Reactions in the Lower Part of the Blast Furnace with Focus on Silicon

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Abstract

The thermodynamic conditions for the behaviour of silicon in the lower part of the blast furnace have been the focus of the thesis. More specifically, the influences of temperature, carbon activity, total gas pressure and Fe reoxidation on silicon have been studied.

Calculations show that an increased temperature gives higher equilibrium ratio between silicon in hot metal and slag. Furthermore, laboratory reduction studies shows that the carbon activity in the cohesive zone increase with an increased reduction time. Increased carbon activity will increase the equilibrium silicon content in liquid metal.

Equilibrium calculations based on tapped hot metal and slag shows that the equilibrium silicon content of the liquid metal phase is higher than measured at tapping. Around the raceway area the equilibrium silicon content is very high. The high equilibrium silicon content makes it important to differ between the conditions under operation and the conditions of samples taken out of the blast furnace before studied. The equilibrium silicon content is strongly correlated to the CO gas partial pressure. Often this partial pressure is changed during sampling and cooling of samples. At tapping the equilibrium partial pressure of CO has been calculated to higher values than the total gas pressure inside the blast furnace.

Metal droplets found in tapped slags are probably formed by reduction of FeO. In the periphery part of the lower part of the blast furnace, it is believed that mainly FeO oxidises silicon in hot metal. It is not expected that the metal droplets in the slag is formed if FeO oxidises dissolved silicon. Instead, the iron droplets may form at reactions with gas, coke carbon or coal powder carbon. Around some droplets increased magnesium content has been found. This may be due to reactions with gaseous magnesium that, according to thermodynamic conditions, is easy to form. It has been reported that much FeO may be formed in the raceway area. The metal droplets may indicate how much FeO that reacts with other components than liquid iron. The iron found in metal droplets in the slag corresponds to between 0.02 and 0.2 wt-% FeO in the slag.

Keywords: blast furnace chemistry, ironmaking, thermodynamics, silicon compounds, combustion, fuel injection, mass balance, slags, pig iron, gases, droplets
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Supplements

The present thesis is based on the following papers:

Supplement 1. “Meltdown behaviour of pellets reduced in a laboratory reduction furnace”
J. Gustavsson, P. Hahlin and P.G. Jönsson

Supplement 2. “Effect of selected model parameters on predicted RAFT data”
J. Gustavsson, A.M.T. Andersson and P.G. Jönsson:

Supplement 3. “Comparison of Calculated Equilibrium and Operation Data for the Blast Furnace with Focus on Silicon”
J. Gustavsson, A.M.T. Andersson and P.G. Jönsson
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Submitted to Ironmaking & Steelmaking, August 2004.

Supplement 4. “A Thermodynamic Study of Silicon containing Gas in a Blast Furnace”
J. Gustavsson, A.M.T. Andersson and P.G. Jönsson
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Supplement 5. “Characteristics of Metal Droplets in Slag Tapped from the Blast Furnace”
J. Gustavsson, M. Shoyeb, D.S. Sarma and P.G. Jönsson
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Appendix 1. “Development of a new Raceway Adiabatic Flame Temperature Calculation Routine for Blast Furnaces with Multiple Material Injection”
J. Gustavsson, A.M.T. Andersson and P.G. Jönsson
Parts of this work were presented in the following conferences:


- Presented at the 61st Ironmaking Conference, Nashville, Tennessee, USA, March 10-13, 2002

II. “Flame Temperature Studies”, J. Gustavsson


III. “Thermodynamic Study of Si Behaviour in BF”, J. Gustavsson

- Presented at the Blast Furnace Seminar, Oulu, Finland, March 30-31, 2004.

IV. ”En Termodynamisk Studie av Kisels Upptärdande i Masugnen”, J. Gustavsson

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Contributions by the author

Supplement 1. Reduction trials: 0%
Sample preparation: 10%
Sample examination: 100%
Writing: 80%

Supplement 2. Literature survey: 100%
Modelling: 100%
Writing: 70%

Supplement 3. Literature survey: 100%
Sampling: 10%
Chemical composition of samples: 0%
Calculations: 100%
Writing: 90%

Supplement 4. Literature survey: 100%
Calculations: 100%
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Supplement 5. Literature survey: 50%
Sample preparation: 0%
Initial evaluation and method evaluation: 60%
SEM examination: 25%
EPMA examination: 0%
Thermo-Calc calculations: 100%
Writing: 70%
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1. Introduction

The main aim of this thesis has been to better understand the behaviour of silicon in the lower part of the blast furnace. The behaviour of silicon depends on several factors, like carbon contents and temperatures in different zones, reactions with FeO, gas pressures in the system, etc. Because of this it has been seen as important to study several different factors in the lower part of the blast furnace. However, it has not been possible to study all factors that influence the behaviour of silicon, why several limitations have been made. The most important limitation is that no kinetic calculations have been made; all calculations are based on equilibrium conditions. The calculated equilibrium conditions have been compared with measured data from different blast furnaces.

The thesis is based on five supplements. Some further work made on Supplement 2 and presented at a conference is presented in Appendix 1. Figure 1 shows the regions of the blast furnace studied in respective supplement.
Supplement 1 deal with a study on pellets that have been reduced in a laboratory furnace with increasing temperature and quenched just before meltdown. The carbon content in the reduced pellets has been compared for different pellet types and reduction conditions. Also, the structure of the iron has been studied. The aim has been to study possible carbon contents in reduced pellets just above and in the cohesive zone. The carbon content influences the silicon behaviour, why it is of importance to study the carbon content at different locations in the lower part of the blast furnace.

Supplement 2 covers adiabatic heat balance calculations around the raceway area. The temperature in the raceway area influences the silicon content in the gas phase. The main aim in the supplement has been to see how changes in injection and blast composition may change the temperature level around the raceway region under different assumptions in the model. The focus in Supplement 2 is to see how changes in the model assumptions affect the calculation results. Since measurement data from the blast furnace is used as indata to the model, measurement errors will also affect the calculation result. By this reason a conference publication was written that studied the effect of measurement errors on the calculation result. This conference publication can be found in Appendix 1.

In Supplement 3, equilibrium conditions at tapping of the blast furnace have been calculated based on the chemical composition of tapped hot metal and slag as well as measured hot metal temperatures from two Swedish blast furnaces. Local calculated equilibrium conditions as well as overall calculated equilibrium conditions are compared with the chemical composition of tapped hot metal and slag. The effect of the total gas pressure in the system on the equilibrium is also studied. In Supplement 4, equilibrium calculations have been performed regarding the amount of silicon in one Swedish blast furnace that can be present in the gas phase around the raceway at different temperatures. Finally, Supplement 5 focuses on metal droplets that have been found in the tapped slag of two Swedish blast furnaces. Possible formation mechanisms of the droplets are discussed.

The work within the supplements of this thesis has mainly been performed within two different projects administrated within the Swedish Steel Producers Association (Jernkontoret), JK2150 and JK21059. The projects have been financed by STEM. Some of the work behind Supplement 2 has also been done within another project (VIP), financed by NUTEK (research grant P11737-1).
1.1 Fundamentals of the blast furnace process

The blast furnace is the dominating process used in the World to reduce iron ores and produce liquid iron (hot metal). It is important to produce good quality hot metal to a low cost and also reduce the emissions to air, ground and water as much as possible. Iron ore contains iron oxide that has to be reduced to iron in the blast furnace. During the reduction, oxygen in the iron ore is transferred to some form of reduction agent. In the blast furnace, mainly coke coal is used as reduction agent, but also other kinds of coal and hydrogen bearers are used. These components are also burnt to give energy required for the reduction of iron and to heat the reduced iron so it melts. The main part of the blast furnace is the shaft, see Figure 2.

Figure 2 Schematic of the zones in the blast furnace shaft [1]
Blast (heated air with oxygen and humidity additions) is blown in through the tuyeres. Usually, also some form of fuel is added through a lance in the tuyere. CO gas, coke and injected fuels will burn due to a reaction with oxygen in the blast. The burning area just inside the tuyeres is usually mentioned as the raceway. Since the gas temperature in the raceway is high (usually about 2000°C) and carbon exists in excess, formed carbon dioxide (CO₂) will react with coal, forming carbon monoxide (CO). Water going into the flame will crack and form hydrogen gas (H₂). Carbon monoxide and hydrogen gas will then pass up through the shaft and act as reduction agents of the iron oxides. Nitrogen gas, hydrogen gas and carbon monoxide leaves the raceway with high temperature. During the passage up in the furnace the gas temperature sinks because heat is used to heat the burden material and also transformed to chemically bonded energy in endothermic (energy consuming) reactions.

Usually gas circulates inside the raceway. Lundh [2] has done a two-dimensional water model study of gas circulation inside the raceway, see Figure 3. This indicates that CO gas formed inside the raceway can circulate and be oxidised by oxygen just inside the tuyeres.

Figure 3  Two-dimensional representation of gas circulation inside the raceway. From water modelling study. [2]
At the top of the blast furnace iron bearers, coke and slag formers are added. The iron bearers mainly consist of Fe$_2$O$_3$, which is reduced in the following steps:

\[
\begin{align*}
\text{Fe}_2\text{O}_3(s) + \frac{1}{3} \text{CO/H}_2(g) & \rightarrow \frac{2}{3} \text{Fe}_3\text{O}_4(s) + \frac{1}{3} \text{CO}_2/\text{H}_2\text{O}(g) \quad (1) \\
\text{Fe}_3\text{O}_4(s) + \text{CO/H}_2(g) & \rightarrow 3 \text{FeO}(s) + \text{CO}_2/\text{H}_2\text{O}(g) \quad (2) \\
\text{FeO}(s) + \text{CO/H}_2(g) & \rightarrow \text{Fe}(s \text{ or } l) + \text{CO}_2/\text{H}_2\text{O}(g) \quad (3)
\end{align*}
\]

In the lower part of the blast furnace the iron will soften and melt, indicated as the cohesive zone in Figure 2. After melting, liquid iron will drop down through the active coke layer and the deadman, see Figure 2. The active coke layer is the coke that flows towards the raceway, where most of the coke is burnt. The deadman consists of coke that does not flow towards the raceway. Coke in the deadman can be located inside the blast furnace for a long time. It will mainly be consumed by dissolving into the liquid iron, but also to some extent in reaction with other species (e.g. MnO, P$_2$O$_5$ and SiO$_2$).

In the lower part of the blast furnace there are also several metal-slag reactions that will go towards equilibrium conditions. To get a better operation of the blast furnace (decreased energy consumption, better hot metal composition, etc.), the equilibrium conditions and the kinetics of the reactions can be controlled by for instance using different slag formers. Liquid iron and slag will flow toward the bottom of the shaft where they are tapped out of the blast furnace.

During the reduction reactions (1) – (3), CO$_2$ and H$_2$O are formed. In the parts of the shaft where the temperatures exceeds 1000°C, some of the formed carbon dioxide will react with carbon in coke and form CO gas according to the reaction:

\[
\text{C} + \text{CO}_2 = 2\text{CO} \quad (4)
\]

This reaction is known as Boudouard’s reaction or the solution-loss reaction. Boudouard’s reaction is important and reduces the amount of reduction agents needed in the blast furnace. However, the reaction consumes a large amount of energy and if the reaction rate is too high the fuel consumption will increase. In almost all situations the latter case dominates over the former case. To decrease the fuel rate in a blast furnace it is therefore important to decrease the reaction rate of Boudouard’s reaction.
The temperature in the blast furnace will decrease towards the top since most reactions need energy and the burden at the top is added at low temperature and is heated by the rising gas. This means that Boudouard’s reaction will occur in the lower part of the blast furnace. Another important factor in a blast furnace is that the resistance of the gas flow through the shaft must be relatively low. In other case, it will be problematic to inject the amounts of gas that is needed and the energy consumption increases. Most resistance for gas flow exists in the cohesive zone. To get a reliable gas passage through the cohesive zone, usually the shape of the cohesive zone is controlled so that gas can pass through the coke layers without passing through the melting metal, see Figure 2. This is done by increasing the temperature in the central part of the blast furnace compared to the periphery and half radius of the shaft. Since the thermal energy is mostly transported in the gas phase, the temperature in the centre of the blast furnace is increased if more gas passes the centre of the blast furnace shaft. To do this, more coke is placed in the central part of the blast furnace than at the periphery (central coke charging). Coke has higher porosity than the iron bearers, which makes it easier for the gas to pass through coke. It is also important that the burden material (especially coke) will not decompose in the shaft. This will otherwise give a high gas resistance in the shaft. Decomposition of material is influenced by the quality of the material, but also on the conditions in the shaft. Coke decomposition shows large influence on the conditions in the dead man. The operational result of the blast furnace will be better with less fines within the dead man.

There are some elements that have high partial gas pressures at the temperatures in the tuyere level, whereof the most important elements are K and Na (alkali metals). Elements that vaporise in the tuyere level will follow the gas stream up in the furnace. When the gas temperature decreases, a large amount of the elements will form solid compounds and follow the solid materials down in the blast furnace shaft, where they can vaporise again. In other words, these elements circulate in the blast furnace. The enrichment of alkali metals strongly affects the behaviour of the solid material inside the blast furnace shaft. Other elements that may circulate in the blast furnace are for instance sulphur and magnesium.

To lower the cost and decrease the emissions of gas in the blast furnace it is important to run the blast furnace with low amounts of coke and other fuels. Most of the ongoing blast furnace research deals with ways to decrease the total fuel consumption and also
replace expensive coke with cheaper fuels. The blast furnace can be controlled mainly by changing the amount, quality, composition and sometimes the temperature of ingoing materials and by charging the ingoing materials in a good way. The material of the blast furnace that is added at the top will take about 5-8 hours to reach the tuyere region. It will therefore take some time from that a change is made in the top charging until it can be noticed in the process. It is therefore important to know what changes to make well before it is obvious that a change has to be done. To reduce the fuel consumption in a blast furnace, work is done on several areas, such as:

- Improvement of the iron ore burden (composition, size, structure etc.).
- Improvements of the quality of all ingoing materials.
- Better control of the blast furnace process.
  - It is important to add the correct amount of fuel. If too much fuel is added the blast furnace will run warm and the gas emissions and fuel consumption increases. If too small amounts of fuel are added, the blast furnace will run cool which amongst other things cause problems to tap hot metal. It usually takes a lot of energy to overcome a cold blast furnace compared with constantly running it at an optimal fuel rate.
  - At the top of the blast furnace, coke and iron ore burden is charged in layers. It is important to control the thickness of the layers. The layer thickness can also be varied within the cross section of the blast furnace top. Having a good control of the charging at the top can save much fuel. The pressure drop inside the shaft is strongly influenced by how the burden is charged.
  - Controlling of the injection and the oxygen and humidity addition to the blast gives a faster response on the process than changing something at the top of the blast furnace. Fuel can be saved by a good control of these parameters. Many reactions and mechanisms are involved in the lower part of the blast furnace. It is important to explore the mechanisms and learn about the interaction between the different mechanisms to be able to better control the blast furnace.
  - The tapping interval and tapping praxis also affects the performance of the blast furnace.
1.2 Literature review on silicon transfer

Silicon enters the blast furnace mainly as silica in coke ash and also in injected materials. The silicon transfer to the hot metal mainly occurs via gas reactions involving SiO(g) and to some extent SiS(g) [3, 4].

Traditionally, the silicon content in hot metal has been higher than the optimal level. In this case, the optimum silicon level is seen as the silicon content that the steel plant wants to minimize the cost in the converter. In the converter, silicon will oxidize and form silica in the slag. Therefore, the silicon content of hot metal will decide the amount of silica formed in the converter. Since a certain amount of slag with certain silica content will be optimal, there exists an optimum silicon level in the hot metal. Nowadays, many large furnaces do not have any problems to produce hot metal with the optimal average silicon content. However, there is a problem to keep the silicon level constant. It has been reported that the most important action to avoid large standard deviations of the silicon content is to control the quality of raw materials [5]. In this section, literature about phenomena that affects the silicon level in hot metal is summarised. Below, some important phenomena that affect the silicon content is listed. These phenomena can usually, in turn, be affected by controlling of the blast furnace operation. Reduction of silica to SiO gas and further reduction of the SiO gas to dissolved silicon is seen as the main transfer mechanism of silicon in the blast furnace. These reactions are assumed to occur around the raceway area. Since the silica activity is much higher in the coke ash than in the slag, it is assumed that most SiO gas is formed from reductions in the coke ash. Below, references on parameters that affect the SiO gasification rate and the SiO reduction rate to dissolved silicon are given.

- The SiO gasification rate is affected by:
  - RAFT (Raceway Adiabatic Flame Temperature) [6-8].
    - Higher RAFT gives more SiO gas [6-8].
    - Lower RAFT often gives low hot metal temperature. To avoid this, the heat losses from the hearth must be decreased [6-8].
    - Parameters that affects RAFT also may affect the position of the cohesive zone, why there are occasions when increased RAFT leads to lower silicon content in hot metal [6, 7].
  - Activity of SiO₂ [9].
- Activity of carbon, and other coke properties.
  - The formation of SiC in coke affects the SiO gas formation [10, 11].
  - SiC + CO = SiO +2C [10].
- Wettability between coke and slag.
  - A decrease in wettability reduces the rate of SiO₂ + C(coke) = SiO + CO [7].
- CO₂, CO₂ and H₂ partial pressures may influence the reaction rate (mainly CO and CO₂) [12].
- An increased total gas pressure will lower the SiO gas formation rate [7].
- A higher blast volume (production) decreases the SiO gas formation rate [7, 13].
- The SiO gas reduction rate to dissolved Si is affected by:
  - Slag composition.
    - FeO activity (SiO + FeO = Fe + SiO₂, Si + 2FeO = SiO₂ + 2Fe) [14-16].
    - Injection of iron ore through the tuyeres can give higher FeO contents in the tuyere region [15, 16] and therefore lower silicon content in hot metal. The oxygen activity at the end of raceway was higher injecting iron ore, measured with oxygen activity probe [16]. There are indications on that the FeO content in the raceway can be high without injection of ore [17]. The high oxygen activity just inside the tuyeres may oxidise iron (usually mentioned as reoxidation) [17-24].
    - A higher slag basicity (lower activity of SiO₂) increases the SiO gas oxidation rate (to SiO₂), but if the basicity is too high the slag viscosity will increase and the SiO oxidation rate decrease [25].
  - HFR (Heat Flow Ratio) also mentioned TFR (Thermal Flow Ratio) [6, 7].
    - A higher HFR decreases the position of the cohesive zone [6, 7].
    - The HFR is defined as \( HFR = \frac{C_{p,s} \cdot M}{C_{p,g} \cdot G} \), where \( C_{p,s} \) is the specific heat of the solids per mass unit, \( C_{p,g} \) is the specific heat of the gas per mass unit, M is the mass flow of solids and G is the mass flow of gas.
  - Height of cohesive zone (especially the root) [10].
    - Lower cohesive zone results in short reaction times and less silicon [10].
  - Carbon activity both in metal and CO/CO₂ ratio [24, 26].
- SiO + C = Si + CO [24, 26, 27].
- SiO + CO = Si + CO₂ [28] (not of any major importance if carbon content in iron is high, [24, 27]).

- Reactions in hearth:
  - In the hearth the silicon reacts with other elements in the direction to equilibrium. The temperature and compositions within the hearth varies between different zones of the hearth, and therefore also the equilibrium conditions. [29]
  - The reaction 2MnO + Si = SiO₂ + 2Mn usually almost reaches equilibrium conditions [29, 5].

### 2. Thermodynamic calculations

To do a thermodynamic calculation, the total free energy in the system has to be expressed as a function of the amount of phases that may form under the conditions given as indata to the calculation. The equilibrium condition is where the total free energy in the system is lowest. Nowadays, most equilibrium calculations are performed using a computer software. Most thermodynamic calculations in this thesis have been performed using the computer software Thermo-Calc [30, 31]. The reason of using this software was that it is flexible and that it can handle many phases at the same time, but also that it was easy to get help to solve problems that occurred during the calculations (the software is mainly developed within the same department as this work was carried out). The Thermo-Calc software reads thermodynamic data from databases that are developed to work with Thermo-Calc. All databases contain thermodynamic data, usually for several phases. So far, there is no single database developed that can handle equilibrium conditions including all the phases found in the blast furnace. By this reason, several databases were combined. Each phase that can be present in the blast furnace was read from the database that best covered that phase. Unfortunately, there does not exist any databases that are perfect. Actually, no companies behind any computer software for thermodynamic calculations have been found that can guarantee that the calculation result will represent the true equilibrium condition.

After reading data from the databases other data have to be given as indata to be able to calculate the amount of each phase that is stable. Different types of data can be given as indata (e.g. total amount of elements, activity of components, temperature, total gas pressure and enthalpy values). Each indata will reduce the degrees of freedom with one.
To be able to perform a calculation there has to be zero degrees of freedom in the system. Thermo-Calc can be used to calculate the stable phases in a system and the amount of the stable phases. Also, activity data can be displayed. Several other types of data can also be displayed (e.g. enthalpy data and free energy data). The route to perform a calculation presented in this thesis has usually been:

1. The aim of the calculation was specified.
2. The elements of interest were specified.
3. The phases of interest were specified.
4. The best available databases covering the elements and phases of interest were combined. Usually there is not possible to find description of phases that covers all elements of interest. In these situations it was needed to neglect the influence of some elements within some phases (e.g. no description of the slag phase including the elements Ti, K and V could be found). Also, some minority elements may be ignored to run into less problems to get the numerical calculations to converge.
5. The indata to the calculations were specified and entered in Thermo-Calc. Usually the amount of each element, the temperature and the total gas pressure was used as indata. In some calculations, the activity of a specie was given instead of the amount of an element (e.g. the carbon activity was given instead of the amount of carbon in the system). In case the activity shall be given as unity, it is usually not possible to set the activity to one. Instead, a command has to be given that the phase shall be stable and that the amount of the phase at equilibrium shall be zero. It would not work to replace the amount of carbon with unity carbon activity relative graphite. This is due to that there are infinite many solutions, since graphite will form when adding enough much carbon. When graphite has formed, adding more carbon would just form more graphite at unity carbon activity relative graphite.
6. The equilibrium condition was calculated. The calculations in Thermo-Calc are performed using numerical methods. In many cases it is hard to get the calculations to converge. There are several ways to get the system to converge better. The most commonly used in this work has been to first suspend all phases except some phases that can include almost all elements (usually the gas, slag and liquid metal phases were the only phases included). To suspend phases means that the phases are not included in the calculations. Usually the calculations converge if only a few phases are included in the calculations. However, the calculation results may be completely wrong. After getting convergence all suspended phases are set as dormant. Dormant means that
the driving force to form the phase is calculated without including the phase in the mass balance. Stable phases were then set as entered, one at a time. Entered means that the phase is completely covered in the calculations.

7. Commands to show the wanted results were entered.

2.1 Used databases in Thermo-Calc

The Slag1 database (TC Fe-containing Slag Database version 1.2, 1992/1998) [32] was used for calculations pertaining to the slag phase and for some solid phases. In the Slag1 database, a liquid metal phase is described using a dilute-solution model in liquid iron. The interaction coefficients are taken from Sigworth and Elliot's work [33] and modified to function as a regular-solution model according to a suggestion by Hillert [34]. The liquid-iron-phase model is not recommended when there is an element except iron with a concentration above 0.1 wt-% [32]. The liquid slag phase is modelled with the IRSID slag model that is based on a quasichemical cell model by Kapoor-Frohberg and modified by Gaye [32]. The database covers the slag system Al₂O₃-CaO-FeO-Fe₂O₃-MgO-SiO₂. More recently also data for Na, Cr, Ni, P and S in the slag phase have been added. The database also includes solid phases [32].

The TCFe3 database (TCSAB Steels/Fe-Alloys Database version 3.0 2002) [35] includes an alloying model for the iron-rich liquid phase that can handle higher amounts of alloying elements than models based on dilute solutions (see Table 1) [35]. It has been reported that there may be problems if several elements have compositions close to the limits [35]. In the case of BF hot metal, the only elements that are close to the limits are carbon and sulphur. From Table 1 it can be seen that only traces of oxygen can be treated. The activity of oxygen is important when calculating metal-slag equilibriums. There are never large amounts of oxygen dissolved in liquid iron (especially in the lower part of the blast furnace), but since only traces can be handled by the database there might be some problems with metal-slag equilibrium calculations. The database can only handle traces of sulphur, which indicates that the reliability of sulphur activities calculated with the model is not high. Despite the limitations with the TCFe3 database, it was in most calculations seen as the best choice for calculation of the iron-rich liquid phase. It was originally developed to be able to reproduce the phase diagrams for the iron-rich corner of the system and is based on experimental data for binary and ternary systems extrapolated to higher order systems [35]. Besides the iron-rich liquid phase the database
also covers solid phases. Intermediate compounds that do not occur in steel are excluded from the TCFe3 database [35].

Table 1  Recommended limits of elements in the liquid metal phase described in the TCFe3 database (wt-%) [35].

<table>
<thead>
<tr>
<th>Element</th>
<th>max</th>
<th>Element</th>
<th>max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>5.0</td>
<td>Nb</td>
<td>5.0</td>
</tr>
<tr>
<td>B</td>
<td>trace</td>
<td>Ni</td>
<td>20.0</td>
</tr>
<tr>
<td>C</td>
<td>5.0</td>
<td>O</td>
<td>trace</td>
</tr>
<tr>
<td>Co</td>
<td>15.0</td>
<td>P</td>
<td>trace</td>
</tr>
<tr>
<td>Cr</td>
<td>30.0</td>
<td>S</td>
<td>trace</td>
</tr>
<tr>
<td>Cu</td>
<td>1.0</td>
<td>Si</td>
<td>5.0</td>
</tr>
<tr>
<td>Mg</td>
<td>trace</td>
<td>Ti</td>
<td>2.0</td>
</tr>
<tr>
<td>Mn</td>
<td>20.0</td>
<td>V</td>
<td>5.0</td>
</tr>
<tr>
<td>Mo</td>
<td>10.0</td>
<td>W</td>
<td>15.0</td>
</tr>
<tr>
<td>N</td>
<td>1.0</td>
<td>Fe</td>
<td>min 50</td>
</tr>
</tbody>
</table>

The SSol2 database (SGTE Solutions Database version 2.1, 1999/2002/2003) [36] includes an alloying model for metal phases. The database covers wider composition ranges than the TCFe3 database. However, the accuracy of the results usually is worse. Comparison between the databases SSol2 and TCFe3 for a typical blast furnace hot metal showed that the calculated activity of most elements was almost equal. However, large differences were found for sulphur and phosphorus. The database has been used in a few cases where the silicon content in the liquid metal was found to be higher than what is covered in the TCFe3 database.

The SSub3 database (SGTE Substances Database version 3.1, 2001/2002) [37] was utilised for calculation of the gas phase. This database can handle all known gas species of importance including the elements that are included in the databases used to describe the other phases. The database is produced by SGTE, Scientific Group Thermodata Europe. The gas phase is described assuming ideal conditions [37]. Thermodynamic data for the gas species comes from several different sources. The database also covers several solid phases [37]. The solid phases covered in the database have only been used in a few calculations.
3. Equipment description

3.1 Production blast furnaces

Results from two different Swedish production blast furnaces have been studied. One of the blast furnaces is blast furnace no. 3 at SSAB Tunnplåt AB in Luleå. The other is blast furnace no. 4 at SSAB Oxelösund AB. The production capacity and some other figures of the blast furnaces can be found in Table 2. Both blast furnaces are operated with fluxed pellets as iron-containing burden.

Table 2  Blast furnace specifications.

<table>
<thead>
<tr>
<th></th>
<th>BF No. 3 SSAB, Luleå, Sweden</th>
<th>BF No. 4 SSAB Oxelösund, Sweden</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production capacity</td>
<td>7000</td>
<td>3000</td>
</tr>
<tr>
<td>(metric ton/24 h)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relined (year)</td>
<td>2000 (rebuilt)</td>
<td>1996</td>
</tr>
<tr>
<td>Hearth diameter (m)</td>
<td>11.4</td>
<td>8.6</td>
</tr>
<tr>
<td>Working volume (m³)</td>
<td>2540</td>
<td>1339</td>
</tr>
<tr>
<td>No. of tuyeres</td>
<td>32</td>
<td>20</td>
</tr>
<tr>
<td>No. of tapholes</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Charging system</td>
<td>Central feed Bell less top</td>
<td>Rotating chute</td>
</tr>
<tr>
<td>Max top overpressure (atm)</td>
<td>1.5</td>
<td>0</td>
</tr>
<tr>
<td>Approx. normal bustling</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pressure (atm) (Note, total</td>
<td>3.7</td>
<td>2.0</td>
</tr>
<tr>
<td>overpressure)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2 LKAB’s Experimental Blast Furnace (EBF)

In some studies, data from the LKAB Experimental Blast Furnace (EBF) have been used. The main specifications of the EBF can be found in Table 3. The gas pressure drop in the EBF is small and the total gas pressure in the lower part of the EBF is only slightly higher than the top gas pressure.
Table 3  LKAB’s EBF specifications.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working volume (m³)</td>
<td>8.2</td>
</tr>
<tr>
<td>Hearth diameter (m)</td>
<td>1.2</td>
</tr>
<tr>
<td>Working height (m)</td>
<td>5.9</td>
</tr>
<tr>
<td>No. of tuyeres</td>
<td>3</td>
</tr>
<tr>
<td>Tuyeres diameter (mm)</td>
<td>54</td>
</tr>
<tr>
<td>Max top overpressure (atm)</td>
<td>1.5</td>
</tr>
<tr>
<td>Charging system</td>
<td>Modified bell type</td>
</tr>
<tr>
<td>Burden distribution</td>
<td>Movable armour</td>
</tr>
<tr>
<td>Injection</td>
<td>Coal, oil, slag formers</td>
</tr>
<tr>
<td>Max blast flow (Nm³/h)</td>
<td>2000</td>
</tr>
<tr>
<td>Blast heating</td>
<td>Pebble heaters</td>
</tr>
<tr>
<td>Max. blast temp. (°C)</td>
<td>1300</td>
</tr>
<tr>
<td>Furnace crew (persons/shift)</td>
<td>5/shift</td>
</tr>
<tr>
<td>Tapping quantity (thm/tap)</td>
<td>1.3 - 1.8</td>
</tr>
<tr>
<td>Tap time (minutes)</td>
<td>5 - 10</td>
</tr>
<tr>
<td>Tapping interval (minutes)</td>
<td>60</td>
</tr>
<tr>
<td>Fuel rate (kg/thm)</td>
<td>510 - 540</td>
</tr>
<tr>
<td>Quenching N₂ gas flow (Nm³/h)</td>
<td>300 - 400</td>
</tr>
</tbody>
</table>

1  The charging system at the time studies included in this thesis was performed. New charging system has been developed since then.
2  Excluding sampling/research staff

3.3 MEFOS’s Reduction-Under-Load Furnace

MEFOS’s Reduction-Under-Load Furnace is used to simulate reduction of different preparations of iron ores. The layout of the experimental set-up is shown in Figure 4. The laboratory furnace is used to simulate the burden material behaviour from the thermal reserve zone down to the cohesive zone or to melting. The furnace consists of two parts, a lower induction coil for heating of reducing gas and an upper induction coil where the sample material is placed. The crucible material and most other materials in the furnace consist of graphite. CO₂ added to ingoing gas would react with graphite in the furnace, forming CO. Because of this, no CO₂ is added with the ingoing gas. Instead, a pre-reduction is performed in another furnace. The pre-reduction is usually done to reach a reduction degree of 30%. After this, the sample material is heated in nitrogen.
atmosphere, usually to 900°C. The heating is performed with constant heating rate within a trial, but can differ between different trials. The reducing gas can be a mixture of N₂, CO and H₂ gases. A trial can continue until melting of the iron or be quenched with nitrogen gas at a certain temperature.

Figure 4  MEFOS’s reduction under load furnace.
4. Review of supplement 1

4.1 Introduction and background

The shape of the cohesive zone in a blast furnace mainly depends on the temperature and gas flow distribution in the blast furnace. These factors also affect the reduction behaviour and the melting point of the burden material. This study focused on the pellet characteristics just before meltdown for two different pellets: olivine and acid pellets. Reduction trials were performed in the reduction-under-load equipment at MEFOS, Luleå, Sweden as a part of the ECSC project “Characterising of the Blast Furnace Cohesive zone at high PCI”. The equipment has been described in a previous section. The material to be tested was placed in a graphite crucible 80 mm in diameter. The sample material was placed on a 20 mm coke pebble layer and another coke pebble layer was placed above the sample material. The sample material particle size was between 10 and 15 mm and the height was around 70 mm. The total sample material weight was around 640 grams.

The ferrous material was pre-reduced in a pre-reduction equipment at LKAB, Malmberget to a reduction degree of 30%, corresponding to the reduction degree in the thermal zone of the blast furnace. The temperature and gas composition for the pre-reduction was set according to the test program used in the MEFOS laboratory reduction under load furnace. The gas flow was, however, set to a lower value. The gas composition was set constant in all trials to 39 % CO, 9 % H₂ and 52 % N₂. This gas composition was chosen based on measurements made by CRM in a production blast furnace with a high PCI rate (around 200 kg/thm) [38]. In the reduction furnace at MEFOS, the burden was first heated to about 900°C in a nitrogen atmosphere before CO and H₂ gas were added. During the test, data were logged every 10 seconds. The main measured data were pressure drop over the charge and shrinkage of the charge. An experimental program for the tests was designed according to statistical planning using the software Modde, developed by Umetrics, Umeå, Sweden [39]. The temperature increase rate, load, and gas flow rate were used as variables during the experiments. Earlier performed trials [38] were run until meltdown of the pellets. From the results of these trials, a model was developed to predict the meltdown temperature as a function of pellet type, temperature increase rate, gas flow and applied load [38]. From this model, the meltdown temperature on the interrupted trials was calculated. Data on the trial conditions, the calculated meltdown
temperature, the maximum temperature in the trials and the crucible contraction in % of the pellets height at start-up for the interrupted trials can be found in Table 4.

Table 4  The trial conditions, maximum temperature in the trials and maximum burden compression (% of the original pellet height).

<table>
<thead>
<tr>
<th>Charge</th>
<th>Gas flow (NL/min)</th>
<th>Temp increase rate (°C/min)</th>
<th>Load (kPa)</th>
<th>Pellet type</th>
<th>Calculated meltdown temperature (°C)</th>
<th>Max temperature in the trial (°C)</th>
<th>Max burden compression (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>507</td>
<td>235</td>
<td>3</td>
<td>49</td>
<td>Olivine</td>
<td>1377</td>
<td>1315</td>
<td>60.7</td>
</tr>
<tr>
<td>508</td>
<td>235</td>
<td>5</td>
<td>49</td>
<td>Olivine</td>
<td>1461</td>
<td>1461</td>
<td>60.8</td>
</tr>
<tr>
<td>509</td>
<td>235</td>
<td>3</td>
<td>100</td>
<td>Olivine</td>
<td>1359</td>
<td>1303</td>
<td>59.5</td>
</tr>
<tr>
<td>510</td>
<td>235</td>
<td>5</td>
<td>100</td>
<td>Olivine</td>
<td>1443</td>
<td>1434</td>
<td>60.5</td>
</tr>
<tr>
<td>511</td>
<td>200</td>
<td>5</td>
<td>49</td>
<td>Olivine</td>
<td>1470</td>
<td>1451</td>
<td>60.6</td>
</tr>
<tr>
<td>512</td>
<td>270</td>
<td>3</td>
<td>100</td>
<td>Olivine</td>
<td>1351</td>
<td>1328</td>
<td>60.4</td>
</tr>
<tr>
<td>513</td>
<td>235</td>
<td>3</td>
<td>49</td>
<td>Acid</td>
<td>1393</td>
<td>1332</td>
<td>54.3</td>
</tr>
<tr>
<td>514</td>
<td>235</td>
<td>5</td>
<td>49</td>
<td>Acid</td>
<td>1467</td>
<td>1448</td>
<td>66.4</td>
</tr>
<tr>
<td>515</td>
<td>235</td>
<td>3</td>
<td>100</td>
<td>Acid</td>
<td>1382</td>
<td>1337</td>
<td>59.0</td>
</tr>
<tr>
<td>516</td>
<td>235</td>
<td>5</td>
<td>100</td>
<td>Acid</td>
<td>1455</td>
<td>1424</td>
<td>60.4</td>
</tr>
<tr>
<td>517</td>
<td>270</td>
<td>3</td>
<td>100</td>
<td>Acid</td>
<td>1396</td>
<td>1332</td>
<td>60.5</td>
</tr>
<tr>
<td>518</td>
<td>200</td>
<td>5</td>
<td>49</td>
<td>Acid</td>
<td>1452</td>
<td>1446</td>
<td>64.4</td>
</tr>
</tbody>
</table>

4.2 Sample preparation and structure of samples

After the interrupted trials the crucibles were filled with epoxy that was allowed to solidify and then cut vertically into two halves. From one of the halves two microscope samples were cut out, one including pellets in the crucible periphery and one in the crucible centre. These samples were polished and studied in an optical microscope. It was found that all samples were completely reduced; no wüstite was found. Furthermore, almost no slag was found. Two different kinds of iron structures were found. One with dendritically formed iron, later called structure 1 and one with a more melted iron structure, later called structure 2. The relative amount of the two iron structures was evaluated. The amount of structure 2, expressed as wt-% of the iron found in structure 2 is summarised in Table 5. The test conditions are also included in the table.
Table 5  Percent of metallic phase represented as structure 2 in wall sample and centre sample respectively in the crucibles from the trials. The test conditions are also included.

<table>
<thead>
<tr>
<th>Charge</th>
<th>Wall sample</th>
<th>Centre sample</th>
<th>Gas flow (N/min)</th>
<th>Temp increase (°C/min)</th>
<th>Load (kPa)</th>
<th>Pellet type</th>
</tr>
</thead>
<tbody>
<tr>
<td>507</td>
<td>78.8</td>
<td>54.4</td>
<td>235</td>
<td>3</td>
<td>49</td>
<td>Olivine</td>
</tr>
<tr>
<td>508</td>
<td>77.7</td>
<td>48.1</td>
<td>235</td>
<td>5</td>
<td>49</td>
<td>Olivine</td>
</tr>
<tr>
<td>509</td>
<td>77.4</td>
<td>39.3</td>
<td>235</td>
<td>3</td>
<td>100</td>
<td>Olivine</td>
</tr>
<tr>
<td>510</td>
<td>66.1</td>
<td>45.3</td>
<td>235</td>
<td>5</td>
<td>100</td>
<td>Olivine</td>
</tr>
<tr>
<td>511</td>
<td>86.0</td>
<td>74.8</td>
<td>200</td>
<td>5</td>
<td>49</td>
<td>Olivine</td>
</tr>
<tr>
<td>512</td>
<td>72.3</td>
<td>48.1</td>
<td>270</td>
<td>3</td>
<td>100</td>
<td>Olivine</td>
</tr>
<tr>
<td>513</td>
<td>93.0</td>
<td>77.5</td>
<td>235</td>
<td>3</td>
<td>49</td>
<td>Acid</td>
</tr>
<tr>
<td>514</td>
<td>90.5</td>
<td>80.9</td>
<td>235</td>
<td>5</td>
<td>49</td>
<td>Acid</td>
</tr>
<tr>
<td>515</td>
<td>91.2</td>
<td>76.5</td>
<td>235</td>
<td>3</td>
<td>100</td>
<td>Acid</td>
</tr>
<tr>
<td>516</td>
<td>71.9</td>
<td>45.9</td>
<td>235</td>
<td>5</td>
<td>100</td>
<td>Acid</td>
</tr>
<tr>
<td>517</td>
<td>92.2</td>
<td>92.0</td>
<td>270</td>
<td>3</td>
<td>100</td>
<td>Acid</td>
</tr>
<tr>
<td>518</td>
<td>93.6</td>
<td>74.0</td>
<td>200</td>
<td>5</td>
<td>49</td>
<td>Acid</td>
</tr>
</tbody>
</table>

4.3 Carbon determination

After the determination of iron structure, the samples were etched with 4% HNO₃ dissolved in ethyl alcohol. Thereafter, the metallic phases were studied. It was found that the iron consisted of free ferrite, pearlite (an eutecticum structure consisting of ferrite and cementite) and free cementite. The carbon content in these phases can approximately be found in the Fe-C phase diagram [40]. By studying the relative amount of the phases found, the carbon content could be estimated. The carbon content was estimated at several positions within each sample. Thereafter the average carbon composition was calculated for the pellet periphery and the pellet centre for pellets located close to the crucible wall, half radius of the crucible and in the crucible centre, see Table 6.

Table 6  Average carbon contents in different charges and at different pellet locations in the pellets.

<table>
<thead>
<tr>
<th>Charge</th>
<th>507</th>
<th>508</th>
<th>509</th>
<th>510</th>
<th>511</th>
<th>512</th>
<th>513</th>
<th>514</th>
<th>515</th>
<th>516</th>
<th>517</th>
<th>518</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flow (N/min)</td>
<td>235</td>
<td>235</td>
<td>235</td>
<td>235</td>
<td>200</td>
<td>270</td>
<td>235</td>
<td>235</td>
<td>235</td>
<td>235</td>
<td>270</td>
<td>200</td>
</tr>
<tr>
<td>Temp increase (°C/min)</td>
<td>3</td>
<td>5</td>
<td>3</td>
<td>5</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>5</td>
<td>3</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Load (kPa)</td>
<td>49</td>
<td>49</td>
<td>100</td>
<td>100</td>
<td>49</td>
<td>100</td>
<td>49</td>
<td>49</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>49</td>
</tr>
<tr>
<td>Pellet type</td>
<td>Olivine</td>
<td>Olivine</td>
<td>Olivine</td>
<td>Olivine</td>
<td>Olivine</td>
<td>Olivine</td>
<td>Acid</td>
<td>Acid</td>
<td>Acid</td>
<td>Acid</td>
<td>Acid</td>
<td>Acid</td>
</tr>
</tbody>
</table>

| Wall sample | %C pellet periphery close to wall | 1.74 | 0.92 | 1.19 | 0.80 | 0.63 | 1.15 | 1.12 | 0.75 | 0.88 | 0.61 | 0.85 | 0.62 |
| Wall sample | %C pellet centre close to wall | 1.26 | 0.75 | 1.32 | 0.78 | 0.68 | 1.28 | 0.90 | 0.71 | 0.93 | 0.70 | 0.88 | 0.53 |
| Wall sample | %C pellet periphery far from wall | 1.11 | 0.78 | 1.09 | 0.75 | 0.81 | 1.16 | 0.95 | 0.80 | 1.10 | 0.62 | 1.14 | 0.75 |
| Wall sample | %C pellet centre far from wall | 0.91 | 0.44 | 0.96 | 0.37 | 0.54 | 0.52 | 1.24 | 0.63 | 1.29 | 0.35 | 0.93 | 0.63 |
| Centre sample | %C pellet periphery | 1.16 | 0.96 | 1.27 | 0.77 | 0.75 | 1.08 | 0.98 | 0.78 | 1.05 | 0.73 | 1.13 | 0.71 |
| Centre sample | %C pellet centre | 0.73 | 0.51 | 0.66 | 0.22 | 0.57 | 0.49 | 0.75 | 0.58 | 0.65 | 0.20 | 0.81 | 0.46 |
4.4 Discussion

A plot on the average of the sixth carbon contents for each charge found in Table 6 versus the calculated meltdown temperature is shown in Figure 5. A straight line in the figure gives an $R^2$ value of 0.79. This indicates that there exists a correlation between the carbon content and the calculated meltdown temperature.

![Figure 5](image.png)

Figure 5 Plot of average calculated meltdown temperature versus carbon contents in the sample. The two different used pellet types are notated.

The difference in carbon content between the crucible wall and the crucible centre is small in comparison to the total carbon content, see Table 6. The average difference of the carbon content can be calculated as 0.17 wt-%, while the average carbon content is 0.83 wt-%. It can though be expected that most of the carbon in the metal phase mostly comes from CO gas that forms dissolved carbon and CO$_2$.

From earlier trials there exist indications that the most important property on the meltdown temperature is the temperature increase rate. A lower temperature increase rate gives longer trials and the reduction is completed at lower temperatures giving more time for carburisation of the metal. This, in turn, decreases the meltdown temperature. It can be concluded that the time for carburisation is important for the carbon content and that the carbon content mainly is controlled by some kinetic step of the carbon dissolution process. It can be expected that the carbon content is dependent upon the reduction
time. The reduction in the MEFOS reduction furnace starts at about 900°C. In Figure 6, the average carbon content in the crucibles is plotted as a function of the time that the pellets have been over 900°C. From the figure, it can be concluded that the reduction time is correlated to the carbon content in the samples.

![Figure 6](image)

Figure 6  Plot of average carbon contents in the sample versus calculated meltdown temperature. The two different used pellet types are notated.

The iron structure of the samples shows that there has been more melted material (structure 2) close to the crucible wall than in the crucible centre, see Table 5. The ratio of structure 1 to structure 2 is supposed to be dependent on exactly how close to the melting point the trial has been interrupted. This differs to some extent between the samples, compare with Table 4 (either the temperature difference between the calculated meltdown temperature and the temperature where the trials were interrupted nor the contraction of the crucibles are constant between the samples). This results in that the ratio of the structures cannot be compared between the samples. Instead, it is more useful to compare the ratio of the amount of structure 2 between the crucible wall and the crucible centre. The reason that the iron close to the crucible wall melts faster than iron in the crucible centre has been assumed to depend on that graphite dissolves into the crucible and reduces the melting point of the iron. From Figure 7 it can be concluded
that the difference in carbon content in the centre of the pellets between the crucible wall and the crucible centre to some extent are correlated to the ratio of structure 2 between the crucible wall and the crucible centre. The corresponding graph, but for the carbon content in the pellet periphery instead of the carbon content in the pellet centre, shows no correlation, see Figure 8. It can therefore be concluded that the reason for the difference in iron structure at least partly occurs because of differences in carbon content in the metal phase in the centre of the pellets between the crucible wall and the crucible centre. The carbon content at the pellet periphery is probably close to equilibrium conditions while the carbon content in the pellet centre depends upon how long time the carburisation process has occurred and the kinetics in carburisation of the iron phase. Close to the crucible wall, the difference of carbon content between the pellet centre and the pellet periphery is small compared with in the crucible centre, indicating that the kinetics of carbon dissolution is better towards the crucible wall. Differences in carbon contents can occur because graphite dissolves directly in the iron, temperature differences in the crucible or that formed CO₂ is reduced to CO by carbon in the graphite wall. An increase of the CO to CO₂ ratio gives higher dissolved carbon contents in the iron phase.

Figure 7 The ratio between the iron phase structure 2 close to the crucible wall and iron phase structure 2 in the crucible centre is plotted versus the difference in carbon content in the pellet centre between the crucible wall and the crucible centre.
Figure 8  The ratio between the iron phase structure 2 close to the crucible wall and iron phase structure 2 in the crucible centre is plotted versus the difference in carbon content in the pellet periphery between the crucible wall and the crucible centre.

The sample was heated in two ways; the gas was preheated before it entered the crucible and the crucible walls were heated with induction. During the trials it was observed that the preheating furnace was regulated to 100% of the maximum power before the maximum temperature was reached. After this, the power to the induction coil that heats the crucible wall was further increased. This indicates that there might have been warmer towards the crucible wall than in the crucible centre at high temperatures. The gas flow through the crucible was set to a very high value that should give a highly turbulent flow through the crucible, which tends to result in an even temperature distribution in the crucible. However, it is possible that this was not enough to get the same temperature all over the crucible. The temperature was just measured close to the crucible wall, which gives no experimental values to confirm that the temperature is equal in all parts of the crucible. If the temperature is higher at the crucible wall this material might be reduced faster than in the crucible centre, resulting in that there are more time to carburise the iron phase. A higher temperature also improves the kinetic conditions of the carbon...
dissolution. This can explain why the carbon content is more equal between the pellet periphery and the pellet wall close to the crucible wall compared with the crucible centre.

5. Review of supplement 2

The Raceway Adiabatic Flame Temperature (RAFT) has been calculated and used in blast furnace control during a long time. The RAFT is calculated as well as used in different ways in different blast furnace plants. At the Swedish blast furnaces, the aim is to keep the RAFT relatively constant by adjusting the oxygen content of the blast in order to have a reliable operation. Therefore, the RAFT calculations are also used to predict the optimum exchange ratios between, for example, coal powder and oxygen content in blast at a constant RAFT value. It should be noted that RAFT is a calculated temperature and not the actual temperature. The actual temperature in the raceway is lower than the RAFT since no heat losses are included in the calculation. The temperature in the raceway also varies in different zones of the raceway. It has been noticed that the temperature profile is influenced by coal injection [41].

Some of the parameters that are used in the calculation of the flame temperature are not easy to set realistic values for, which makes it necessary to come up with assumptions. This project was initiated to study the effect of the model assumptions on the predicted RAFT. In RAFT all heat losses are ignored and it is usually assumed that all injectants are completely burnt to CO and H₂. In this study the heat losses are ignored but the effect of burning degree on the injectants are studied. In order to focus the efforts, it was decided not to study the effect of input data on the model predictions. That was to be carried out in a separate project.

It was decided that data from the LKAB experimental blast furnace (EBF) located at MEFOS in Luleå, Sweden should be used in the calculations. In the EBF tests, both pulverized coal (PCI) and slag formers have been injected through the tuyeres. The slag former of most interest was BOF slag. Therefore, it was decided that both the effect of coal powder and BOF slag injection on the predicted RAFT should be studied. From the literature it can be seen that much research efforts have been done on how PCI injection affects the RAFT [42-46]. However, no references on the effect of BOF slag injection on the RAFT have been found in the open literature.
In the initial stage of the project, the most relevant variables were selected in discussions with representants from industry. The following six model parameters were chosen:

1. Coke temperature factor. The temperature of all solid and liquid materials in the raceway region was assumed to have the same temperature. This temperature is often assumed to be a constant multiplied with the calculated RAFT value. This is not true, but since the temperature is not easy to estimate the assumption is used also in the present model. Since there are big uncertainties with the real temperature in the raceway region, the coke temperature factor was varied from 0.6 to 0.9.

2. Degree of silica reduction. Silicon introduced in the raceway region is mainly introduced as SiO$_2$ and some silicon as SiC, since some SiO$_2$ in coke will react with C and form SiC before the coke arrives to the raceway region. When silicon leaves the raceway zone it was assumed that silicon will be present as either SiO$_2$ or SiO gas. It was also assumed that ingoing SiC can pass through the raceway without reacting. In the present study all extreme cases was studied.

3. Coal powder burning degree, was varied between 50 and 100%. If the coal burning degree is too low the unburnt coal powder particles will block the gas passage through the coke layers in the blast furnace and stop the process. It was therefore not seen meaningful to include burning degrees below 50%.

4. Reduction degree of some components in injected BOF slag when leaving raceway. It was varied between 0 and 100%. The components that are reduced are FeO, Fe$_3$O$_4$, Fe$_2$O$_3$, SiO$_2$, MnO and V$_2$O$_5$. It has been assumed that all components are reduced to the same degree, which is not realistic. However, it is simply done to determine if the reduction degree will influence the calculated RAFT value.

5. Enthalpy of coke burning in blast furnace. This value is often assumed to be the same as of graphite, 110.532 kJ/mole [47]. In literature [48, 49] it was shown that the value is higher; the references gives 123.1 resp. 125.9 kJ/mole. In the parameter study the value was varied within the range 105 and 130 kJ/mole.

6. Cp value of coke. No value was found in the literature. The value for graphite was used, $C_{P,\text{graphite}} = 1423.95 + 0.3537046T - 72434114/T$ [J/(kg, K)] [47]. The constant in the Cp value was varied between 1100 and 1700.

The aim with the study was to determine which of these parameters that have the largest influence on the RAFT calculations.
The effect of the studied six parameters on the:

- maximum temperature difference in the calculation of the RAFT,
- change in oxygen in the blast/change in coal powder rate to retain the RAFT,
- change in oxygen in the blast/change in BOF slag rate to retain the RAFT,

are summarised in Figure 9. The results indicate that one needs to specify what the RAFT values should be used for before determining which of the studied parameters that is of the greatest importance to consider more in detail. If the objective is to predict the RAFT, it is clear that the coke burning enthalpy has the greatest effect on the RAFT predictions. Furthermore, it is necessary to take into account the variation of the coke temperature factor and the reduction of silica and silicon carbide. The only parameter that can be said to have negligible effect on the RAFT is the reduction degree of the injected slag.

![Figure 9](image)

**Figure 9** Summary of influences on RAFT calculation by assuming different conceivable values on uncertain parameters.
Often, the RAFT value is kept constant by adjusting the oxygen content in the blast. The change in oxygen that has to be done when changing coal powder injection rate or BOF slag injection rate was found to have an almost linear fit. The slope of the lines varied when inserting different values on the studied uncertain parameters. The maximum difference in slope is plotted in Figure 9, inserting values within the ranges of the uncertain parameters. Both the influence of changes in coal powder rate and BOF slag injection rate were examined. It could be seen that the burning degree of coal powder had the largest effect on the amount of oxygen in the blast that has to be provided to keep the RAFT constant when injecting coal powder. Furthermore, the coke temperature factor and the coke burning enthalpy also need to be taken into account. The only parameter that can be said to have no effect on the ratio between the oxygen content and the blast coal powder rate is the reduction degree of the injected slag.

As seen in Figure 9, the silica and silicon carbide reduction tendency and the reduction degree of the injected slag components shows the largest calculation uncertainty on the amount of oxygen that needs to be added to the blast in order to keep the RAFT value constant when BOF slag is injected. The only parameter that can be neglected is the burning degree of the coal powder.

An extension to this study is presented in Appendix 1. Measurements from the blast furnace are used as indata in the RAFT model. There always exist measurement errors in these values. It could be concluded that if the measurement errors are within reasonable ranges, the effect of the assumptions in the model shows larger influence on the RAFT value than the errors in blast furnace measurements.

6. Review of supplement 3

Equilibrium calculations between hot metal and slag were performed using analysis of tapped hot metal and slag from two Swedish blast furnaces. Most of the samples were taken from blast furnace no. 4 at SSAB Oxelösund AB. The samples from Oxelösund were taken in another project [50]. Also two tappings from blast furnace no. 3 at SSAB Tunnplåt in Luleå have been studied. Blast furnace no. 3 in Luleå is larger than blast furnace no. 4 in Oxelösund (see Table 2) and produces hot metal with lower silicon content.
The calculations showed that hot metal and slag were close to local equilibrium with each other. However, when the composition of the gas phase, that was calculated to be in equilibrium with the tapped slag and hot metal, was calculated it was shown that the carbon monoxide partial pressure was higher than the total gas pressure in the bustle-ring, see Figure 10. In the figure it can be seen that the difference between calculated equilibrium total gas pressure and the blast pressure is larger for blast furnace no. 4 in Oxelösund than for blast furnace no. 3 in Luleå. This can be seen as an indication to that blast furnace no. 3 in Luleå is closer to equilibrium at tapping than blast furnace no. 4 in Oxelösund.

![Equilibrium gas pressure and blast pressure](image)

**Figure 10** Calculated equilibrium total gas pressure for gas phase in equilibrium between tapped hot metal and slag for Oxelösund and Luleå (two last taps). Blast pressure is indicated by dotted line.

If the total gas pressure of the gas was set to represent the total gas pressure in the bustle-ring some carbon monoxide gas was formed at equilibrium. The gas was formed from dissolved carbon and silica in the slag, increasing the silicon content of the hot metal. One example on the effect of the total gas pressure on the equilibrium composition can be found in Table 7. The table shows calculation results based on average slag and hot
metal compositions as well as the average hot metal temperature during one tapping in Luleå (tap no. 6027) at different total gas pressures in the system. It can be seen that the hot metal and slag are close to equilibrium with each other at high total gas pressures. The exception is the FeO content. The reason for the bad correspondence for FeO is probably that the thermodynamic constants used in the calculations still are not perfect. Another reason may be that FeO is reduced by coke or graphite carbon rather than dissolved carbon in the hot metal.

Table 7  Results of equilibrium calculations with Thermo-Calc at different total gas pressures for Luleå BF (average values for tap no. 6027).

<table>
<thead>
<tr>
<th>Component</th>
<th>Normalised measured composition (wt-%)</th>
<th>Total gas pressure: 0.987 atm</th>
<th>Total gas pressure: 3.652 atm</th>
<th>Total gas pressure: 4.580 atm</th>
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<tr>
<td></td>
<td></td>
<td>Equilibrium composition (wt-%)</td>
<td>Equilibrium activity</td>
<td>Equilibrium composition (wt-%)</td>
</tr>
<tr>
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<td></td>
<td>Equilibrium composition (wt-%)</td>
<td>Equilibrium activity</td>
<td>Equilibrium composition (wt-%)</td>
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<td>5.40E-01</td>
<td>4.34</td>
<td>4.41</td>
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<td>1.53E-03</td>
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<td>0.16</td>
<td>7.22E-03</td>
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<td>(CaO)</td>
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<td>6.98E-04</td>
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<td>(S)</td>
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<td>(A/O₂)</td>
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<td>9.24E-02</td>
<td>12.5</td>
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<tr>
<td>(MgO)</td>
<td>17.5</td>
<td>2.45E-05</td>
<td>17.7</td>
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<td>6.68E-06</td>
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<td>5.88E-06</td>
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<tr>
<td>SiO</td>
<td>5.31E-06</td>
<td>4.04E-06</td>
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<td>2.41E-06</td>
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<td>O₂</td>
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<td>1.39E-15</td>
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<td>L₉₅₇₉₅</td>
<td>0.0018</td>
<td>0.0017</td>
<td>0.0051</td>
<td>0.0059</td>
</tr>
<tr>
<td>L₉₅₇₅₂</td>
<td>63</td>
<td>16</td>
<td>45</td>
<td>59</td>
</tr>
<tr>
<td>L₉₅₇₅₂₅</td>
<td>1.2</td>
<td>0.15</td>
<td>0.75</td>
<td>0.96</td>
</tr>
<tr>
<td>L₅₇₅₉₅₅</td>
<td>20</td>
<td>114</td>
<td>23</td>
<td>19</td>
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</table>
The calculations were performed using the computer software Thermo-Calc [30, 31]. For liquid metal the database TCFe3 [35] was used, for liquid slag the database Slag1 [32] was used and for gas the database SSub3 [37] was used. Also, some solid phases were considered in the calculation. Mainly the solid phases described in the TCFe3 database were considered. Solid phases found in the Slag1 database that were not described in the TCFe3 database were also considered. The effect of some elements was neglected in the calculations, due to numerical problems in Thermo-Calc. The elements that were not considered in the calculations due to this reason were P, Cr, Ni, Cu and Mo. Further, some elements had to be neglected in the slag phase because of lack of data in the slag database. The only elements considered in the slag phase were Al, Ca, Fe, Mg, Mn, Na, O, S and Si. Other elements, like K, P, Ti and V had to be neglected from the calculations. The measured content of Ti and V in the liquid metal was included in the calculations of activities in the liquid metal. However, because these elements were not included in the slag phase, the equilibrium distribution between the slag and liquid metal phase could not be calculated.

The TCFe3 database is based on a model that can treat higher levels of alloying elements than models based on dilute solutions. It could be concluded that the calculated activities of different elements using the TCFe3 database for a typical hot metal composition differed from the activities calculated using the dilute solution model. It was seen that predicted values of for instance silicon, showed large deviation between different models. Since silicon was shown to be of importance for the equilibrium distribution, the activity of silicon was also compared to measured silicon contents in the Fe-C-Si system. The calculated equilibrium silicon activity using the TCFe3 database showed some deviation from the measured. However, the error range in the measurements was pretty high, why the calculated and measured silicon activities could be seen to correspond with each other. Because the error ranges in many equilibrium measurements are rather high, the calculated activities can deviate from the real activities.

The activity of different elements in a liquid metal phase is often calculated using models for dissolved elements in liquid iron at infinite dilution. These models can usually just handle low levels of dissolved elements. Two different models based on this kind of assumptions were compared with the result from the TCFe3 model, see Figure 11. It can be seen that some elements shows big differences.
Another database in Thermo-Calc that can be used to calculate the activity in the liquid metal phase is the SSol2 database. This database covers wider composition range than the TCFe3 database. However, TCFe3 is more reliable within the composition ranges that it is developed to handle. In Supplement 4, initial calculations showed that the calculated liquid metal phase consisted of more than 5 wt-% Si, which is the maximum amount that TCFe3 covers. Because of this the SSol2 database was used. By this reason also the activity coefficients using the SSol2 database is given in Figure 11. The treatment of sulphur was shown to be extremely bad in the SSol2 database. The activity coefficient of sulphur was calculated to 589 for the hot metal used to calculate Figure 11.

Figure 11  Activity coefficients for a hot metal calculated with different models. The hot metal composition is taken as the average measured tapping analyses during tapping no. 42512 in BF no. 4 at SSAB Oxelösund.
7. Review of supplement 4

The thermodynamic conditions for formation of silicon-containing gas around the raceway area have been calculated. The amounts of ingoing materials in the calculations were selected based on a typical situation in blast furnace no. 3 at SSAB in Luleå. The chemical compositions and specific amounts of ash from three different coke types, three different coal powder types and one typical blast air composition were selected. Based on these specific compositions, thermodynamic calculations were performed including one coke ash, one coal powder ash and the blast air at a certain time as indata. Other indata to the calculations were temperature, total gas pressure and carbon activity in the system. The composition (expressed as kg per metric ton of hot metal) of the selected materials can be found in Table 8. The carbon content can not be found in the table, the reason is that the carbon activity was given as indata to the calculations instead of the amount of carbon.

Table 8  Consumption of coke, coal powder and blast used in the calculations. The consumption is given as kg/thm.

<table>
<thead>
<tr>
<th></th>
<th>Coke 1</th>
<th>Coke 2</th>
<th>Coke 3</th>
<th>Coal 1</th>
<th>Coal 2</th>
<th>Coal 3</th>
<th>Blast</th>
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<tr>
<td>Fe</td>
<td>1.989</td>
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<td>SiO₂</td>
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<td>0.371</td>
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<td>-</td>
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<td>0.006</td>
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<td>1.335</td>
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<td>914.281</td>
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</table>

There are several materials existing in the blast furnace that are not included in the calculations (for instance liquid iron and slag arriving from iron ore and slag formers added through the blast furnace top). The reason not to include them is that most silicon-containing gases are assumed to form from the ashes before mixing with other materials. In the thermodynamic calculations the amount of each element, the temperature and the total gas pressure are given as indata. From this, the stable phase composition is calculated. Including other materials than the ones selected would give the result that all
materials would mix, giving less silica activity in the system and by this reason lower amount of silicon in the gas phase.

The calculations were performed using the computer software Thermo-Calc, described previously. The databases used were Slag1 for the slag phase, SSol2 for all phases included in the database and SSub3 for all phases included in the database except those included from other databases (e.g. liquid metal oxides and gas).

The results of the calculations show that large amounts of silicon, according to thermodynamical conditions, can exist around the raceway area. Figure 12 shows the equilibrium silicon distribution between phases at different temperatures when mixing coal 1 (see Table 8), different coke ashes and the blast air in conditions where graphite is stable. The total gas pressure in the calculation was set to the total gas pressure measured in the bustle-ring (3.7 atm). Figure 13 is almost the same as Figure 12, but it shows the effect of different coal powder ashes instead of different coke ashes. From Figures 12 and 13 it can be seen that the temperature is the most important factor for how much silicon that can be found in the gas phase.
Figure 12 Equilibrium silicon distribution between phases at different temperatures using different coke qualities. Coal 1 is injected.

Figure 13 Equilibrium silicon distribution between phases at different temperatures using different coal powders. Coke 1 is used.
Figure 14 shows the effect of total gas pressure on how much silicon that according to calculated thermodynamic conditions can be found in the gas phase at different temperatures. The calculations were based on Coke 1, Coal 1 and Blast as given in Table 8. Graphite was assumed to be stable. It can be seen that the total gas pressure shows large influence on the calculated equilibrium amount of silicon in the gas phase at low temperatures.

![Graph showing the effect of total gas pressure on the equilibrium amount of silicon in the gas phase.](image)

Figure 14  The effect of total gas pressure on the equilibrium amount of silicon in the gas phase expressed as percent of silicon in the system that is found in the gas phase.

It could also be calculated that there might be possible to form a liquid metal phase with high silicon content inside the ashes. The silicon content was calculated to be between 5 and 35 wt-%. The only iron included in the calculations was iron from the ashes. In reality, iron also from other materials will be found in the system, which will lead to a reduced silicon content.

The effect of different carbon activities (relative to graphite) on the calculated equilibrium amount of silicon in the gas phase were calculated, see Figure 15. The calculations were based on Coke 1, Coal 1 and Blast as given in Table 8. The total gas pressure was set to
3.7 atm. From the figure it can be seen that at low temperatures, an increased carbon activity increases the amount of silicon in the gas phase. This is due to that a higher carbon activity increases the driving force for the reaction where silica reacts with carbon, forming SiO and CO gas. At high temperatures there is a tendency that increasing carbon activities decreases the amount of silicon in the gas phase. This is mostly due to that solid SiC forms at a higher carbon activity.

![Graph showing the effect of carbon activity on the equilibrium amount of silicon in the gas phase.](image)

Figure 15 The effect of carbon activity on the equilibrium amount of silicon in the gas phase expressed as percent of silicon in the system that is found in the gas phase.

8. Review of supplement 5

Tapped slag from blast furnace no. 3 at SSAB in Luleå was studied in SEM. Also, a few samples from blast furnace no. 4 at SSAB Oxelösund were studied. The phases found were a glass phase and small metal droplets. In areas of the slag that was cooled more slowly also some phases that probably have been formed during cooling of the samples were found. The only thing that was found interesting to study further was the metal droplets. All these looked almost spherical in the SEM. The determined diameter
distribution of metal droplets in a cross-section of each sample can be found in Figure 16. It can be seen that almost all droplets were below 2 µm in diameter. No big difference between the samples from Luleå (S01 to S09) and the samples from Oxelösund (S10 to S12) could be noticed.

![Figure 16](image)

Figure 16  Distribution of droplet diameters in cross-sections of different samples.

Back in 1983, Fornander [51] claimed that a typical metal droplet taken from slag in blast furnaces in the 70’s was a couple of tenth micrometer in diameter. This is somewhere in between 10 and 100 times a typical diameter found in this study. Note, that neither the blast furnace studied nor the amount of droplets was mentioned in Fornander’s study. Besides the size determinations, the area fractions of droplets within the examined cross-section of each sample were also measured. Figure 17 shows the percentage of the examined area that is covered with droplets in the different samples studied. The x-axis in the figure shows a dimensionless slag time that is equal to zero when the slag begins to flow out of the blast furnace and equal to one at plugging of the blast furnace.
From Figure 17 it can be seen that most metal droplets are present in the beginning of the slag tapping. In the beginning of the slag tapping most slag comes from the periphery of the blast furnace, close to the tap hole. It can also be assumed that slag from the centre of the blast furnace mostly will be tapped in the middle of the tapping. In the end of the tapping mostly slag from the periphery on the opposite side of the tap hole will flow out, but also slag that flows down to the hearth region. Overall, the results indicate that most droplets are found in the periphery of the blast furnace. It can also be seen that the amounts of droplets varies between different tappings. Too few samples have been analysed to conclude if there exists a correlation between process variables and the amount of droplets.

It has been reported that iron is oxidised in the raceway region of the blast furnace (usually mentioned as reoxidation, because the iron has first been reduced in the shaft and is than partly oxidised again in the raceway region) [17-24]. The FeO formed during reoxidation will mainly be found in the periphery of the blast furnace. The droplets may form as a result of reduction of this FeO, this would explain why more droplets are found.
in the periphery of the blast furnace. FeO can be reduced by a number of reactions, for instance:

- \( \text{FeO}(l) + C(\text{graphite, coke or coal powder}) = \text{Fe}(l) + \text{CO}(g) \)  

- \( \text{FeO}(l) + \text{Mg}(g) = \text{Fe}(l) + \text{MgO}(l) \)  

- \( \text{FeO}(l) + \text{SiO}(g) = \text{Fe}(l) + \text{SiO}_2(l) \)  

- \( \text{FeO}(l) + \text{CO}(g) = \text{Fe}(l) + \text{CO}_2(g) \)  

- \( \text{FeO}(l) + C = \text{Fe}(l) + \text{CO}(g) \)  

- \( 2\text{FeO}(l) + \text{Si} = 2\text{Fe}(l) + \text{SiO}_2(l) \)  

- \( \text{FeO}(l) + \text{Mn} = \text{Fe}(l) + \text{MnO}(l) \)  

The first four reactions may lead to the formation of metal droplets. The three last reactions contain metal droplets on both sides of the reaction, why it can be assumed that the iron that is formed is transferred to the metal droplet on the left side of the reaction. If an even distribution of droplets is assumed within each sample, the volume fraction of droplets will be almost the same as the area fraction of droplets within a cross-section. Assuming that the density of slag and liquid metal is 2800 resp. 6800 kg/m³, it can be calculated that formation of droplets would lower the FeO content in the slag with between 0.02 and 0.2 wt-% for the studied samples. Some studies of reoxidation claims that the FeO content of the slag can be around 30 wt-% within the raceway. Compared to this value, only small amounts of FeO are needed to form metal droplets. It is therefore likely that FeO also reduces elements in metal droplets according to reactions (9), (10) and (11).
Figure 18 contains two element mappings of metal droplets and surrounding slag. In both mappings it can be seen that the metal droplets contain mostly iron. The difference between the mappings can be seen in the slag surrounding the droplets. In the left mapping, it can be seen that the surrounding slag is homogeneous. In the right mapping, it can be seen that there exists an enrichment of magnesium close to the metal droplets.

Enrichment of magnesium has been found around some of the metal droplets. All locations found with magnesium enrichment have been in contact with metal droplets. There may be different explanations of seeing MgO enrichment close to the metal droplets. One may be that magnesio-wüstite can exist higher up in the furnace and that the wüstite is reduced, leaving metal droplets and magnesia. However, if this would be the case, magnesia enrichment also should be found in other locations than around the droplets if most FeO is reduced without formation of new droplets.

Another possible formation mechanism is that magnesium gas is oxidised according to reaction (6). The partial pressure of Mg gas can be high at high temperatures. To study this, thermodynamic calculations were performed. As indata to the calculations a typical composition and amount of hot metal and slag from one tapping of blast furnace no. 3 at
SSAB Tunnplåt as well as the hot metal temperature from the same tapping were used. The total gas pressure was set equal to the total gas pressure measured in the bustle-ring during the tapping, 3.7 atm. The equilibrium ratio between the amount of Si resp. Mg in the gas phase and the total amount of Si resp. Mg in the system were calculated at different temperatures. The results of the calculation can be found in Figure 19. From the figure it can be seen that it is easier to form Mg-containing gas than Si-containing gas. It can also be seen that there can exist much more Mg gas at high temperatures than at low temperatures. It can therefore be expected that Mg containing gas formed at high temperatures have to oxidise at lower temperatures.

Figure 19  Calculated concentration of Mg and Si, in system consisting of tapped slag and hot metal, that would be found in gas phase at equilibrium (no gas from blast included in calculations).
9. Discussion

9.1 Thermodynamics for reactions including silicon

In Supplements 3 and 4 the thermodynamic conditions for silicon behaviour is calculated. It was concluded that the equilibrium silicon content mainly is affected by:

- **Temperature**
  - Increased temperature gives higher equilibrium ratio between silicon in hot metal and silicon in slag.

- **Total gas pressure**
  - In Supplement 3 it is showed that increased total gas pressure (or rather increased CO partial gas pressure) gives lower equilibrium ratio between silicon in hot metal and silicon in slag. In many cases the total gas pressure increases with increasing temperatures (due to larger gas volumes). In these cases the silicon content of hot metal will increase, due to higher temperatures.

- **Carbon activity**
  - Increased carbon activity increases the equilibrium ratio between silicon in hot metal and silicon in slag. At high carbon activities solid SiC may form. At normal tapping conditions (Supplement 3) no SiC has formed in the calculations. However, calculations of equilibrium conditions in coal powder and coke ash (Supplement 4) shows that SiC is formed at high carbon activities. This is especially significant in temperatures between 1600°C and 1800°C.

- **Hot metal and slag analysis**
  - Affects the activity of silicon in the system through the concentration of silicon in respective phase as well as through interaction phenomenon with other species.

The above mentioned parameters affect the silicon content. As mentioned earlier, there are many more parameters affecting the kinetics for silicon’s behaviour. It is widely accepted that silicon-containing gases are formed around the raceway. Also, that SiO and SiS gas is reduced under the formation of dissolved silicon in liquid iron. However, it is still unknown exactly how much silicon that will dissolve in the liquid metal in the tuyere level of the blast furnace shaft. It has been reported that many samples taken in this area shows extremely high silicon content in the metal phase [e.g. 23]. Equilibrium calculations made in this study (Supplement 3 and 4) indicate that the silicon content in the tuyere level may increase during sampling and cooling, which may indicate that the extremely
high silicon contents found refers to cooling conditions rather than operational conditions. This will be further discussed below.

As mentioned earlier and in Supplement 5, it is assumed that the silicon content below the raceway will decrease due to reduction of FeO that is oxidised (reoxidised) in the raceway region. It is reported that no slag flows in to the raceway region [15]. Liquid iron may, however, be present. Taking recirculation of gas in the raceway into account (see Figure 3), it is possible that some liquid iron will flow into the raceway and be oxidised. It can be expected that the amount of liquid metal going in into the raceway will vary with the liquid metal flow in the shaft. The distribution of liquid metal flow in the shaft depends to a large extent on the shape of the cohesive zone [15], fines generation from injected materials, etc. It can therefore be expected that also the reoxidation rate of liquid iron is affected by this kind of phenomenon. However, the knowledge about reoxidation phenomenon are today limited. Further studies would be of importance.

9.2 Operational conditions versus conditions of sampled materials

Much information available on the internal state of the blast furnace comes from dissection of cooled blast furnaces or from samples taken with sonds in the shaft. In both these cases the materials studied are cooled before studying. Therefore, the samples do not represent conditions in the blast furnace under operation. Reactions and phase transformations may occur during cooling of samples. Also, the gas phase usually can not be kept under operational conditions during the cooling. This thesis concentrates on reactions in the hearth and tuyere region. In these regions the temperature is high and many species are liquid or gaseous. These conditions will make this region more sensitive to cooling conditions than other zones of the blast furnace, where most species are solid. One way to try to find out what may happen during cooling is to calculate the equilibrium conditions. Usually it can be expected that the reactions will go towards equilibrium, even if they usually do not reach equilibrium. In Supplement 3 it could be calculated that there sometimes exist local equilibriums between two phases in the blast furnace, but no location has been found where equilibrium exists between all phases present. All equilibrium calculations performed (in Supplements 3 and 4), points out that the equilibrium silicon content is higher than measured or higher than it is realistic to assume that it actually is. It is therefore likely that the silicon content will increase during cool-down. However, decreases of the temperature decreases the equilibrium silicon content.
of the liquid metal phase, which may tend to lower the silicon content in the liquid metal phase during cool-down.

The calculated equilibrium silicon content also showed a strong correlation to the partial pressure of carbon monoxide gas (Supplement 3). During tapping, the calculated equilibrium carbon monoxide pressure in the system was calculated to be higher than the total gas pressure in the system. If the partial pressure of carbon monoxide gas was set equal to the total gas pressure in the bustle-ring, the equilibrium silicon content in the hot metal becomes higher than measured. In many cases the partial pressure of carbon monoxide is lower during cooling of samples than at operation (e.g. during quenching of a blast furnace with nitrogen gas). During this kind of cooling it can be expected that the silicon content in the liquid metal phase drastically increases, especially in areas where the flow of nitrogen is high (e.g. around the area that was the raceway during normal operation). Below the cohesive zone it can also be expected that several elements to some extent will be found in the gas phase, e.g. Na, K, S and Mg. Changing the gas atmosphere will also affect the distribution of elements between the gas phase and other phases.

The above discussion points out that one has to be careful when drawing conclusions based on material sampled in the lower part of the blast furnace. However, taking reactions during cooling of samples into account, evaluation of sampled material can be a good way to better understand the blast furnace process.

9.3 Metal droplets in slag

The reoxidation phenomena reported to occur in the raceway may influence the silicon content in hot metal. According to thermodynamics, much FeO may oxidise silicon if gas formation is prevented. Probably FeO also will be reduced by carbon, forming CO gas. The carbon can be either in the form of dissolved carbon in liquid metal, graphite, coke carbon or coal powder carbon. The metal droplets observed in the tapped slag may have been formed in any of the three latter reactions. The results in Supplement 5 indicate that the metal droplets are formed during reduction of FeO in the slag, in reactions where liquid metal is not involved as reactant. However, to form the observed metal droplets, only small amounts of FeO have to be reduced (between 0.02 and 0.2 wt-%). As comparison, the amount of FeO that must be reduced to oxidise a certain amount of silicon in hot metal can be estimated. If it is assumed that FeO shall oxidise for instance 1 wt-% silicon in the hot metal, and that the specific slag amount is 170 kg/thm, then about
30 wt-% FeO in the slag has to be reduced. Since only small amounts of FeO must be reduced to form droplets, there may still exist FeO to oxidise some silicon in the hot metal.

It is also reported that slag formed higher up in the furnace is not found in the raceway area [15]. In the raceway an acid slag may form. However, much of the ashes from coke and injectants will probably not form a slag. The amount of slag around the raceway therefore should be rather low. Therefore, it is seen unlikely to form large amounts of slag in the raceway. Also, it can not be expected that any large amounts of dissolved silicon shall be oxidised by FeO.

9.4 Change of coal powder flow
In blast furnace no. 3 at SSAB in Luleå it has been showed that increases of the coal powder flow increases the silicon content and the temperature of hot metal. One of the aims with this work was to explain the mechanisms leading to this phenomenon. It has not been possible to do a quantitative determination of the mechanisms. There are many mechanisms affecting the silicon content of hot metal. It can be expected that some mechanisms will lower the silicon content at coal powder injection. However, most mechanisms will work toward an increased silicon content. If the only change of the directly controllable parameters of the blast furnace is to increase the coal powder flow, the burning rate of coke will decrease (see Supplement 2). This reduces the descending rate of the burden and reduces the hot metal production rate. The amount of gas formation per time unit should, however, be relatively unaffected, increasing the reduction potential of the gas per unit produced hot metal. It can therefore be expected that the reduction of the burden will occur higher up in the shaft, increasing the time for carburisation of the iron (see Supplement 1). The equilibrium composition of silicon in the hot metal is to a high extent correlated to the carbon content (see Supplement 3). Thus, it can be expected that a higher carbon content will lead to an increased silicon content of hot metal.

The decreased hot metal production rate tends to increase the heat level in the blast furnace. The only part of the blast furnace where the heat level maybe will decrease is the raceway region. This phenomenon is treated in Supplement 2. Coal powder is not preheated when entering the raceway, as the coke is. Coke carbon also has another structure than coal powder carbon and usually releases more energy at combustion, which
further will reduce the burning temperature when less coke is burnt. Also, the coal powder contains some humidity (water). The water will be cracked in the raceway, further reducing the burning temperature. Because of the higher temperature in other parts of the furnace it can, on the other hand, be assumed that the temperature of coke entering the raceway will increase which will tend to increase the temperature in the raceway. In the RAFT model described in Supplement 2, it is assumed that the coke temperature is directly proportional to the RAFT. The above discussion indicates that this probably is not true. Decreases of the gas temperature in the raceway tend to decrease the SiO and SiS gas formation rate. However, if it is assumed that the coke temperature is not directly proportional to the RAFT, the effect should not be as high as the changes of the RAFT value indicates.

The above mentioned effects of changing the coal powder flow rate on the silicon content, will take some time to occur. There may also be other changes that show faster effect on the silicon content. It has been reported that oxygen in the raceway first is burnt to CO₂ followed by CO₂ reduction by carbon to CO [52]. It has also been reported that the oxygen potential of the gas will be faster reduced inside the tuyeres during coal powder injection, mainly due to faster burning to CO₂ [41]. This may reduce the reoxidation tendencies of iron to FeO. It can be assumed that some of the FeO formed in the raceway region will oxidise silicon (see Supplement 5). By this reason, an increased coal powder flow may increase the silicon content of hot metal. The decrease of hot metal production may result in a lower reoxidation degree in the raceway, but also less silicon in hot metal to oxidise. The increased temperature in most parts of the blast furnace will increase the equilibrium silicon content of the hot metal. Increased temperature also increases the volume of the gas, probably resulting in higher pressure drop in the blast furnace. The higher total gas pressure will decrease the equilibrium silicon content, but not as much as the temperature will increase the equilibrium silicon content.

10. Conclusions

In Supplement 1, the meltdown behaviour of pellets reduced under different conditions in a reduction-under-load furnace has been examined. Twelve different trials were carried out where the experiments were interrupted just before meltdown. The crucibles used were made of graphite. The pellet type, the temperature increase rate, the gas flow and the applied load over the crucible were changed between the trials in accordance to statistical
planning. Samples from the interrupted trials were studied in optical microscope and it was found that all iron oxides in the samples were reduced to iron. By etching of the samples, the iron phase structures could be examined and thereby the carbon content could be estimated using a phase diagram.

The specific conclusions from the study are:

- The meltdown temperature of reduced pellets is mainly determined by the dissolved carbon content in the metal phase.
- The carbon content in the samples is determined by the reduction properties. A lower temperature increase rate has been shown to result in higher carbon contents. This is probably caused by longer reduction times that makes the reduction completed at lower temperatures, which gives more time for carburisation. Because higher dissolved carbon content in hot metal reduces the melting temperature, the kinetics of carburisation has a major influence on the meltdown temperature.
- Two different iron structures were found, one structure formed in solid phase and another melted structure. More melted structure was found close to the crucible wall. The carbon contents were slightly higher in the pellet centre for pellets sampled close to the crucible wall than for pellets sampled in the crucible centre. No difference could be found for the carbon content at the pellet surface.
- Only small differences in carbon content were found for pellets close to carbon bearing material and pellets far from carbon bearing material. This indicates that the carburisation mainly occurs by the reaction where CO forms carbon dissolved in the metal and CO₂.

In Supplement 2, a model for the prediction of the Raceway Adiabatic Flame Temperature (RAFT) based on a mass and heat balance of the raceway region has been developed. The new feature with this model in comparison to previously published models is that it takes the effect of injected materials, that are not fuel or reduction agents, on the RAFT into account. More specifically, the effect of injected BOF slag on the RAFT has been considered. A parameter study on how different assumptions affects the model result has been performed. The following parameters were varied in the calculations: (i) Coke temperature factor, (ii) Degree of silica reduction, (iii) Coal powder burning degree, (iv) Reduction degree of some components in injected BOF slag when leaving raceway, (v) Enthalpy of coke burning in blast furnace and (vi) Cp value of coke. The RAFT model predictions were also used to predict the exchange ratios between
The following parameters were found to have the largest influence on the maximum temperature difference in the calculation of the RAFT:

- The coke burning enthalpy (287°C)
- The coke temperature factor (221°C)
- The silica and silicon carbide reduction (198°C)

Coal powder injection was included as a part of the calculations. The following parameters were found to have the largest influence on the maximum change in the ratio between the oxygen content in the blast and the change in coal powder rate:

- The burning degree of coal powder (0.0105 %O₂/(kg/thm))
- The coke temperature factor (0.0056 %O₂/(kg/thm))
- The coke burning enthalpy (0.0051 %O₂/(kg/thm))

Injection of BOF slag was also taken into account in the predictions. The following parameters were found to have the largest influence on the maximum change in the ratio between the oxygen content in the blast and the change in the BOF slag rate:

- The silica and silicon carbide reduction (0.0087 %O₂/(kg/thm))
- The effect of the reduction degree of injected slag components (0.0064 %O₂/(kg/thm))

In Supplement 3, measured composition values of blast furnace hot metal and slag were used to calculate an equilibrium gas phase composition. The equilibrium gas pressure was found to be much higher than the total gas pressure for all parts of the blast furnace. One conclusion therefore is that, from a thermodynamic point of view, CO gas should form from reactions between slag and hot metal in the lower part of the blast furnace. During
these reactions the silicon content would increase. Since the reactions involve several phases, they are probably slow and gas nucleation will be an obstacle. It can, on the other hand, be concluded that the silicon content in the lower part of the blast furnace can not decrease due to reactions between gas, hot metal and slag, since that reaction would go in the opposite direction as the equilibrium reaction.

Other conclusions drawn from the study are:

- The activity coefficients of elements in hot metal differ for different hot-metal compositions. It can therefore not be recommended to design general models in which the activity coefficients are set as constants.
- Silicon can not be oxidised by a CO gas reaction in the lower part of the blast furnace.
- The dominating oxygen source in the lower part of the blast furnace at tapping would be the reduction of silica. Considering the system thermodynamics, the driving force for this reaction is strong.
- Reactions involving gas formation do not reach equilibrium conditions in the lower part of the blast furnace.
- The reactions among slag, hot metal and gas were closer to equilibrium conditions in BF No. 3 at SSAB Luleå than in BF No. 4 at SSAB Oxelösund.
- The actual distribution of elements between slag and metal are close to equilibrium at the higher oxygen potential that corresponds to the calculated high CO partial pressure at which no gas is generated.

In Supplement 4, a thermodynamic study of the effect of i) coke and coal powder qualities, ii) total gas pressure, and iii) graphite activity on the silicon distribution in a blast furnace was carried out. Calculations were made for different temperatures. The specific conclusions from the study are:

- More silicon can dissolve in the liquid metal phase in the tuyere level than measured in hot metal at tapping.
- According to thermodynamics, silicon can be transferred to hot metal through the gas phase (mainly as SiO and SiS gas).
- The amount of silicon in the gas phase may be influenced by the total gas pressure, giving less silicon in the gas phase at high total gas pressures.
• Much silicon can exist in the gas phase even at lower carbon activities (0.5 relative to graphite) at temperatures of 1600°C and above. At temperatures higher than 1600°C, higher carbon activity levels do not necessarily give higher equilibrium amounts of silicon in the gas.

• It is thermodynamically possible to find high silicon content metal droplets inside the coke pieces around the raceway.

In Supplement 5, samples taken during tapping of two different Swedish blast furnaces have been studied in SEM. The only interesting thing to study further was seen to be small metal droplets found in the slag. The two studied blast furnaces were blast furnace no. 3 at SSAB in Luleå and blast furnace no. 4 at SSAB Oxelösund. The specific conclusions from the study are:

• The metal droplets detected in blast furnace slag samples were very small in size, with diameters less than 8 µm and the vast majority less than 2 µm.

• Droplet size distribution was found to be relatively independent of the sampling time point in the tapping period.

• The metal droplets contained mostly iron and small amounts of carbon (approximately 1 wt-%). The silicon concentration in the droplets was lower than the silicon concentration in the hot metal. No bubbles or holes were observed inside the droplets.

• The volume fraction of droplets was quite small. The area fraction of droplets in sample cross-sections varied from approx. 0.01 to 0.1%. The area fraction was highest in the beginning of the slag tapping.

11. Future work

11.1 Blast furnace field

This work has concentrated on studying equilibrium conditions in the lower part of the blast furnace. To explain all reactions in the lower part of the blast furnace, also kinetic aspects need to be studied. This can be done using, for example, fundamental mathematical modelling of the lower part of the blast furnace, so called Computational Fluid Dynamics (CFD) modeling. However, the conditions inside the blast furnace shaft are changing with time in a way that it so far has been almost impossible to make fundamental mathematical models. It is, for example, very hard to define reasonable boundary conditions for the calculations. Those, in turn, will to a large degree effect the
predictions. One way is to define these boundary conditions from available experimental data from blast furnace excavations. Of course, it is also necessary to use all available experimental data to verify any future mathematical modelling results. However, it is out of the scope in this thesis to give any detailed suggestions on how these fundamental mathematical models of the lower part of the blast furnace can be made.

Maybe future CFD models can be used to give a clearer picture on how much iron that is oxidised (reoxidised) in the raceway at different situations. It can be expected that the reoxidation varies with the shape of the cohesive zone, the production rate etc. Since the reoxidation phenomenon is seen to affect the silicon content of hot metal, it is important with a better understanding of reoxidation to be able to reduce the variations in silicon content of hot metal.

In this work, the distribution of metal droplets found in blast furnace slag has been studied. However, too few samples have been studied to correlate the volume fraction of droplets with other measurements from the blast furnace. If more samples are studied, it can be evaluated how for instance the blast volume rate (production rate), the total gas pressure and the coal powder injection rate affects the amount of droplets. This can be valuable information to predict how much iron that is oxidised in the raceway area and how much silicon that will be oxidised by FeO in the slag. However, it should be pointed out that it is an extensive job to get enough data on iron droplets to get some statistical base for comparison with different operational conditions.

11.2 Thermodynamic calculations

Also, in the thermodynamic field it would be interesting with some future work. Still there does not exist thermodynamic data to be sure that calculated equilibrium conditions are in accordance with real equilibrium conditions. To get this kind of data it is important to do more controlled experiments to experimentally find out equilibrium conditions. Comparisons of sample compositions from the blast furnace with equilibrium calculations made in this thesis show some strange relationships. The most obvious is that the calculated Fe content in the tapped slag is much higher than measured. Actually, the opposite would be expected due to that also small metallic iron droplets are included in the analysis of the sampled material.
The author’s opinion is that the industry would prefer one computer software that covers calculations of thermodynamic related issues, instead of several small softwares that only covers parts of the thermodynamic calculations. It would be interesting to get for instance the equilibrium phase distribution, component activities, phase density and the viscosity of liquid phases presented in the same software.

Most thermodynamic calculations in this thesis have been performed using the Thermo-Calc software. Some further development of the software and the databases used would be recommended. The slag databases are developed for iron-containing slags, in the blast furnace there are almost no iron in the slag. There should be better coverage in the slag databases for slags with low Fe contents. Also, the author would like to see an overview of the values for oxygen activity versus oxygen content in the databases. Another lack in the thermodynamic calculations is that several slag components are not included in today’s versions of the Thermo-Calc slag databases. From blast furnace point of view, it would be interesting to be able to include TiO$_2$, K$_2$O and VO$_x$ (x can take various values, several species of vanadium can be found) in the slag phase. In Swedish ore based steel industry the amount of vanadium is higher than in many other countries. For this reason it would be interesting with a Swedish research initiative to better evaluate the thermodynamic behaviour of vanadium compounds and to include the results in the Thermo-Calc databases.

It would be interesting for the pyro-metallurgical industry to get a better tool to calculate equilibrium conditions. In today’s version of Thermo-Calc usually several databases have to be combined to do a thermodynamic calculation representative for pyro-metallurgical processes. It can not be expected that the industry shall combine thermodynamic data from several databases the way it works now. If combinations shall be done all databases have to be directly compatible, using the same definitions of pure elements and the same name of the same species and phases.

Also, the numerical treatment in Thermo-Calc should be developed so that the calculations converge better. Sometimes meta-stable equilibriums have been shown as stable equilibriums (for instance, sometimes a solid metal phase is shown to be stable when a liquid metal phase should be stable. In these situations further numerical treatment has shown liquid metal phase to be stable). Many pyro-metallurgical process industries develop on-line process models. In these models thermodynamic calculations
are often needed. If the numerical treatment within Thermo-Calc is improved towards less convergence problems, it should be interesting to call Thermo-Calc as a sub-routine to do thermodynamic calculations from within the on-line process models.

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