average concentration for [C], [Si], [S], [Mn] and [V] in hot metal for each trial tap
- Fig. 11 Difference between routine sample concentration and tap average concentration for slag components for each trial tap
- Fig. 12 Probability of obtaining a sample having a tap average concentration of the elements carbon, vanadium, silicon, sulphur and manganese in the hot metal, given in minutes after tap startup
- Fig. 13 Probability of obtaining a sample having a tap average concentration of the elements carbon, vanadium, silicon, sulphur and manganese in the hot metal, given in minutes after the start of slag flow
- Fig. 14 Probability of obtaining a sample having a tap average concentration of the studied slag components, in minutes after the start of slag flow
- Fig. 15 Difference between average concentration calculated from two samples and overall tap average concentration of [C], [Si], [S], [Mn] and [V] for each tap
- Fig. 16 Difference between average concentration calculated from two samples and overall tap average concentration for some slag components for each tap



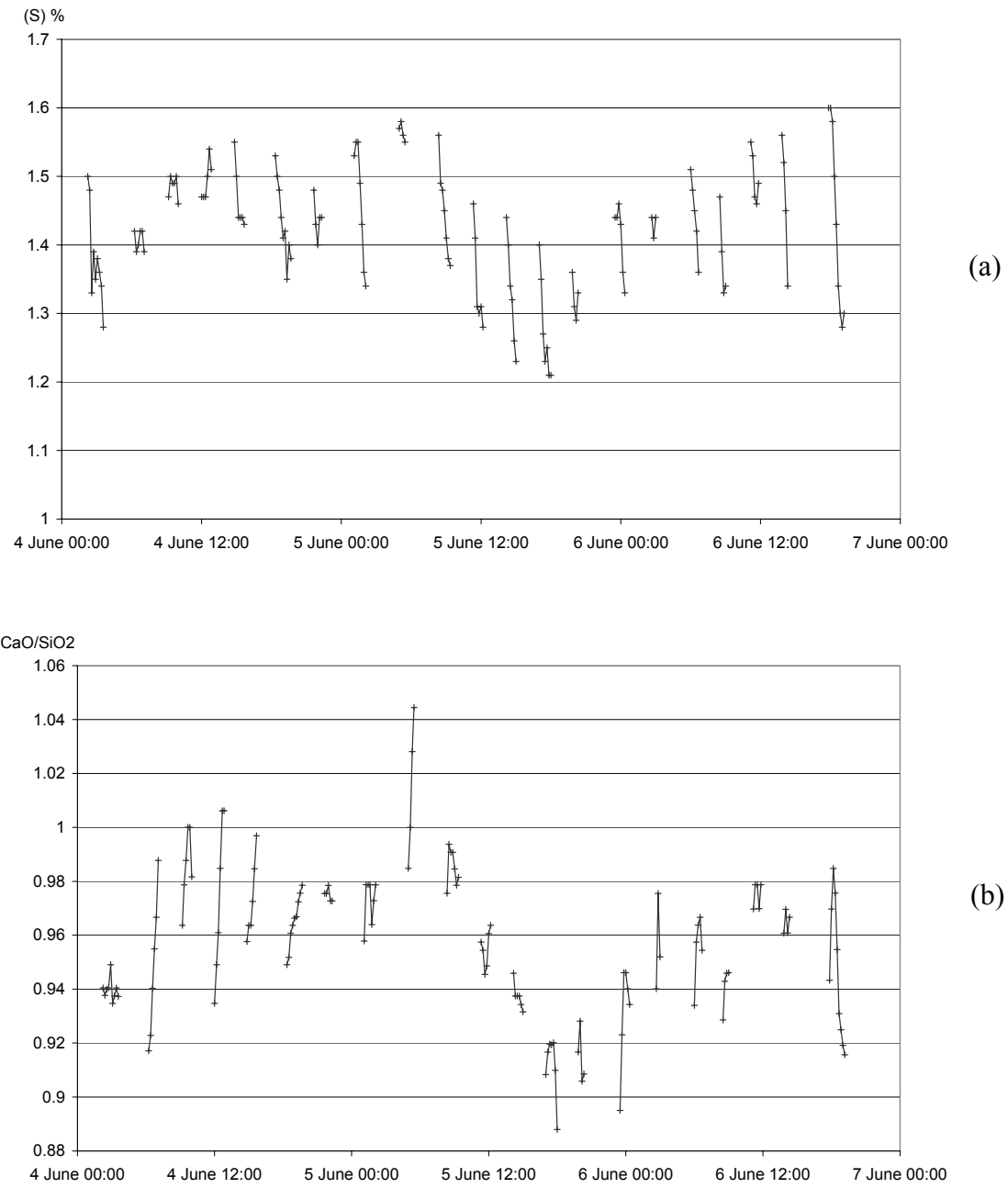
**Fig. 1** Variation in carbon, silicon and sulphur content in hot metal during tapping for a period of 68 hours



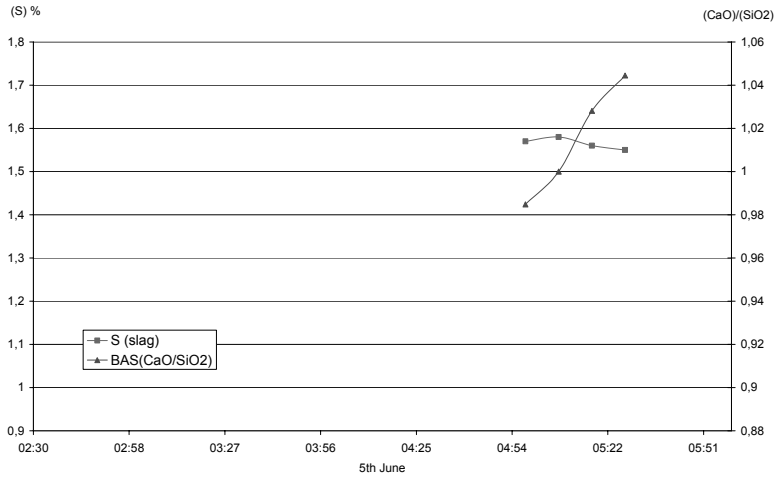
**Fig. 2** Variation in hot-metal composition for three different taps



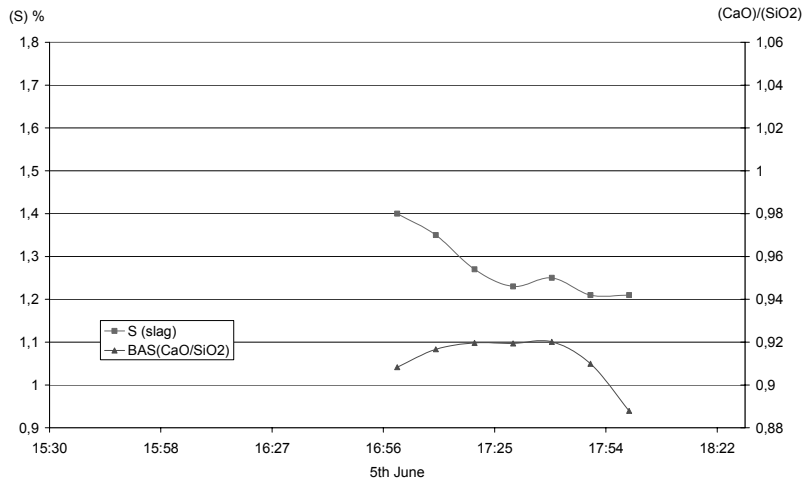
**Fig. 3 Temperature increase in hot metal during tapping for a period of 68 hours**



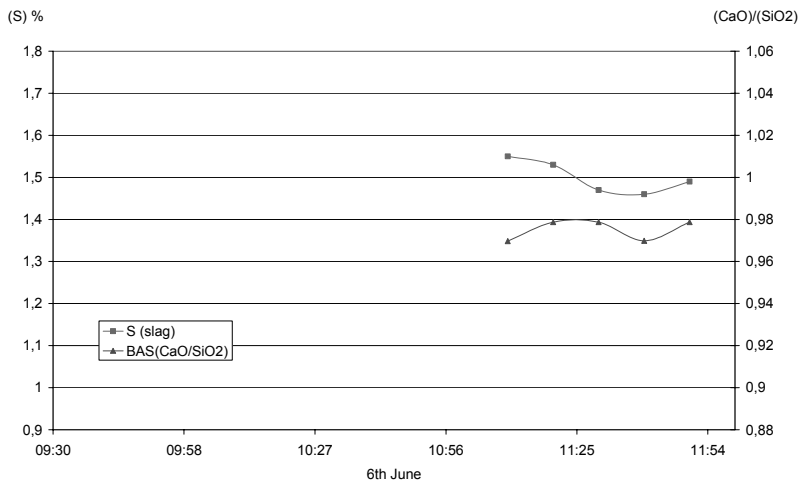
**Fig. 4 Variation in slag sulphur content and basicity during tapping for a period of 68 hours**



(a)

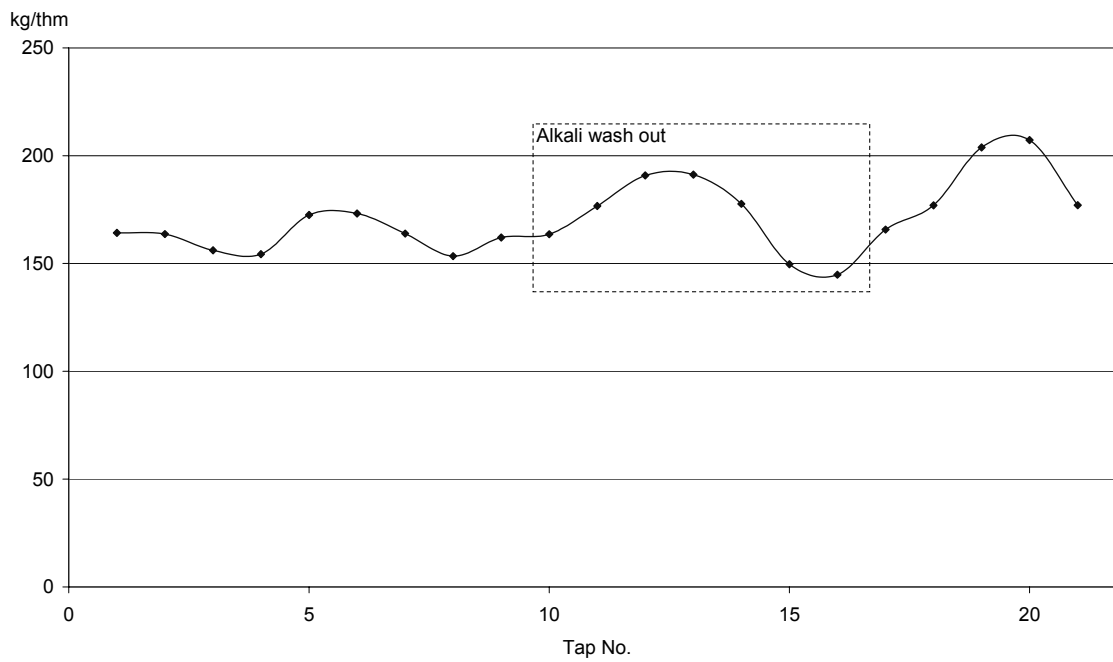


(b)



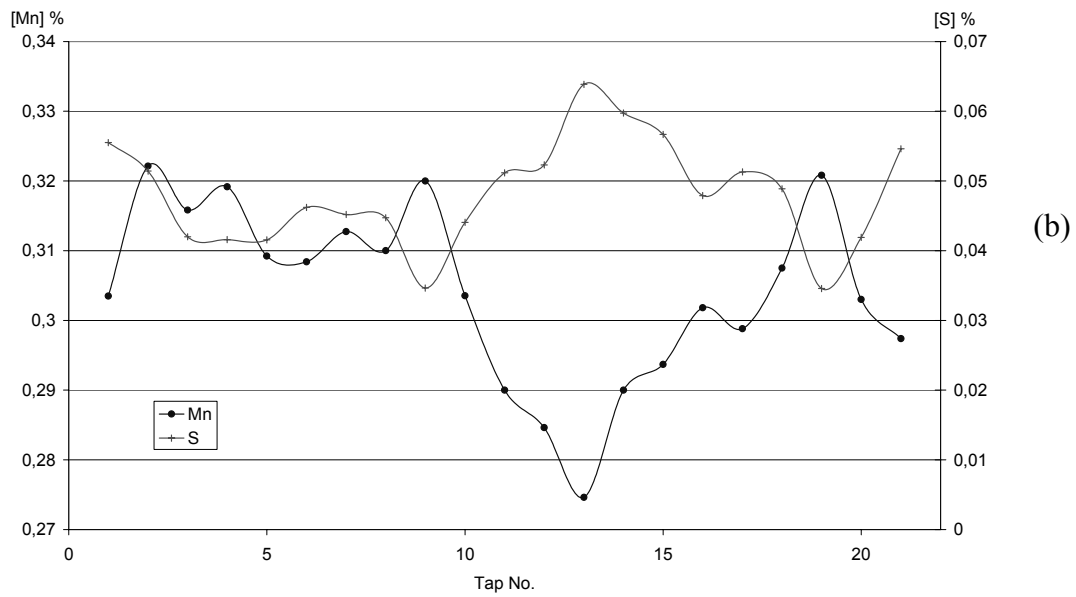
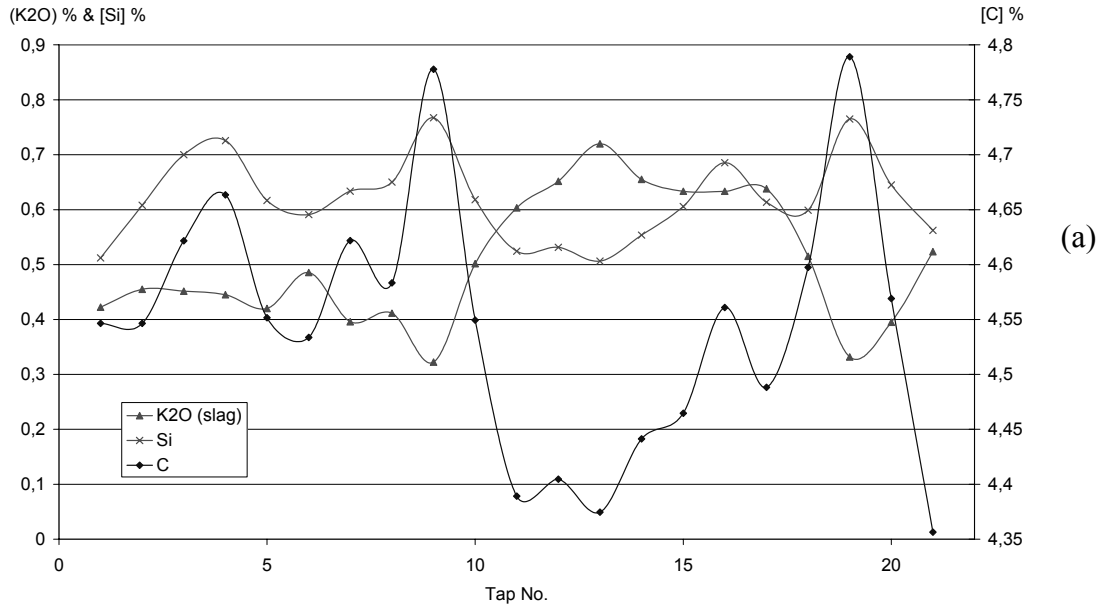
(c)

**Fig. 5 Variation in slag sulphur content and basicity for 3 different taps**

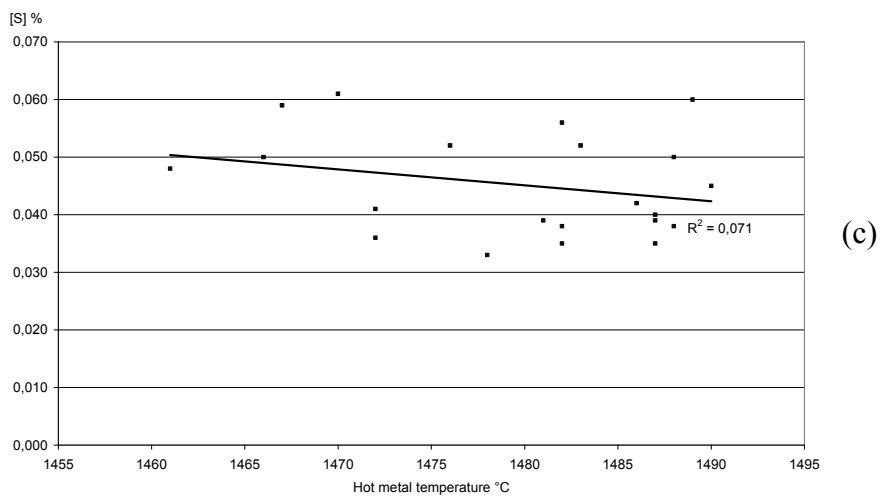
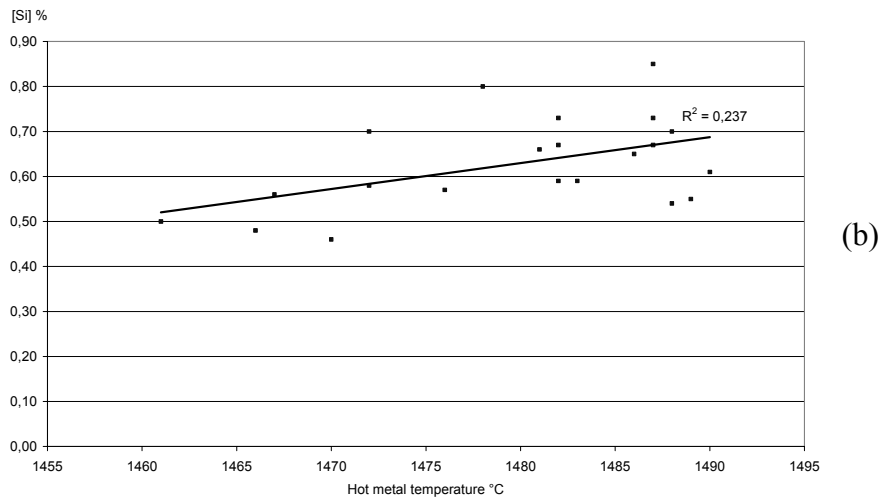
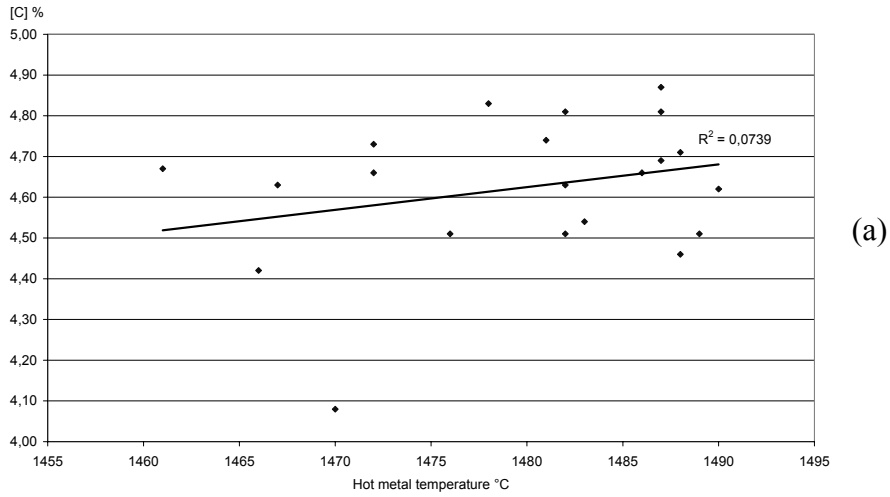


**Fig. 6** Calculated slag amounts for the 21 taps

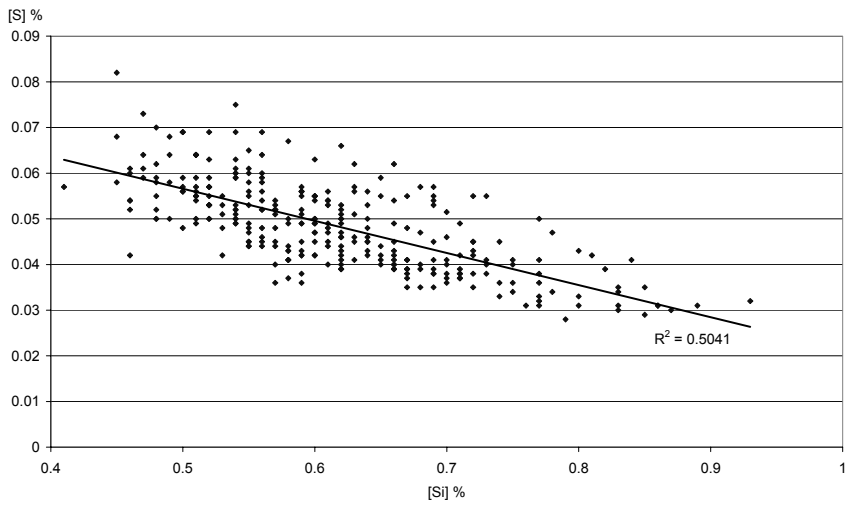
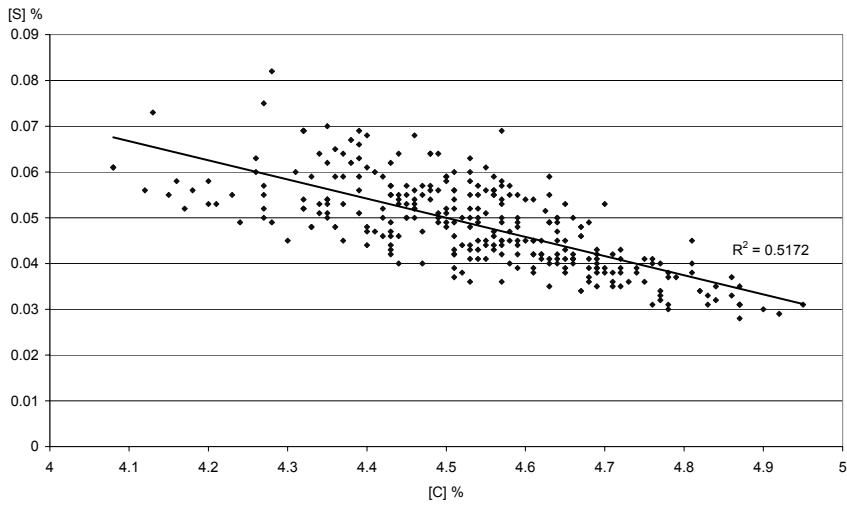
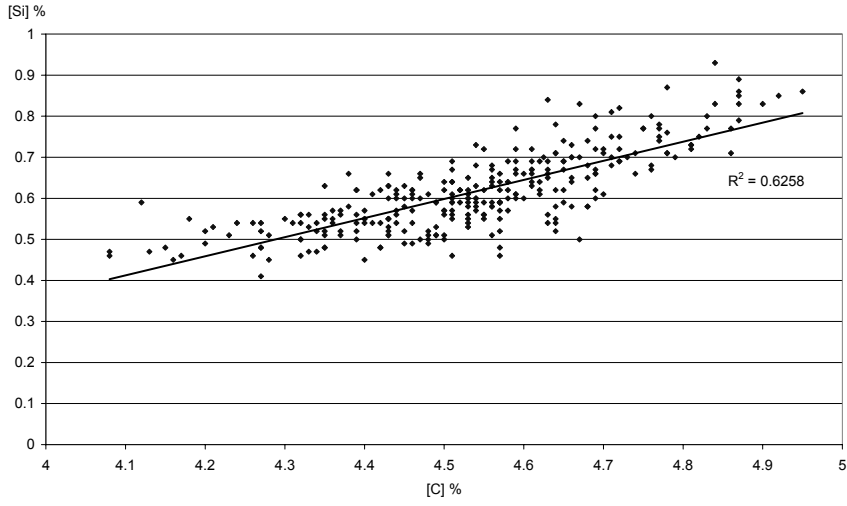




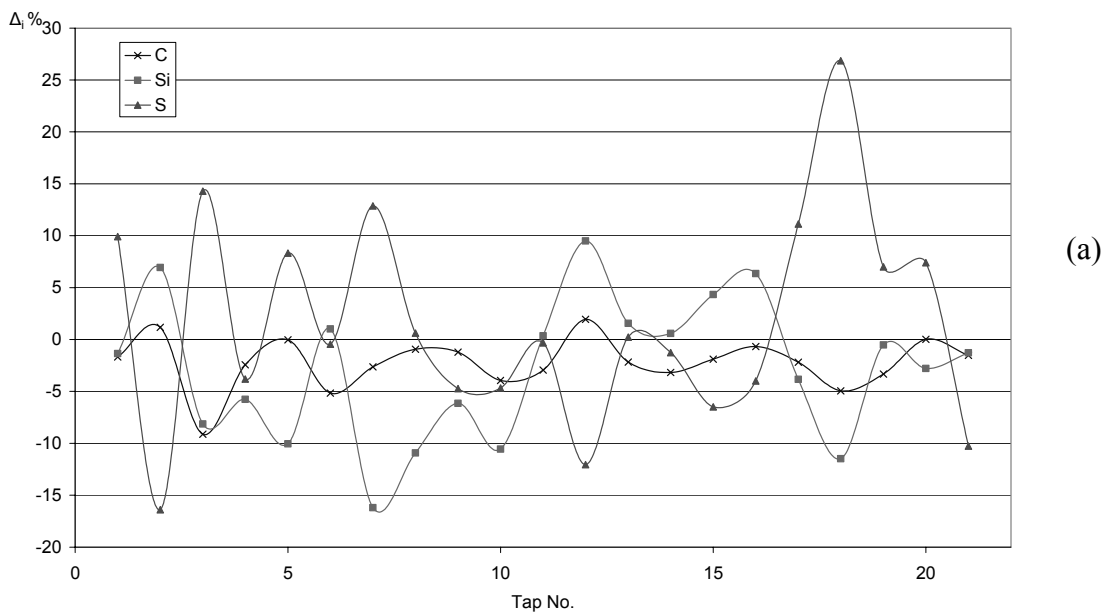
**Fig. 7 Some hot-metal and slag average elemental/component concentrations from 21 taps, illustrating the alkali washout.**



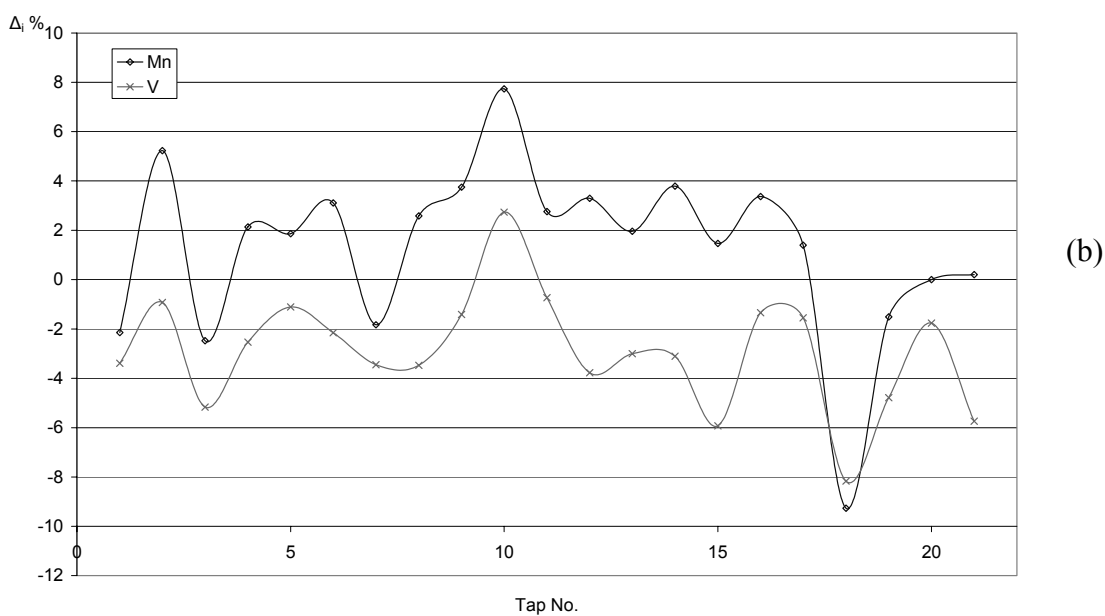
**Fig. 8 Hot-metal temperature versus [C], [Si] and [S] concentration**



**Fig. 9** Correlation between [C] and [Si], [C] and [S], and [Si] and [S] for 21 taps

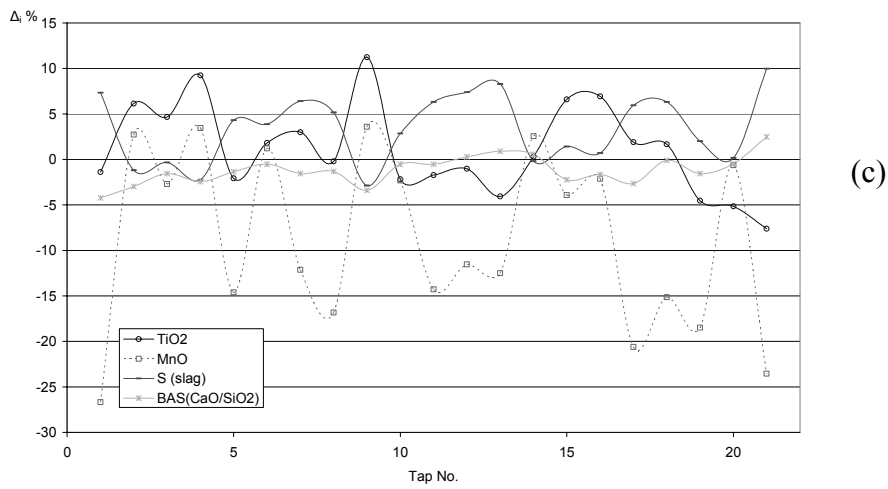
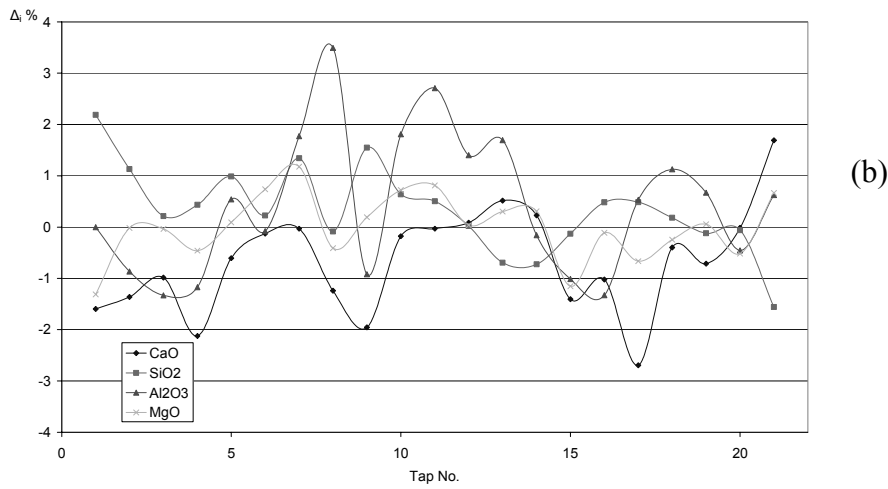
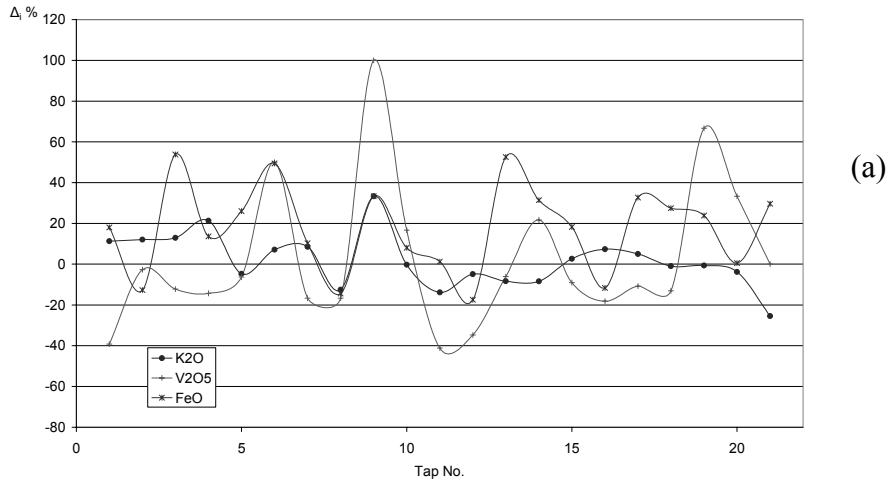


(a)

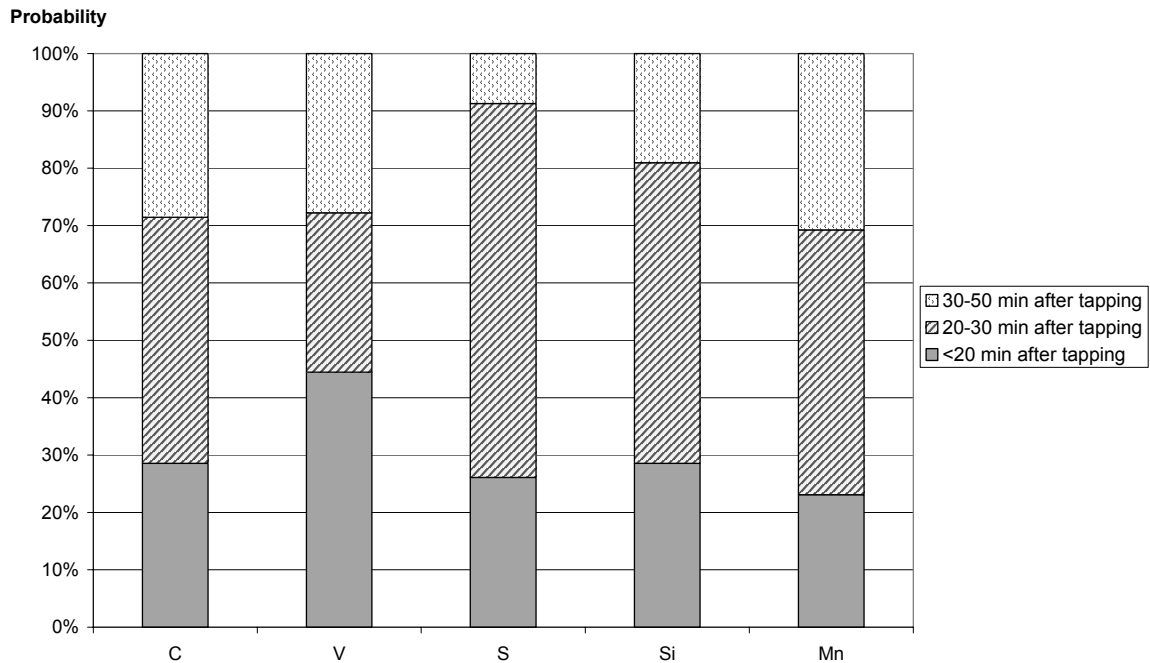


(b)

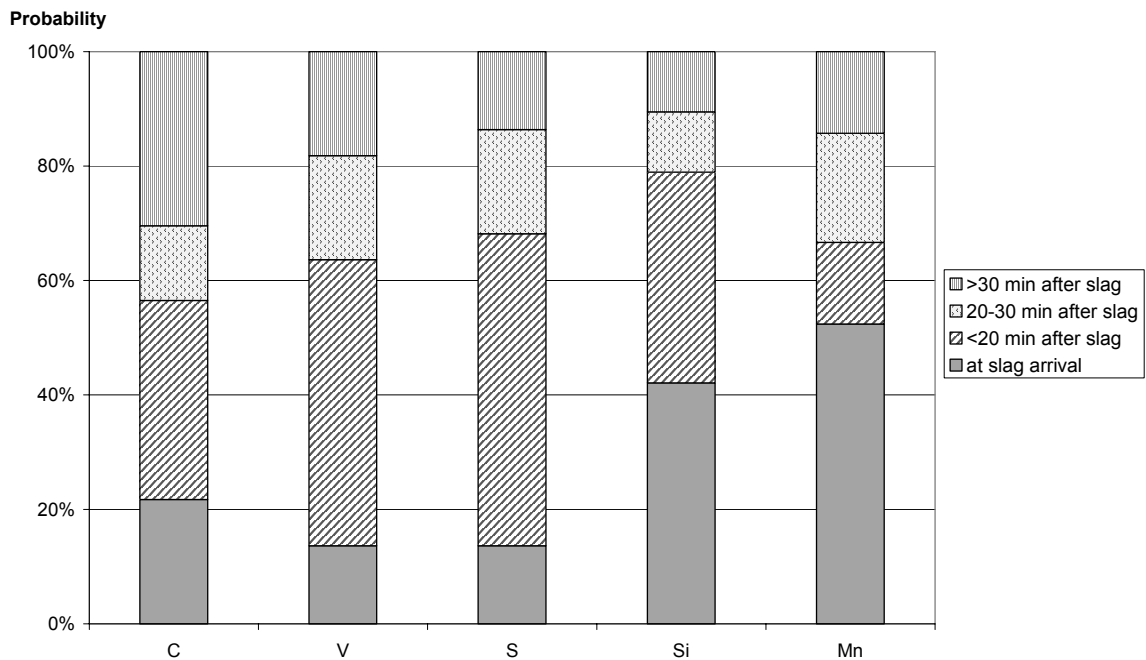
**Fig. 10** Difference between routine sample concentration and tap average concentration for [C], [Si], [S], [Mn] and [V] in hot metal for each trial tap



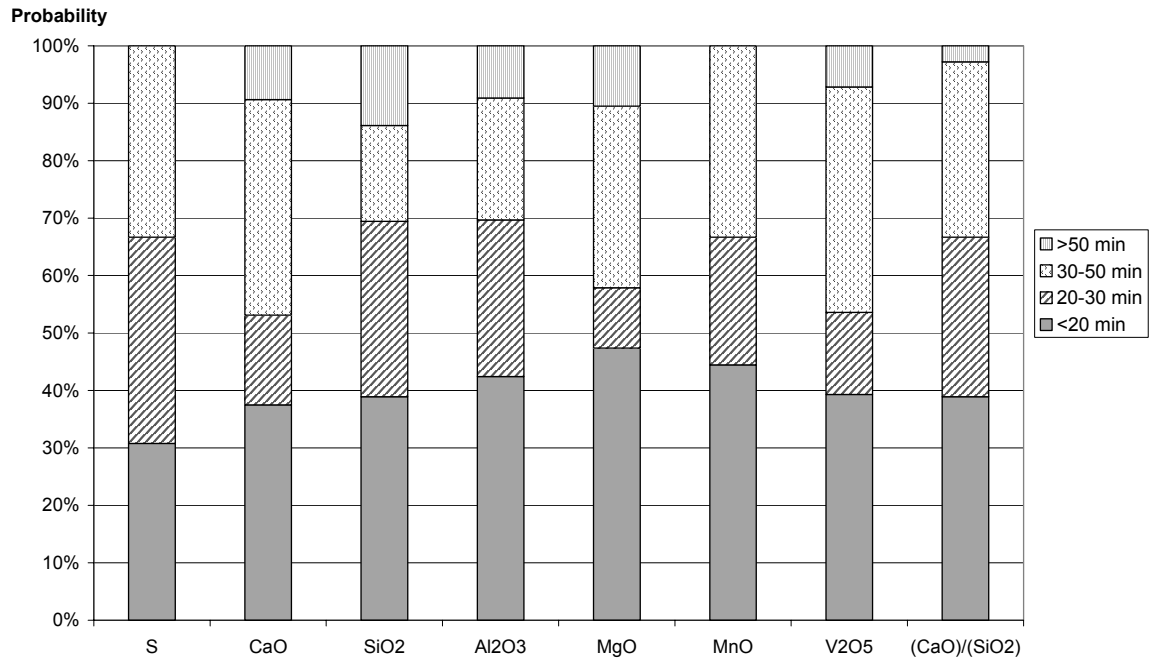
**Fig. 11** Difference between routine sample concentration and tap average concentration for slag components for each trial tap



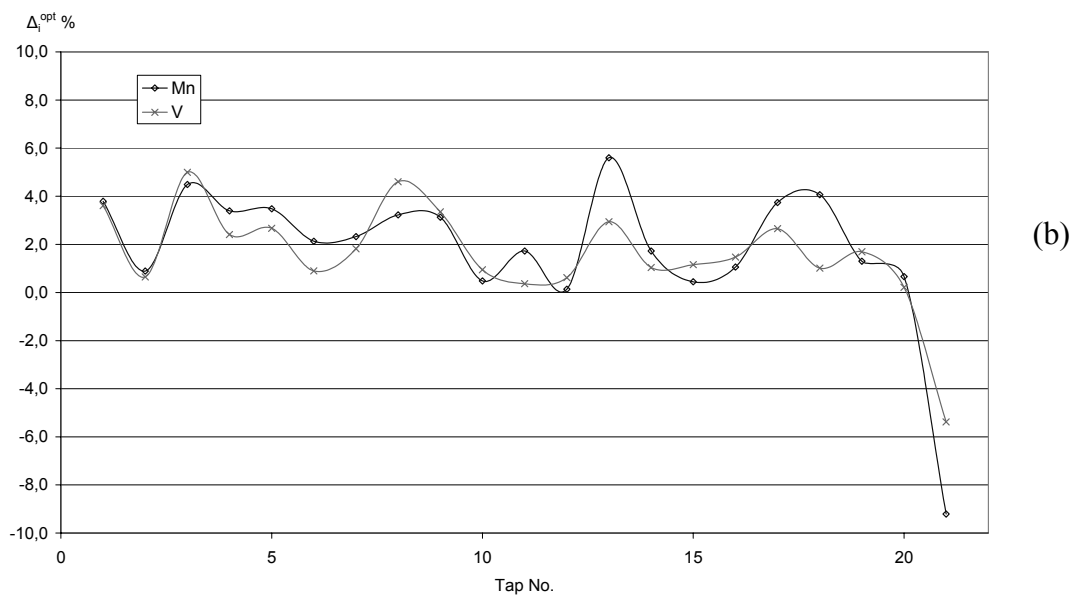
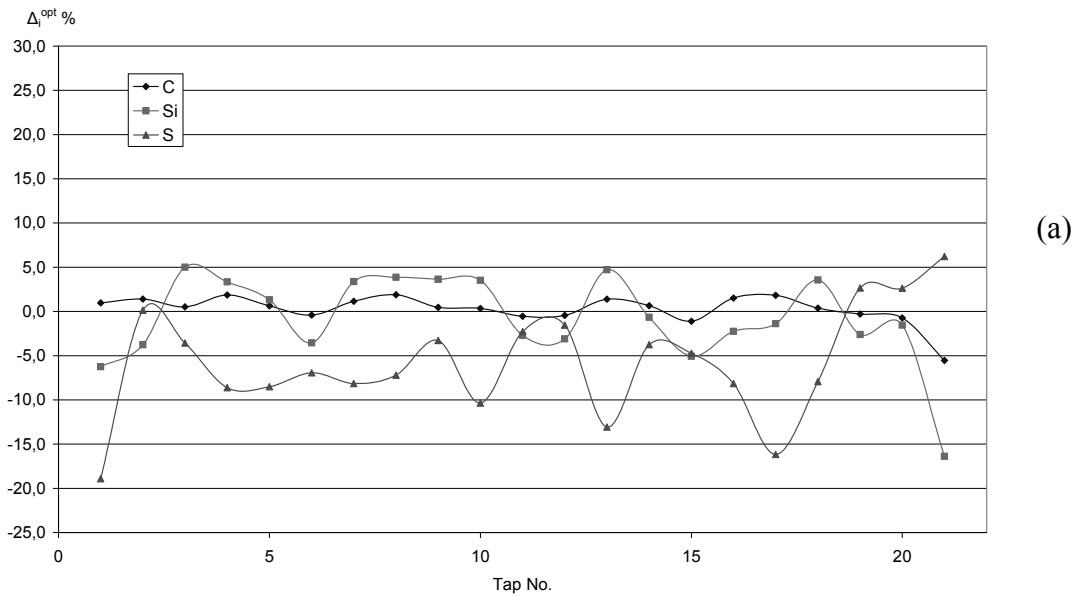
**Fig. 12** Probability of obtaining a sample having a tap average concentration of the elements carbon, vanadium, silicon, sulphur and manganese in the hot metal, given in minutes after tap startup



**Fig. 13** Probability of obtaining a sample having a tap average concentration of the elements carbon, vanadium, silicon, sulphur and manganese in the hot metal, given in minutes after the start of slag flow

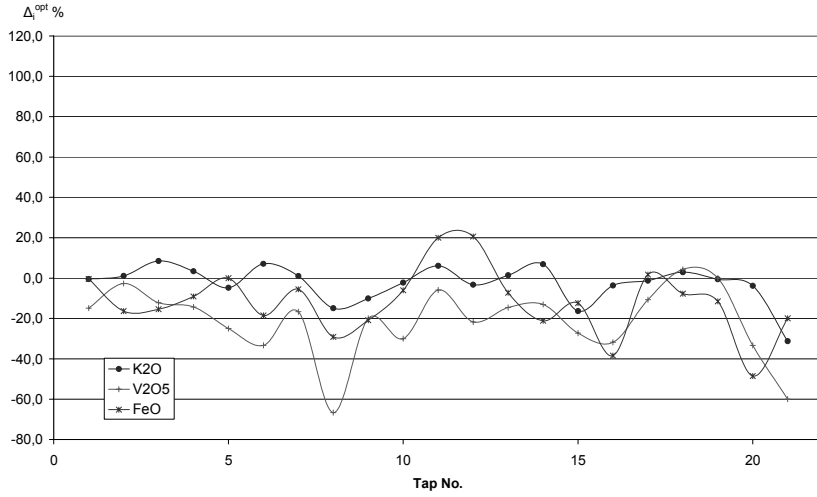


**Fig. 14** Probability of obtaining a sample having a tap average concentration of the studied slag components, in minutes after the start of slag flow

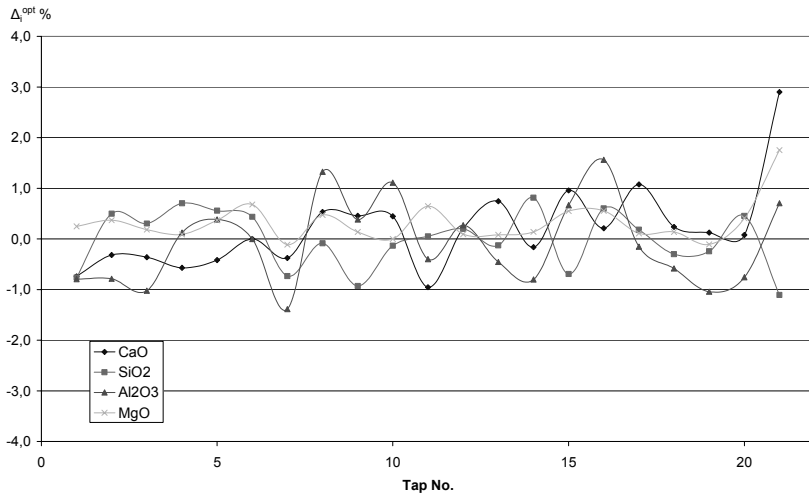


**Fig. 15** Difference between average concentration calculated from two samples and overall tap average concentration of [C], [Si], [S], [Mn] and [V] for each tap

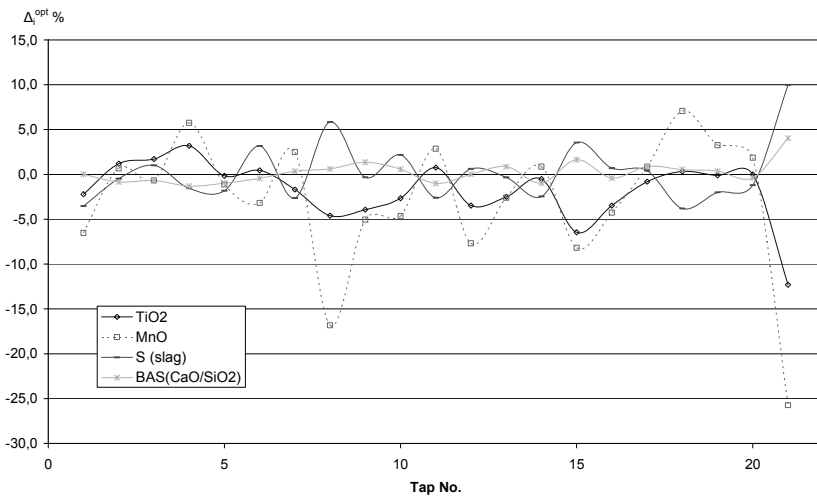




(a)



(b)



(c)

**Fig. 16** Difference between average concentration calculated from two samples and overall tap average concentration for some slag components for each tap

## **Supplement 3**

A Study of some Elemental Distributions Between Slag and Hot Metal  
During Tapping of the Blast Furnace

**A.J. Andersson**, A.M.T. Andersson and P.G. Jönsson

ISRN KTH/MSE--03/59--SE+APRMETU/ART

*Submitted to Steel Research*

# A STUDY OF SOME ELEMENTAL DISTRIBUTIONS BETWEEN SLAG AND HOT METAL DURING TAPPING OF THE BLAST FURNACE

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## Abstract

This report presents a unique investigation of the distribution of elements between slag and hot metal from a blast furnace through calculation of distribution coefficients from actual production data. First, samples of slag and hot metal tapped from a commercial blast furnace were taken continually at 10-minute intervals for a production period of 68 hours. Distribution coefficients of manganese, silicon, sulphur and vanadium were then calculated from the results of the sample analyses.

A major conclusion drawn from examination of the results was that the behaviour of the studied elements was as could be expected when approaching the equilibrium reactions from thermodynamic theory. The distributions of the elements in the slag-metal system showed clear tendencies which did not appear to be influenced by the operational conditions of the furnace. For example, for manganese, vanadium and sulphur, it was found that a higher basicity led to a decreased  $L_{Mn}$  and  $L_V$ , but an increased  $L_S$ , which is according to theory. Another observed relationship was that slag basicity increased with an increased carbon content in the hot metal, which indicated that  $SiO_2$  was reduced to  $[Si]$  when the oxygen potential decreased. Furthermore it was found that sulphur and silica behaviour likened that of acidic slag components, while the manganese oxide and vanadium oxide behaviour was similar to that of basic slag components.

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## Keywords

blast furnace, distribution coefficients, hot metal, slag, silicon, sulphur, manganese, vanadium

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# 1. Introduction

Blast furnace (BF) ironmaking is very complex due to its non-isothermal, high-temperature and multiphase counter-current operation, where solid materials are added at the top of the furnace, gaseous materials are blown into the lower part, and liquid products are tapped from the bottom. The process is also often operated under pressure and at very high temperatures, which makes sampling the furnace content and directly measuring process characteristics in most cases impractical, if not impossible. The primary methods used to further our knowledge on the ongoing BF process are laboratory-scale experimentation and excavation of quenched blast furnaces. Conclusions are then drawn from the findings and applied to the production process. Since laboratory-scale studies are normally simplified, their results often prove to be inappropriate for application to the production BF process. One of the subjects frequently investigated in laboratory experiments is the distribution of different elements at equilibrium in slag-metal-gas systems. Studies have shown, however, that equilibrium is seldom reached among these phases [1,2,3].

Another way of studying equilibrium among slag-metal-gas reactions is to calculate distribution coefficients from actual production data. Data on calculated distribution coefficients of silicon ( $L_{Si} = 15-50$ ) [3,4], sulphur ( $L_S = 10-90$ ) [3,5,6,7,8], manganese ( $L_{Mn} = 0.3-1.8$ ) [3,7,8,9] and vanadium ( $L_V = 1-9$ ) [10] from various blast furnaces can be found in the literature. The investigation covered in this report employed production data from a commercial blast furnace at SSAB Oxelösund AB in Sweden. A unique study was conducted in which slag and hot-metal samples were taken every 10 minutes during tapping for a period of 68 hours. Distribution coefficients of manganese, silicon, sulphur and vanadium were then determined from analysis results.

The first part of the paper describes the thermodynamic theory used in the determination of distribution coefficients as well as the procedure used in obtaining the production data. In the second part, investigation results regarding the variation in distribution coefficients during tapping and between taps are presented and discussed.

## 2. Theoretical background

The main reactions in a blast furnace are heterogeneous slag-metal-gas reactions. Although the reactions normally go through the gas phase, a common way to present the degree of the reduction of oxides is to use distribution coefficients. This is possible due to the fact that most of the elements of interest leave the furnace through the slag or the hot-metal phase. Only CO, CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O and some S leave the furnace with the gas through the top. Since the blast furnace is assumed to operate at steady state the distribution coefficient,  $L_i$ , for a general slag-metal distribution can be expressed on the form

$$L_i = \frac{(\%i)}{[\%i]} \quad (1)$$

where parentheses indicate slag phase and brackets indicate metal phase of element  $i$ . The distribution coefficients provide information about how the elements behave in the blast furnace, i.e. how much oxide remains in the slag and how much oxide is reduced to the elements contained in the hot metal. The equilibrium distribution coefficients are influenced by three factors: temperature, oxygen potential and basicity. In the present work the basicity is expressed as

$$\text{Basicity} = \frac{(\%CaO)}{(\%SiO_2)} \quad (2)$$

In order to investigate the thermodynamic relationships that play a role in the distribution of elements between slag and metal, an approach involving the oxygen potential was applied to the sulphur distribution. The equilibrium sulphur distribution,  $L_S$ , between slag and metal can be expressed by the following equation [11]

$$\log L_S = \log \frac{(\%S)}{[\%S]} = -\frac{935}{T} + 1.375 + \log C_S + \log f_S - \log a_O \quad (3)$$

where  $T$  is the temperature in Kelvin,  $C_S$  is the sulphide capacity,  $f_S$  is the activity coefficient for sulphur in the metal phase and  $a_O$  is the oxygen activity in the metal phase. The oxygen activity  $a_O$  can be related to the partial pressure of oxygen by the following reaction [12]



$$\Delta G^0 = -RT \ln K_i \quad (5)$$

$$\Delta G_4^0 = -117152 - 2.887 \cdot T \quad (\text{J/mol}) \quad (6)$$

$$K_6 = \frac{a_o}{\sqrt{p_{O_2}}} \quad (7)$$

The activity coefficient of dissolved elements in the metal phase was estimated using Wagner's equation:

$$\log f_j = \sum (e_j^i \cdot [\%i]) \quad (8)$$

where  $f_j$  is the activity coefficient for element  $j$  in the liquid metal phase,  $i$  represents the dissolved elements in the liquid metal phase and  $e_j^i$  is the interaction parameter for element  $j$ . It should be pointed out that Wagner's equation is, strictly speaking, only valid for dilute solutions, i.e. the metal should not contain more than 1 wt% of the dissolved elements. However, it is often used in published literature [1,8] at higher contents of alloying elements for estimations of activities and activity coefficients. The interaction parameters were in the present work taken from a compilation carried out by Engh.[13] The sulphide capacity  $C_S$  was calculated by using the KTH model.[14] This model allows calculation of the sulphide capacity as a function of slag composition and temperature.

### 3. Obtaining the production data

#### 3.1. Blast furnace information

Production data from June 2003 for blast furnace No. 4 at SSAB Oxelösund have been used. For the No.4 furnace the annual production is ~1000 ktonnes, the capacity 3000 tonne/24h, the hearth diameter 8.6 m and the working volume 1339 m<sup>3</sup>. The furnace is equipped with a rotating chute and the last relining was done in 1996. During the study the furnace operated on a 100% pellet burden and had PCI (Pulverized Coal Injection) as complement reduction material, slag fluxes (BOF-slag and limestone) and Mn-additives in form of briquettes. The production data for the studied period can be seen in Table 1.

The aimed-for composition of hot metal in the studied blast furnace was: C > 4.25%; Si 0.32-0.72%; S < 0.090% and Mn 0.25-0.35%. For the slag, components concentrations of S < 1.8%; MgO < 18% and basicity > 0.88 were target. The actual composition of hot metal and slag for each tap during the studied period can be seen in Table 2.

### 3.2. Sampling of hot metal and slag

Samples of hot metal and slag were taken with a 10-minute interval during tapping of the BF for a total period of 68 hours.[15] The temperature of the hot metal was measured at the same time as the sampling. Each sampling was carried out according to the normal practice followed at the steel plant for the standard single sampling per tap. The hot-metal temperature was measured and the hot-metal sample was taken, using a lollipop sampler, in the area directly following the skimmer. The slag sample was obtained from the beginning of the slag runner using a scoop. The process was running on an ordinary burden mixture and the operational conditions during the period included some natural variations, such as a minor decrease in the blast of 15% for 6 hours due to a surplus of hot metal in the steel plant, an alkali washout and a lengthy four-hour tapping.

## 4. Results and discussion

### 4.1. Effect of operational status on the distribution coefficients

The sulphur distribution coefficient versus distribution coefficient of manganese (Figure 1) is an example on the correlation between different distribution coefficients for a period of 68 hours. During this period the furnace was tapped 21 times, with tap times ranging from 80 to 220 minutes. The total period of 68 hours encompassed different “operational” states: one alkali wash out occurred, a minor decrease in blast flow and an extremely long tapping for 220 minutes. All these different operational states were compared with a “normal” state where the furnace run on ordinary burden and blast flow. It is interesting to note that even though these operational states cause the hot-metal and slag composition to vary [15], the correlations between different distribution coefficients follow the same trend irrespective of the operational status. As can be seen in Figure 1, a high value of  $L_S$  related to a low  $L_{Mn}$ , irrespective if looking at the “normal” period or the periods with an alkali wash out, a reduced blast flow or a long tapping. It was found in the present study that variations in the operational conditions did not influence the correlation trends between  $L_i$  versus  $L_j$ , for the cases when  $i$  and  $j$  were represented as manganese, silicon, sulphur or vanadium. This observation suggests that the thermodynamic relations between the studied elemental

slag-metal distributions were not influenced by the above-mentioned operational variations in the blast furnace during the studied period.

## 4.2. Parameters influencing the distribution coefficients

The present study focuses on the measured effects of (i) temperature, (ii) basicity and (iii) oxygen potential on the distribution coefficients. The hot-metal temperature had an average standard variation of only 10.6°C for 21 taps (the highest standard variation for one tapping was 18°C), and a great deal of the variation could be explained through heat losses.[15] Consequently, the temperature behaviour was judged to be quite stable, and therefore the influence from the hot-metal temperature on the present results was disregarded. The rest of this section will thus cover the influence of oxygen potential and basicity on the elemental distribution between the hot metal and slag.

### 4.2.1. Effect of oxygen potential on the $L_S$ , $L_{Si}$ and $L_{Mn}$ relationships

The measured sulphur distributions between slag and metal varied from 20 up to 50 with an average value around 32. In Figure 2 the relations for  $L_S$  with  $L_{Si}$  and  $L_{Mn}$ , respectively, are illustrated.

The calculation of the equilibrium sulphur distribution as a function of the oxygen partial pressure using equations (3)-(8) was done using only the overall average values of slag and metal compositions from the whole studied period, see Table 2. For the calculation of sulphide capacity, the average slag composition was normalised to the four components  $Al_2O_3$  (13.4%),  $CaO$  (33.1%),  $MgO$  (18.9%) and  $SiO_2$  (34.6%). The assumed temperature was kept constant at 1500 °C, because it was believed to be a representative value for the tapping temperature during the same period.[15] The KTH model [14] was used to calculate the average sulphide capacity to  $7.06 \cdot 10^{-5}$ , which is of the same order of magnitude as corresponding values reported for blast furnace slags.[8] In Figure 3, the calculated  $L_S$  from equation (3) as a function of  $p_{O_2}$  is shown as a solid unbroken line. The broken vertical lines in Figure 3, mark the oxygen partial pressures at equilibrium for the following slag-metal reactions [12]



$$\Delta G_9^0 = -405045 + 122.424 \cdot T \quad (J/mol) \quad (10)$$



$$\Delta G_{11}^0 = -814881 + 214.881 \cdot T \quad (J/mol) \quad (12)$$





$$\Delta G_{13}^0 = -135471 - 44.256 \cdot T \quad (\text{J/mol}) \quad (14)$$

For the calculation of the activity of  $\text{SiO}_2$  and the activity coefficient of  $\text{MnO}$  in the slag, the empirical expressions suggested by Ohta and Suito [16] were used. It has earlier been shown that Ohta and Suito's expressions for  $1600^\circ\text{C}$  can be used as approximations at temperatures down to  $1500^\circ\text{C}$  [11]. The same assumption was made in the present work. The calculated activity of  $\text{SiO}_2$  was 0.05 (standard state  $\text{SiO}_2$  (s)) and the activity coefficient of  $\text{MnO}$  was 2.50 (standard state  $\text{MnO}(\text{s})$ ). The activities of manganese, silicon and carbon in the hot metal were estimated using the dilute solution model (see equation (8)).

As seen in Figure 3, the oxygen partial pressure calculated from the manganese-oxygen equilibrium in equations (9) and (10) was around  $4 \cdot 10^{-14}$  atm. This corresponds to a  $L_S$  value that is too low to be in equilibrium with the experimentally determined sulphur distributions, extending from 20 to 50.

The oxygen partial pressure calculated from the  $\text{Si}/\text{O}/\text{SiO}_2$  equilibrium in equations (11) and (12) (around  $2 \cdot 10^{-15}$  atm, see Figure 3) was clearly lower than that of the  $\text{Mn}/\text{O}/\text{MnO}$  equilibrium in equations (9) and (10). This resulted in a higher equilibrium sulphur distribution ( $L_{Si}$  around 10), which could be considered as comparable with the measured sulphur distributions, ranging from 20 to 50.

The oxygen partial pressure from the  $\text{C}/\text{O}/\text{CO}$  equilibrium in equations (13) and (14) was calculated at two different values of  $p_{CO}$ , 1 and 0.5 atm, respectively. The resulting oxygen partial pressures were slightly lower than the  $\text{Si}/\text{O}/\text{SiO}_2$  equilibrium (around  $10^{-16}$ ), and therefore rendered an equilibrium  $L_S$  of 15-30, as can be seen in Figure 3. This equilibrium sulphur distribution is rather close to the actual  $L_S$  values.

#### 4.2.2. *Effect of basicity and carbon on distributions*

The results showed a relation between slag basicity and carbon in hot metal, where a high carbon content correlate to a high basicity, see Figure 4. This reduces the possibility to only study the effect of basicity on distribution coefficients due to the influence of carbon content. High carbon content in the hot metal involve a low oxygen potential according to equation (13) and (14). The oxygen potential ( $p_{O_2}$ ) is related to the activity of oxygen ( $a_o$ ) through equation (4) and (7). The basicity is correlated to

the oxygen ion activity ( $a_{O^{2-}}$ ) and a high oxygen ion activity leads to a high basicity. This is due to the fact that oxides behave as acids in the slag, pick up of oxygen ions ( $O^{2-}$ ) and basic oxides tend to release oxygen ions in the slag.

The distribution of an element between hot metal and slag, at equilibrium, is correlated to the relationship between oxygen potential, temperature and the oxygen ion activity. The relationships for these parameters are expressed for sulphur, silicon, vanadium and manganese and are evaluated qualitatively in the present work.

For sulphur equation (15) and (16) shows the relationship



$$\frac{(\%S)}{[\%S]} = \frac{K_s \cdot a_{O^{2-}} \cdot f_s}{\gamma_{S^{2-}} \cdot a_o} \quad (16)$$

where the equilibrium constant  $K_S$  depends on temperature. In the present study, the temperature, as mention before, is considered as a constant and the influence on the present results could thus be disregarded. In equation (16) a high activity of oxygen ion ( $a_{O^{2-}}$ ) and a low oxygen activity ( $a_o$ ) both contribute to an increased in  $L_S$ . This behaviour is illustrated in Figure 5 where high basicity represents high  $L_S$  and in Figure 6 the correlation with high carbon in hot metal corresponds to high  $L_S$ .

For silicon, having a corresponding acidic slag component  $SiO_2$ , the same relationship with oxygen activity and oxygen ion activity can be expressed with equations (17) - (19)



$$\frac{(\%SiO_4^{4-})}{[\%Si]} = \frac{K_{Si} \cdot f_{Si} \cdot a_o^2 \cdot a_{O^{2-}}^2}{\gamma_{SiO_4^{4-}}} \quad (18)$$

$$\frac{(\%Si)}{[\%Si]} = \frac{M_{Si}}{M_{SiO_4^{4-}}} \cdot \frac{K_{Si} \cdot f_{Si} \cdot a_o^2 \cdot a_{O^{2-}}^2}{\gamma_{SiO_4^{4-}}} \quad (19)$$

A high basicity, i.e. high  $a_{O^{2-}}$ , should result in high  $L_{Si}$ . This behaviour could not be observed in Figure 5, where an increase of basicity decreased  $L_{Si}$ . However, in Figure 5, the effect of basicity on  $L_{Si}$ , is obscured by the fact that the basicity is also a function of the  $SiO_2$  - content in the slag. On the other hand a low oxygen activity in the hot metal should be detrimental for  $L_{Si}$ , and in Figure 6, the increase of [%C] (i.e. decrease of  $a_o$ ) decreased the  $L_{Si}$ .

For manganese, related to the basic slag component MnO, the opposite correlation compared to sulphur can be seen in equation (20) and (21)



$$\frac{(\% \text{Mn})}{[\% \text{Mn}]} = \frac{K_{\text{Mn}} \cdot f_{\text{Mn}^{2+}} \cdot a_{\text{O}}}{\gamma_{\text{Mn}^{2+}} \cdot a_{\text{O}^{2-}}} \quad (21)$$

For the distribution of manganese, a low basicity, a low activity of oxygen ion ( $a_{\text{O}^{2-}}$ ), and a high oxygen activity ( $a_{\text{O}}$ ) will increase  $L_{\text{Mn}}$ . This is exemplified in Figure 5, where a low basicity leads to a high  $L_{\text{Mn}}$  and in Figure 6 the correlation with low carbon content in hot metal relates to a high  $L_{\text{Mn}}$ .

Vanadium oxide in iron- and steelmaking slags behave as an amphoteric component, i.e. in an acidic slag vanadium oxide will behave as a base and in a basic slag vanadium oxide will behave as an acid.[17] Vanadium oxide can also be in different valence states and in the literature it is concluded that  $\text{V}^{5+}$  dominates at high basicity and oxidizing conditions.[18] In blast furnace, where the basicity often is very low (basicity  $\leq 1$ ) and the conditions are reducing, the vanadium takes the valence state  $\text{V}^{3+}$  or sometimes  $\text{V}^{4+}$ . [18,19] In this work it has been assumed that the valence state is  $\text{V}^{3+}$  and the ion in the slag is  $\text{VO}^+$ . The relationship with oxygen activity and basicity can thus be expressed in equations (22) - (24)



$$\frac{(\% \text{VO}^+)}{[\% \text{V}]} = \sqrt{\frac{K_{\text{V}} \cdot f_{\text{V}^{3+}}^2 \cdot a_{\text{O}}^3}{\gamma_{\text{VO}^+}^2 \cdot a_{\text{O}^{2-}}}} \quad (23)$$

$$\frac{(\% \text{V})}{[\% \text{V}]} = \frac{M_{\text{V}}}{M_{\text{VO}^+}} \sqrt{\frac{K_{\text{V}} \cdot f_{\text{V}^{3+}}^2 \cdot a_{\text{O}}^3}{\gamma_{\text{VO}^+}^2 \cdot a_{\text{O}^{2-}}}} \quad (24)$$

For a high oxygen activity ( $a_{\text{O}}$ ) and a low basicity, activity of oxygen ion ( $a_{\text{O}^{2-}}$ ), the  $L_{\text{V}}$  would be high. Figure 5 shows that a low basicity represents high  $L_{\text{V}}$  and Figure 6 show the correlation that a decreased carbon content in the hot metal corresponds to high  $L_{\text{V}}$ . This is in accordance with the theory.

Figure 7a) and b) shows the added effect of basicity and [%C] on the distribution of Si, S, Mn and V. The taps were divided into two groups, by finding the median basicity of the taps. The first group (low basicity) had a basicity lower than the median basicity of 0.956, while the second group (high basicity) had basicities higher than 0.956. This principle, dividing the basicity into a high and a low group, was done according to

literature [18,19]. The variation of  $L_i$  with [%C] for the low basicity taps and high basicity taps, are indicated in Figure 7a) and b) by the solid and broken lines, respectively.

Figure 7a) indicates that the distributions for the two slag components with an acidic behaviour (sulphur and silicon) were increased when the basicity increased, since the broken lines are slightly above the solid lines. The opposite behaviour can be observed for the distribution corresponding to the element V and Mn in Figure 7b), where the broken lines are below the solid lines. Since it has been assumed that vanadium and manganese as oxides components have a basic behaviour, the different behaviour (compared to Figure 7a) is quite reasonable.

## 5. Conclusions

The major conclusions from the study was that the distribution coefficients from the blast furnace follows the behaviour that can be expected when looking at the equilibrium reactions from a thermodynamic point of view. The studied slag-metal distributions were also showing strong, trend-like relationships, which was not affected by the operational status of the furnace during the studied period. It was shown that a higher basicity decreased  $L_{Mn}$  and  $L_V$ , whereas the  $L_S$  increased and this was according to theory.

The more specific conclusions are as follows:

- I. The equilibrium sulphur distribution calculated by assuming that the reaction  $[Mn] + \frac{1}{2} O_2 \leftrightarrow (MnO)$  determined the oxygen potential, was significantly lower than the measured sulphur distributions between slag and metal.
- II. The equilibrium sulphur distribution calculated by assuming that the reaction  $[Si] + O_2 (g) \leftrightarrow (SiO_2)$  determined the oxygen potential, was lower than the measured sulphur distributions, but still of the same magnitude
- III. The oxygen partial pressures calculated at two different  $p_{CO}$  from the reaction  $[C] + \frac{1}{2} O_2 (g) \leftrightarrow CO(g)$  were somewhat lower compared to the Si/O/SiO<sub>2</sub> reaction and thus the corresponding equilibrium sulphur distributions were closer to the actual.
- IV. The basicity of the slag increased with an increased content of carbon in the hot metal, which indicated that SiO<sub>2</sub> was reduced to [Si] when the oxygen potential was decreased.

V. Sulphur and silica exhibited behaviour of acidic slag components, while manganese oxide and vanadium oxide exhibited behaviour of basic slag components.

## **Acknowledgment**

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**List of symbols**

$a_i$	activity of species $i$
$a_{O^{2-}}$	oxygen ion activity
$C_S$	sulphide capacity
$e_j^i$	interaction parameter for species $i$ on species $j$
$f_i$	activity coefficient for species $i$ in liquid metal when $[\%i] \rightarrow 0$
$\Delta G_i^0$	change in Gibbs standard free energy for equation $i$ , J/mol
$K_i$	equilibrium constant for species $i$
$L_i$	distribution coefficient for species $i$
$M_i$	molar weight for species $i$
$p_{O_2}$	oxygen potential
$T$	temperature in Kelvin, °K
$(i)$	concentration of species $i$ in slag, wt-%
$[i]$	concentration of species $i$ in hot metal, wt-%
$\gamma_i$	activity coefficient for species $i$ in slag when $x_i \rightarrow 1$
$x_i$	molar fraction for species $i$

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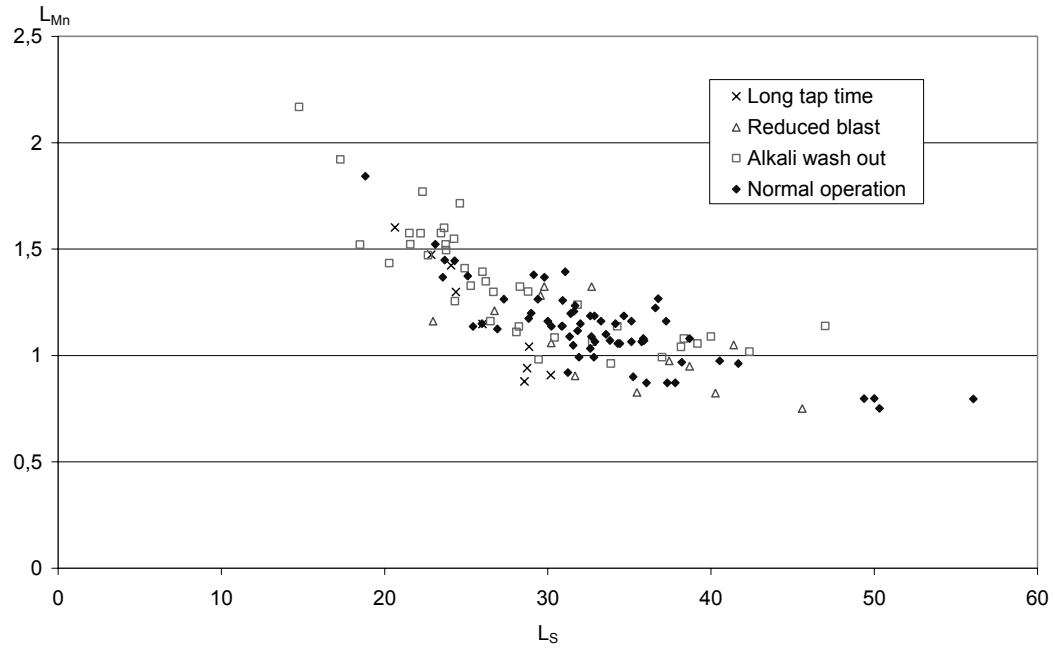
**Table 1 Production data from blast furnace No.4 at SSAB Oxelösund during the studied period in June 2003.**

	Amount	Unit
Blast volume	114700	Nm <sup>3</sup> /h
Blast temperature	1033	°C
Steam	7.5	g/Nm <sup>3</sup>
Oxygen	4.8	%
Production	2858	metric ton/24h
Cooling effect	22796	MJ/h
Material charged		
Pellet	1427	kg/thm
Slag fluxes (BOF-slag and limestone)	~70	kg/thm
Mn briquettes	65	kg/thm
Coke	~360	kg/thm
PCI	~100	kg/thm
Calculated slag (avg)	171	kg/thm



**Table 2 The average composition of hot metal and slag for each tapping during the studied period in June 2003 [wt%].**

Tapping	Tap length (min)	Temp (°C)	Hot-metal composition								Slag composition									
			C	Si	Mn	P	S	V	Ti	Fe	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	FeO	MnO	V <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	K <sub>2</sub> O	S
1	204	1475	4.55	0.51	0.30	0.038	0.056	0.278	0.141	98.59	31.53	33.56	12.60	17.96	0.27	0.55	0.082	2.41	0.42	1.38
2	169	1479	4.55	0.61	0.32	0.039	0.051	0.286	0.165	98.52	31.60	33.33	12.70	17.93	0.28	0.49	0.062	2.22	0.46	1.41
3	121	1492	4.62	0.70	0.32	0.039	0.042	0.281	0.179	98.40	32.22	32.70	13.03	18.07	0.26	0.49	0.068	2.04	0.45	1.49
4	119	1495	4.66	0.73	0.32	0.039	0.042	0.283	0.181	98.43	32.18	33.07	13.08	18.18	0.22	0.44	0.058	1.99	0.45	1.49
5	124	1493	4.55	0.62	0.31	0.038	0.042	0.278	0.160	98.54	31.93	32.82	12.95	18.13	0.23	0.45	0.053	2.09	0.42	1.47
6	189	1486	4.53	0.59	0.31	0.039	0.046	0.279	0.157	98.52	31.80	32.96	12.70	17.98	0.29	0.45	0.060	2.20	0.49	1.43
7	112	1487	4.62	0.63	0.31	0.039	0.045	0.285	0.167	98.43	31.92	32.74	12.98	17.82	0.25	0.48	0.060	2.14	0.40	1.44
8	191	1489	4.58	0.65	0.31	0.038	0.045	0.279	0.166	98.52	32.13	33.03	12.93	18.11	0.34	0.43	0.060	2.05	0.41	1.46
9	151	1496	4.78	0.77	0.32	0.040	0.035	0.294	0.205	98.17	32.75	32.30	13.05	18.18	0.24	0.35	0.025	1.78	0.32	1.57
10	178	1494	4.55	0.62	0.30	0.038	0.044	0.279	0.164	98.56	31.96	32.44	12.86	18.00	0.21	0.43	0.043	2.10	0.50	1.45
11	126	1490	4.39	0.52	0.29	0.039	0.051	0.274	0.135	98.66	31.50	32.98	12.55	18.08	0.27	0.53	0.085	2.43	0.60	1.35
12	126	1486	4.40	0.53	0.28	0.038	0.052	0.273	0.135	98.68	31.43	33.53	12.37	17.98	0.32	0.52	0.077	2.45	0.65	1.33
13	138	1493	4.37	0.51	0.27	0.038	0.064	0.269	0.121	98.81	30.67	33.64	12.56	17.89	0.33	0.61	0.117	2.56	0.72	1.27
14	84	1490	4.44	0.55	0.29	0.038	0.060	0.278	0.136	98.73	30.85	33.73	12.50	17.98	0.34	0.59	0.115	2.43	0.66	1.32
15	196	1489	4.46	0.61	0.29	0.038	0.057	0.275	0.147	98.65	31.30	33.63	12.52	18.20	0.23	0.47	0.055	2.30	0.63	1.41
16	111	1483	4.56	0.69	0.30	0.039	0.048	0.285	0.175	98.60	31.63	33.10	12.80	18.00	0.37	0.47	0.073	2.11	0.63	1.43
17	178	1490	4.49	0.61	0.30	0.038	0.051	0.274	0.154	98.68	31.56	33.04	13.12	18.08	0.23	0.47	0.056	2.22	0.64	1.44
18	91	1490	4.60	0.60	0.31	0.039	0.049	0.283	0.162	98.66	31.43	33.40	12.88	18.18	0.23	0.50	0.058	2.24	0.52	1.38
19	116	1497	4.79	0.77	0.32	0.040	0.035	0.286	0.198	98.43	32.16	32.98	13.44	18.32	0.23	0.37	0.030	1.81	0.33	1.50
20	101	1495	4.57	0.65	0.30	0.037	0.042	0.278	0.174	98.58	31.88	33.05	13.20	18.33	0.43	0.40	0.045	1.94	0.40	1.47
21	234	1487	4.36	0.56	0.30	0.039	0.055	0.276	0.153	98.71	31.39	33.17	12.61	18.38	0.26	0.46	0.050	2.35	0.52	1.44



**Figure 1 Correlation between  $L_S$  and  $L_{Mn}$  during different operational conditions.**

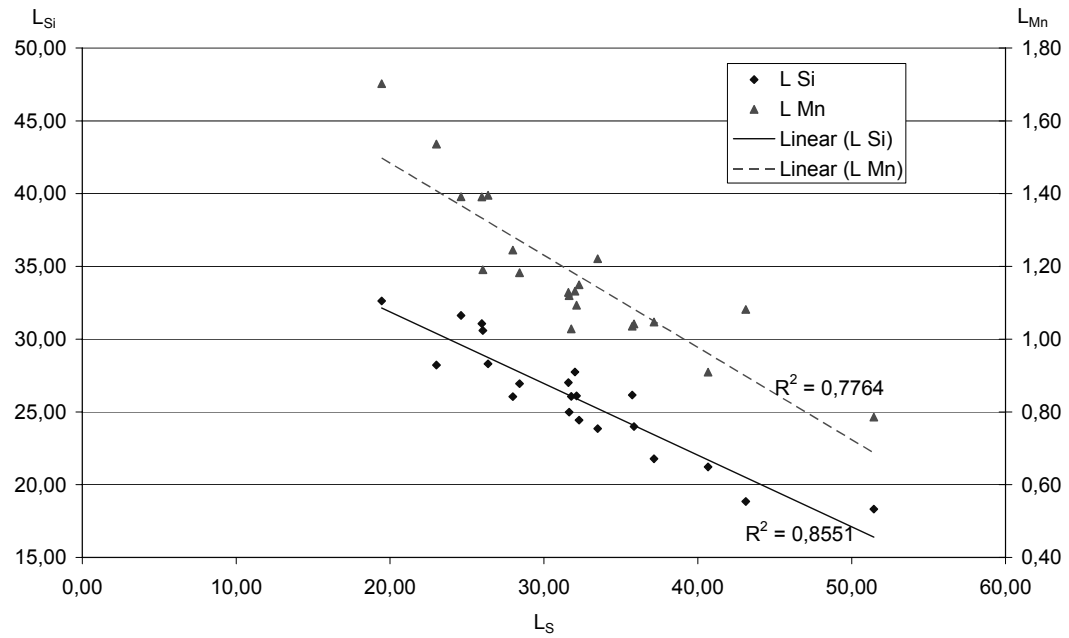
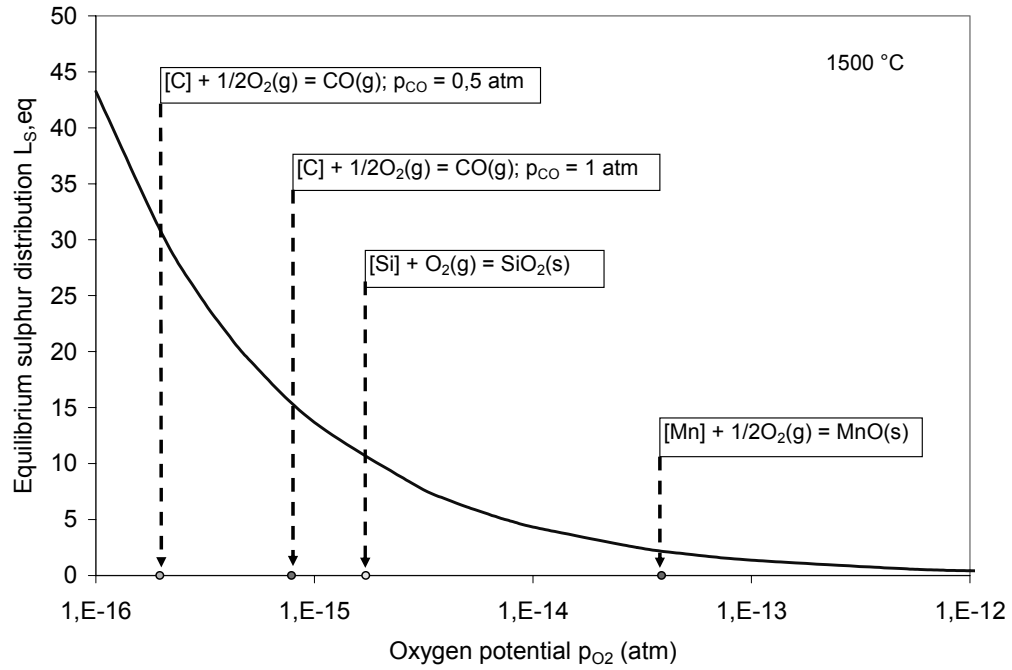
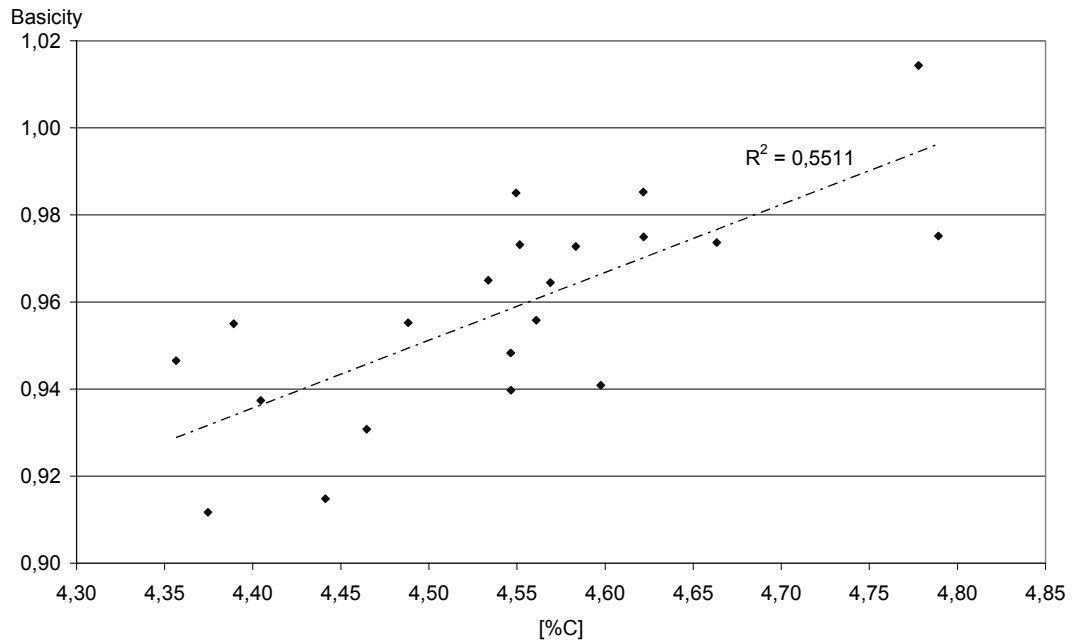


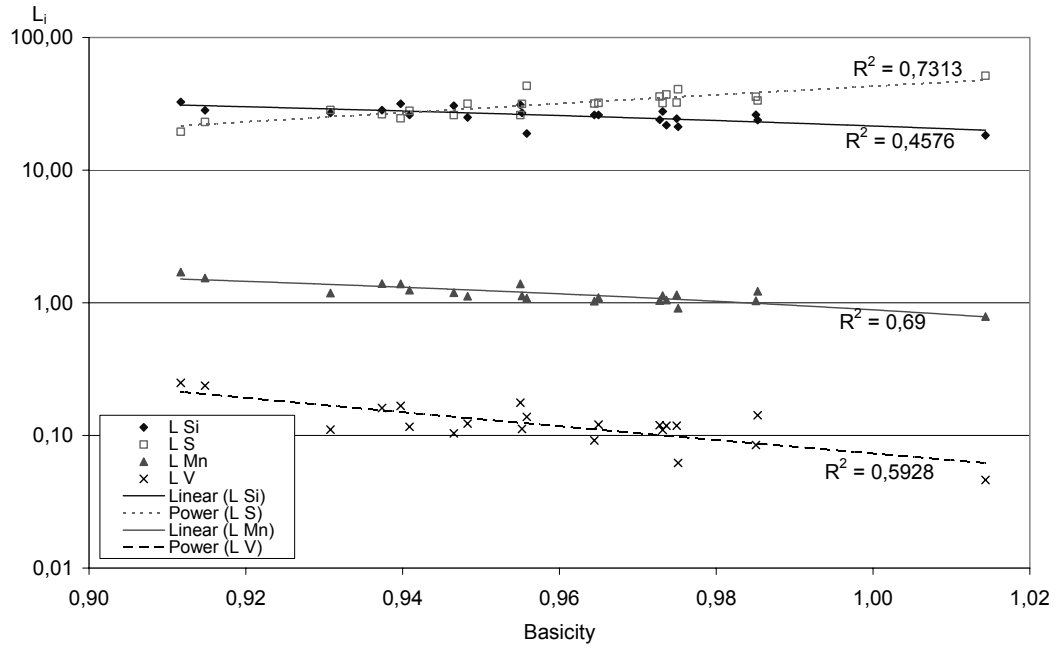
Figure 2 The correlation between  $L_S$  and  $L_{Si}$  and  $L_{Mn}$  as average values from 21 taps.



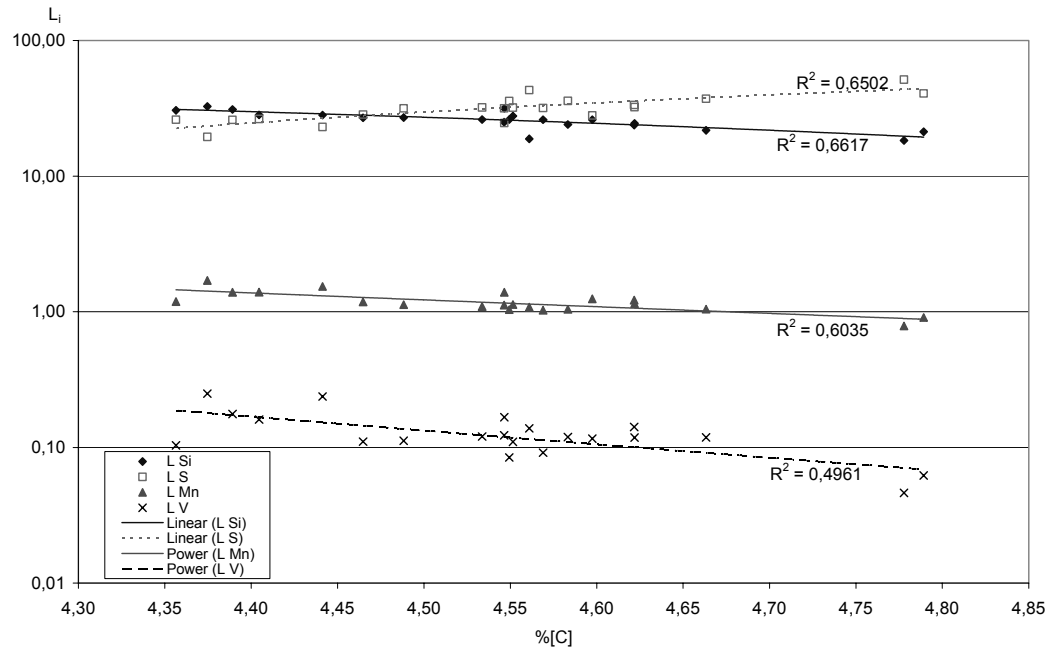
**Figure 3** The theoretical equilibrium for sulphur distribution as a function of partial pressure of oxygen and the partial pressure at equilibrium for equations (9) – (14), at 1500°C. For C/O/CO the equilibrium was calculated for  $p_{CO} = 0.5 \text{ atm}$  and  $1 \text{ atm}$ .



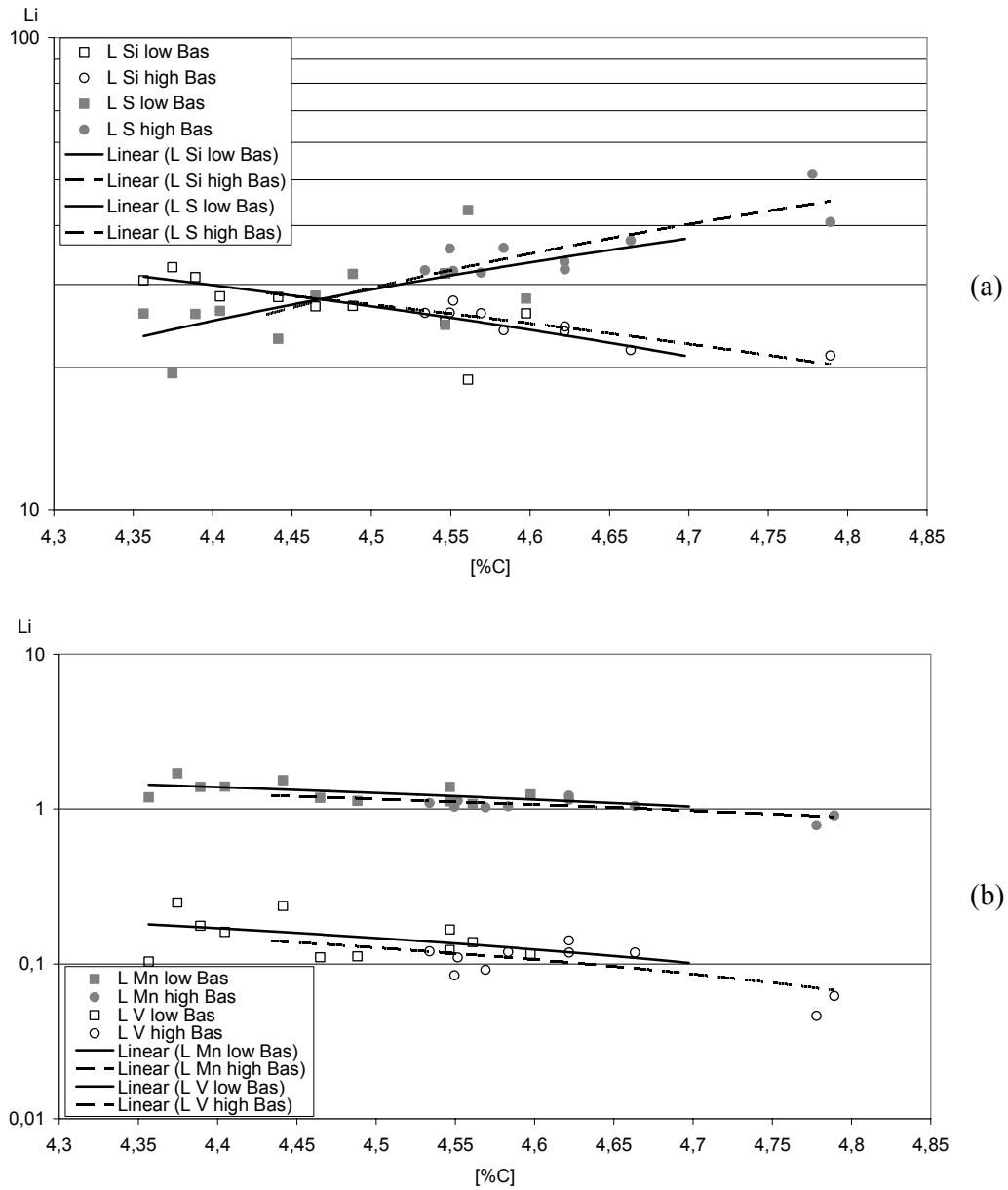
**Figure 4** Correlation between carbon in hot metal and basicity as average value for 21 taps.



**Figure 5** The correlation between the slag basicity and the distribution coefficients for 21 taps (average values).



**Figure 6** The correlation between carbon in hot metal and distribution coefficients during 21 taps (average values).



**Figure 7** The added effect of basicity and carbon in hot metal on the distribution coefficients  $L_{Si}$ ,  $L_S$ ,  $L_{Mn}$  and  $L_V$ . The basicity was split in two groups, where high basicity  $> 0.956$ .