A pre-study of Hot Metal Desulphurization

Master’s degree project

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ABSTRACT

In this thesis work, some basic concepts about desulphurization of hot metal have been done based on a literature study. Two experimental trials have also been carried out to study the slags: one consider as a reference and in the other trial, the amount of calcium carbide was reduced by 150 kg. The average carbide efficiency has been improved from 21.3% in trial 1 to 26.0% in trail 2. Metal droplets containing iron oxides are found in three of eight heats and most of metal droplets are surrounded by Ti-compounds. The slags mainly consisted of (Ca, O, Si) and (Ca, S), with some low content of other elements.

Key words: Desulphurization, hot metal, SEM analysis
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CONTENTS

Abstract .............................................................................................................................................. 1
Acknowledgement .............................................................................................................................. 2
1 Introduction ....................................................................................................................................... 5
2 Theory .............................................................................................................................................. 6
   2.1 Process Route ............................................................................................................................... 6
   2.2 Desulphurization ......................................................................................................................... 7
       2.2.1 General Theory .................................................................................................................... 7
       2.2.2 Desulfurizers ....................................................................................................................... 9
       2.2.3 Desulphurization Process Description at SSAB Oxelösund ............................................. 10
   2.3 Desulphurization Kinetics .......................................................................................................... 13
   2.4 Slag Properties .......................................................................................................................... 16
       2.4.1 Composition .......................................................................................................................... 17
       2.4.2 Viscosity .............................................................................................................................. 17
       2.4.3 Basicity ................................................................................................................................ 17
       2.4.4 Slag Modifier ........................................................................................................................ 18
   2.5 Metal droplets formation ............................................................................................................. 19
   2.6 Analyzing methods ..................................................................................................................... 21
       2.6.1 Scanning electron microscope (SEM) equipped with energy dispersive spectrometry (EDS) .......................................................................................................................... 21
       2.6.2 Petrography .......................................................................................................................... 22
       2.6.3 Electrolytic extraction .......................................................................................................... 23
       2.6.4 X-ray Fluorescence (XRF) Spectrometry ............................................................................ 24
       2.6.5 Combustion Infrared Detection ............................................................................................ 24
   2.7 Metal- and slag samples from desulphurization in SSAB Luleå ............................................. 25
       2.7.1 Slag sample preparation ......................................................................................................... 25
   2.8 Titanium compounds .................................................................................................................. 26
3 Experiment ......................................................................................................................................... 29
   3.1 Composition of hot metal samples .............................................................................................. 29
1 INTRODUCTION

The demands on steel grades with a low sulfur content will increase drastically in the nearest decades because these grades have improved material properties, lower sulfur inclusions and less cracking tendencies. A low sulfur content iron is a prerequisite for producing a steel grade with a low sulfur content. So the major effort has been concentrating on the pretreatment of hot metal before converter to achieve a low sulfur content in the hot metal. To remove sulfur to an acceptable level is not so difficult. But there is one problem during desulphurization at the steel company SSAB: the iron losses in the slag are as high as 4.6% of the total produced metal. One part of the slag from desulphurization will be recycled to the blast furnace after crushing and magnet separation. In this way, the iron losses can be lowered. So a project is carried out to reduce the metal losses by modifying the slag properties by mixing the mineral nepheline syenite with calcium carbide.

The aim of this thesis work is to learn the basic concepts about the desulphurization process of hot metal in reality. Also to learn the analyzing tools such as SEM is one propurse. Two simple trials have been done: one trial using the amount of calcium carbide that the computer suggested according to the mass of hot metal, temperature and ingoing and outgoing content of sulfur; the other trial is done by reducing 150 kg calcium carbide from the amount calculated by the computer. In the study, both metal droplets and the slag surrounding the metal droplets has been studied using SEM.
2 THEORY

2.1 Process Route

Figure 1 shows the metallurgy process route at SSAB. The process is explained in the following parts.

Figure 1 The metallurgical process at SSAB

(I) Raw Material

At the steel plants of SSAB in Sweden, the production is iron ore-based and the pellets used in the blast furnace are from LKAB. Thus, this implies a high content of titanium and vanadium compared to the other pellet types. Coke is used in the blast furnace to reduce iron ore and it is one of the major sources of sulfur coming to the hot metal. Other sources of sulfur are the iron ore and the fuels used in different furnaces.

(II) Blast Furnace

In a blast furnace, the coke reacts directly and indirectly with the iron pellets to produce the metallic iron. Raw materials are charged from the top of blast furnace and it usually takes 8 hours to get hot metal at the furnace bottom. The reduction reactions can be described to take place as follows: $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$.

The hot metal from the blast furnace contains high contents of carbon, usually about 4.5%. This high content of carbon is beneficial for the desulphurization of hot metal. When tapping, the hot metal is tapped into a torpedo car, for transportation from the blast furnace to the steel shop.
**(III) Desulphurization of hot metal**

In the blast furnace, the slag has to take up both alkali metals and other impurities, such as sulfur and phosphorus. A low basicity slag is needed to remove alkali metals, while a high basicity slag is necessary for a good desulphurization. In other words, the blast furnace process is not effective for the desulphurization process.

To desulphurise before converting the hot metal to crude steel is useful and it is a result of the increasing requirements on the sulfur content. It can be done in a torpedo car or in a ladle and the later one is more modern. Desulphurization in a torpedo car has difficulties in getting a homogenous result and using the desulphurizor effectively.

**(IV) LD Process**

In this step crude steel is made by blowing oxygen gas in to the hot metal bath. Dissolved carbon reacts with oxygen and the content of carbon decreases to around 0.06% at Oxelösund. Before charging the hot metal into the LD converter, scraps are usually added to utilize the heat generated during oxidation reactions. In this step, the desulphurization process is not promoted because of the high activity of oxygen.

**(V) Ladle Metallurgy**

This step is also called the secondary refining process of steelmaking. During ladle treatment, steel gets adjustments both with respect to composition and temperature. Also, inclusions from desoxidation of the steel and other impurities such as hydrogen and nitrogen are decreased to reach the final requirements of the products. Sometimes it is necessary to desulphurise the steel to get a very low content of sulfur. This is done after desoxidation when the content of oxygen is lower. So the desulphurization is a process that is done through the whole production chain.

**(VI) Continuous Casting**

After adjustments during ladle treatments, the steel melt is ready to be cast into a solid form. In SSAB, the steel is cast continuously into slabs.

**2.2 Desulphurization**

**2.2.1 General Theory**

During desulphurization the sulfur in the metal bath is reduced into the slag phase
accompained with an oxidation of oxygen into the metal bath. A general reaction can be written as follows:

$$S + MeO \leftrightarrow MeS + O$$ (1)

where $S$ and $O$ is dissolved sulfur and oxygen in the hot metal respectively; MeO and MeS is sulfide and oxide in the slag respectively.

Usually calcium is added to react with sulfur, either directly injected into the melt or as an important component in the slag. The most common and cheap reagent for sulfur removal is lime, CaO. The reaction can be written as follows:

$$CaO(s) + S \leftrightarrow CaS(s) + O$$ (2)

The Gibbs free energy for reaction (2) is the following:

$$\Delta G^\circ = 110 \ 000 - 31,1 T \ (J/mol)$$ (3)

The equilibrium constant $K$ for the reaction (2) is following:

$$K = \frac{a_O \cdot a_{CaS}}{a_S \cdot a_{CaO}} = \frac{a_O \cdot a_{CaS}}{f_S [\%S] \cdot a_{CaO}} = \exp\left(\frac{-\Delta G^\circ}{RT}\right)$$ (4)

where $a_O$ and $a_S$ is the activity of dissolved oxygen and sulfur in the melt; $a_{CaS}$ and $a_{CaO}$ is the activity of CaS and CaO in the slag; $f_S$ is the activity coefficient and $[\%S]$ is the dissolved sulfur in mass%.

From equation (4), the content of sulfur can be calculated as follows:

$$[\%S] = \frac{a_O \cdot a_{CaS}}{f_S K \cdot a_{CaO}}$$ (5)

The activity of CaO can be set to be $a_{CaO}$=1 if the slag is saturated with CaO. The activity coefficient of sulfur ($f_S$) can be calculated by the Wagner expression. The oxygen activity can be measured while the activity of CaS is more difficult to get. The equilibrium content of sulfur is based on reaction (2). If a more effective reagent is used, a lower equilibrium content of sulfur can be achieved.

Reaction (2) can also be written as follows:

$$(O^2-) + S \leftrightarrow (S^2-) + O$$ (6)

It is coming from the two following equations:

$$(O^2-) + 1/2 \ S_2 (g) \leftrightarrow (S^2-) +1/2 \ O_2 (g)$$ (7)
\[ S + \frac{1}{2} O_2(g) \leftrightarrow \frac{1}{2} S_2(g) + O \]  

(8)

From the equilibrium constant of reaction (7), one parameter called sulfide capacity \( C_s \), which used to describe the ability of a slag to pick up sulfur, is defined as follows:

\[ C_s = (\%S) \cdot \sqrt{\frac{P_{O_2}}{P_{S_2}}} \]  

(9)

where (\%S) is sulfur content in the slag and \( P_{O_2} \) and \( P_{S_2} \) is the partial pressure of \( O_2 \) and \( S_2 \).

With help of equation (9), the equilibrium constant of reaction (8) can be written as follows:

\[
\log K = \log \left( \frac{a_O}{a_S} \cdot \sqrt{\frac{P_{O_2}}{P_{S_2}}} \right) = \log \left( \frac{a_O}{f_S[\%S]} \cdot \frac{\%S}{C_S} \right) = -\frac{935}{T} + 1.375
\]

(10)

which gives the equilibrium sulfur distribution ratio \( L_S \) between the slag and the melt to be:

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

(11)

It is important that a slag can keep the sulfur present in the slag phase, so that the melt can remain the result of the desulphurization. From expression (11), it is obvious that the desulphurization process is promoted by a high sulfur capacity and activity coefficient of sulfur. All these three parameters are depending on temperature, so the influence of it on the sulfur distribution ratio is complex.

2.2.2 Desulfurizers

Except lime, there are other common desulfurizers such as calcium carbide (CaC\(_2\)), magnesium (Mg) and soda (NaCO\(_3\)). All these three are more effective desulfurizers than CaO, but they are more costly.

(I) \( CaC_2 \) powder

The desulphurization reaction of CaC\(_2\) with sulfur is shown as follows:

\[ CaC_2(s) + S \leftrightarrow CaS(s) + 2C \]  

(12)

The affinity between calcium and sulfur is strong, which can lead to a direct
reaction between the elements. The reaction can be more easily achieved if the powder is directly injected to the melt. At SSAB Oxelösund, the desulphurization process uses CaC\textsubscript{2} blended with carbon powder. The reaction is exothermal and the generated heat can reduce the temperature loss of the melt.

(II) **Mg powder**

The desulphurization reaction can be written as follows:

$$Mg(g) + S \leftrightarrow MgS(s)$$  \hspace{1cm} (13)

With Mg powder, very low sulfur contents can be achieved. The problem with Mg powder is that the vapor pressure of Mg is high, so that Mg bubbles forms when Mg powder is injected to the melt. Mg powder is usually blended with other desulfurizers to avoid a too violent reaction with the melt. Magnesium can dissolve in the melt, which can prevent resulphurization. This means that the reaction (13) will go to left and the sulfur will return to the melt.

(III) **Soda ashes**

Soda (Na\textsubscript{2}CO\textsubscript{3}) has a melting temperature of 851°C. It is stable until 1200°C, which is lower than the steelmaking temperature. So once soda is in contact with the hot metal, it decomposes to Na\textsubscript{2}O and CO\textsubscript{2}. Na\textsubscript{2}O can be reduced by dissolved carbon into Na-gas. Both Na\textsubscript{2}O and Na-gas can react with sulfur intensively according to the following reactions:

$$Na_2O(l) + S \leftrightarrow Na_2S(l) + O$$  \hspace{1cm} (14)

$$Na (g) + S \leftrightarrow Na_2S(l)$$  \hspace{1cm} (15)

Soda ashes are added into the hot metal at the end of the desulphurization process for mono-injection with calcium carbide. Soda ashes can promote separation of hot metal from slag and iron losses in slag is lower. The problem with soda ashes is that it gives a violent gas evolution, which is not desired for the environment inside steelmaking plant.

2.2.3 Desulphurization Process Description at SSAB Oxelösund

The hot metal desulphurization process can be done in a ladle or in a torpedo-car,
and the latter way is used at SSAB Oxelösund. Molten iron is tapped into a torpedo-car from a blast furnace and is transported to a BOF-shop. The hot metal desulphurization process is an external pre-treatment of iron. It takes advantage of the high content of carbon, which implies a low activity of oxygen. A low activity of oxygen makes the desulphurization process more effective according to equation (5).

After the torpedo-car is fully filled and the weight is measured, it is transported to the desulphurization station. Before starting the desulphurization process, a temperature and a composition sample of the hot metal are taken. The composition analysis gives the initial content of sulfur, which is one important parameter to decide the amount of desulfurizing agent to be added. The desulfurizing agent used at SSAB Oxelösund is a powder mixture of 95% calcium carbide (CaC₂) and 5% carbon. The injection system can be described as follows: The powder is stored in a silo, which is connected with a dispenser to ensure a better control of the desulphurizor flow. Calcium carbide is dangerous in contact with any moisture. Therefore, the storage of calcium carbide is inside a house and is kept dry as much as possible. The gas carrier used is nitrogen gas and the lance is a kind of straight bottom discharger with 2 holes. The lance is lowered through the opening in the middle of the torpedo-car when injecting the desulphurization agent. The direction of the gas flow is along the long side of the torpedo-car. The turbulence is introduced when injecting powder and gas is the only way used to stir the melt during the desulphurization process. Because of the shape of the torpedo-car, it is difficult to achieve homogeneity in the reactor.

The amount of reagent is recommended by the process control system based on four parameters: a) temperature of hot metal, b) initial content of sulfur, c) final content of sulfur and d) the amount of hot metal. The average amount of calcium carbide used is around 1.5 ton for a torpedo-car.

During blowing of the desulphurization agent, the reaction is intensive inside the torpedo-car, which leads to splashing of hot metal outside of the torpedo-car and a strong shaking of the lance. The solid flow rate for the desulphurization process is about 48-54 kg/min. The blowing time can vary depending on the four parameters, but the average blowing time is about 30 minutes. After the desulphurization is finished,
the final composition sample is taken from the hot metal. Similarly as for the first sample, the rest of the sampler is thrown in the torpedo-car. The sulfur content after desulphurization is below 50 ppm.

After the desulphurization process, the torpedo-car is transported to another place for tapping. There are three tracks for the torpedo-cars, two of them are normally used because they are beside a tapping hole on the floor where the tracks exist. The melt is tapped into a transport ladle with a volume of 160 ton. The transportation of the ladle is controlled by the process control system and there are two tracks for the transport ladle at the floor below the torpedo-car. Usually when the transport ladle is not fully filled, it will wait for the next torpedo-car. In order to reduce the temperature loss, a mixture of oxides is added to cover the surface of the hot metal. When filling a partly filled ladle, the smoke generation is much less than when filling an empty ladle. There is a gas removal system in order to minimize the gas in the factory. When filling the transport ladle, the torpedo-car needs to be rotated and the operator needs to control how much the torpedo-car will rotate. When there is no demand from the BOF-shop, the torpedo-car will stay on the track without a cover over the tapping hole.

After tapping from the torpedo-car, it is time for slag skimming. Before slag removal, both temperature and composition samples are taken. This is because the inhomogeneity of desulphurization in the torpedo-car, which results in different sulfur contents at the end of desulphurization in the torpedo-car and in the transport ladle. The most common method to remove the sulfur-rich slag is to tilt the transport ladle and rake the slag by a slag skimmer. When deslagging, nitrogen gas is introduced from the bottom plug of the transport ladle and is used to force the slag move in the direction towards the spout. This reduces the number of deslagging strokes as well as the iron losses. However, the slag can’t be removed totally and the deslagging process is terminated by the operator based on the judgement.

After the deslagging process, the hot metal is ready for charging into a BOF to produce crude steel.
2.3 Desulphurization Kinetics

The desulphurization rate can be described as the equation below \(^{(1)}\):

\[
\frac{d[\%S]}{dt} = K \left( [\%S] - [\%S_{eq}] \right)
\]  \hspace{1cm} (16)

where:

\([\%S]\) is the sulfur content at time \(t\); \([\%S_{eq}]\) is the equilibrium sulfur content; \(K\) is a constant. The constant \(K\) can vary with the reagents used in the desulphurization process.

The most important parameters that influence the effect of desulphurization are the properties of the top slag, the oxygen activity and the injection conditions. In an earlier study \(^{(2)}\), four different top slag conditions have been tested. The experimental results show that it is important to control the initial condition of the slag. A low solid loading was found to be favorable for a slag/metal and plume desulphurization. Also, it was shown that the oxygen content is crucial for the process.

The four different top slag conditions are shown as follows:

i) no initial slag

ii) a dry slag with 60% CaO and 40% SiO\(_2\)

iii) a liquid slag (a kind of continuous casting powder with a melting point of 1135ºC)

iv) a dry slag modified by injecting aluminum into the metal before carbide injection

The effect of the top slags can be shown by plotting the change of sulfur content during the process by **Figure 2 and 3**: 
The change of sulfur content during the desulphurization process for injection with no initial slag and injection with dry slag (2).

The biggest difference is that in Figure 2 there is a period of 30-50 seconds (2) where the sulfur content does not change significantly as shown in Figure 3. This period is called the incubation time during which the injected calcium carbide is inefficiently used.

Figure 4 shows the apparent sulfur ratio over the injected calcium carbide amount. The ratio is calculated by assuming that all the sulfides go to the slag phase. The sulfide amount is the change of the sulfur content in the hot metal. So the ratio is the change of sulfur content in the hot metal over the sulfur content in the hot metal.
The apparent sulfur partition ratio for injections with dry slag over the injected calcium carbide amount is shown in Figure 4. The figure is for injections with a dry slag and a lower partition ratio in the beginning of the injection is shown here. The incubation time in Figure 4 is shown as the amount of injected carbide of 3.5 kg (1.4 kg /t.H.M.). After passing the incubation time, the partition ratio of sulfur increases with an increased injection mass. The value of 0.1 is obtained by making an interception with the line with y-axis. According to the author, a high injection rate in the initial stage will decrease the incubation time. The same plotting is done for the injections with the liquid slag as shown in Figure 5. Here no incubation period can be found. By comparing these figures, it is possible to conclude that the liquid slag has better slag properties than the solid slag which can maintain the desulphurization product in the slag phase in the initial stage.

Figure 5 The apparent sulfur partition ratio for injections with liquid slag over the injected calcium carbide amount is shown in Figure 5.
The reason for the incubation period for injections with no slag can be explained by the fact of a poor protection of the hot metal surface. The hot metal surface is easier to oxidize by the oxygen in the atmosphere without a top slag, which leads to a formation of FeO. According to earlier studies, both FeO and CaS are effective fluxes that can reduce the melting temperature of the CaO-based slags. According to the author, the desulphurization product together with CaS can form a sulfur-saturated slag in the beginning of the injection. Because of the high activity of the FeO in the slag, the sulfur tends to return to the hot metal by the reversed desulphurization reaction. After passing the incubation period, the amount of unreacted carbide increases in the slag and deoxidizes the slag and reacts with the hot metal.

For injections with dry slag, the incubation time is observed because of the chemical property of the slag. According to the author, a mixture of solid CaO and SiO$_2$ cannot dissolve the desulphurization product CaS. After passing the incubation period, the amount of unreacted carbide increases in the slag. This reduces the portion of FeO and also provides the slag with a reducing property.

For injections with liquid slag, CaS from desulphurization process is absorbed in the slag phase at the start of injection. For injections with slag modified with aluminum, the apparent sulfur partition ratio is even higher because of the low oxygen content in the hot metal. Also, calcium aluminosilicate with a high sulfide capacity forms and prevents the reversal of sulfur back to the hot metal at the start of the process.

### 2.4 Slag Properties

In order to get an effective desulphurization, the slag should have properties such as: a high sulfide capacity, a high basicity and a high fluidity. It is also known that a high amount of slag is promoted for the desulphurization process. Usually slag is a multi-component phase, based on oxides such as CaO, SiO$_2$ and Al$_2$O$_3$. It is important to choose a slag with a suitable chemical composition, which can influence both the
basicity and the fluidity of the slag. A basic slag has higher amount of basic oxides which is a network breaker, so that more oxygen ions \((O^2-)\) exist in the slag phase. These oxygen ions can later react with dissolved sulfur in the melt.\(^{(3)}\)

### 2.4.1 Composition

Slag is formed during refining processes. Additions such as oxides \(\text{CaO}, \text{MgO}\) and iron oxides to slag is done to obtain the desired physicochemical properties of slag. Properties of slag are decided by the composition and the structure of slab. Oxides can be acidic and basic. Acidic oxides such as \(\text{SiO}_2\) and \(\text{P}_2\text{O}_5\) are also called network former while basic oxides such as \(\text{CaO}, \text{MgO}\) and \(\text{Na}_2\text{O}\) are called network breakers. Also, \(\text{Al}_2\text{O}_3\) acts as a network breaker in an acidic slag and a network former in a basic slag.\(^{(4)}\)

### 2.4.2 Viscosity

Slag viscosity is directly related to the temperature and composition of the slag. Also, solid particles that exist in slag can influence the viscosity. Generally, the slag viscosity decreases with an increased temperature for all slag compositions. The viscosity can be expressed according to equation (17)\(^{(4)}\):

\[
\eta_0 = A \cdot e^{\left(\frac{E}{RT}\right)} \tag{17}
\]

where \(\eta_0\) is viscosity, \(A\) is an empirical constant, \(E\) is the activation energy, \(R\) is the gas constant and \(T\) is the temperature.

Basic oxides added to an acidic slag containing \(\text{SiO}_2\) will reduce the viscosity of the slag quickly by reacting with silica network.

Solid particles increase the viscosity according to equation (18)\(^{(4)}\):

\[
\eta = \eta_0 \cdot (1 - \varepsilon)^{-2.5} \tag{18}
\]

where \(\varepsilon\) is volume fraction of solid particles.

### 2.4.3 Basicity

There are two kinds of definitions of the basicity: ionic and molecular basicity. Ionic definition implies the ability of slag to give oxygen ion. Molecular definition is more useful in practical. Commonly, basicity \(B\) can be written in two ways according
to molecular definition as following:

\[ B = \frac{CaO \text{ (weight percent)}}{SiO_2 \text{ (weight percent)}} \]

\[ B = \frac{CaO+MgO \text{ (weight percent)}}{SiO_2+Al_2O_3 \text{ (weight percent)}} \]

To get an efficient desulphurization, high basicity slag is more favorable.

### 2.4.4 Slag Modifier

In order to separate hot metal from slag more easily, flux agents, for example fluorspar can be added to slag and modify the properties of the slag. The flux agents form compounds with impurities existing in metal. In this way, they are separated from hot metal. Fluorspar additions to steelmaking slags are made because it can reduce viscosity of slags and lower the melting temperature of slags. Fluorspar additions have no effect on the sulfur distribution parameter. But it can attack refractory and cause environmental problem. Also the price of fluorspar is high. Because of these, the usage of fluorspar is reduced in steel industry in Sweden. Other minerals are studied in order to find a mineral which can replace fluorspar and give same result. In a recent study \(^{(5)}\) two mainly investigated minerals are nepheline syenite and ilmenite.

Fluorspar is an excellent flux agent which can increase slag fluidity and also increase velocity of lime dissolving in slag. But production of fluorspar is low and it is expensive.

Nepheline syenite is a kind of mineral which consisted of three separate minerals: nepheline (NaAlSiO₄), albite ((Ca,Na)(Al,Si)AlSi₂O₈) and microcline (KAlSi₃O₈). Nepheline syenite is mainly used in glass industry to remove FeO. After this, nepheline syenite tailing (NST) is obtained. NST consists of 50% SiO₂, 20%Al₂O₃, 10%FeO, 15% alkalis (Na₂O, K₂O) and rest oxides.\(^{(5)}\) In steel industry, the mineral was first used to replace fluorspar in secondary steelmaking slags.

According to the literature study \(^{(5)}\), fluorspar can fully be replaced by nepheline syenite. Even though slag with nepheline syenite can’t reach as low viscosity as with fluorspar, the difference is not remarkable. Earlier studies in the literature study focused on the steel desulphurization slags, while the latest study from 2004 (a
monograph by Freissmuth) tested different slag modifiers used for the hot metal pretreatment. A mixture of lime and calcium carbide together with 12-15% nepheline syenite was tested in 51 heats. The mixture gave a reduced slag amount from 3 ton to 1.94 ton for 240 ton of hot metal. Also, the study showed that an addition of aluminum gave an improved sulfide capacity with a minimum aluminum content of 0.005 wt%. By adding aluminum, a dicalcium silicates formation is inhibited. Instead a layer of aluminum is formed around lime particles, which can make transportation of sulfur to lime surface easier.

Generally fluxes have two functions in a steelmaking process. One is to lower the melting temperature of the slag so that a high basicity slag can be used to remove impurities. Another is to reduce the viscosity of slag in order to promote slag-metal reactions. (6)

Ilmentite sand consists of FeTiO₃. B.N.Singh et al used ilmentite sand instead of fluorspar in an open heart steelmaking furnace. The basicity of the slag in the open hearth furnace was high, so it was imperative to add a flux agent to increase the slag fluidity as well as to promote the lime dissolution. CaO and SiO₂ can form mono-, di- and tricalcium silicates. Dicalcium silicates formed around lime have high melting temperatures (2130°C) and therefore they prevent further dissolution of lime. So a flux agent needs to be added in order to avoid a formation of dicalcium silicates. The experimental results showed that ilmentite can fluidize slag as well as fluorspar, but the weight ratio of ilmentite to fluorspar was about 2:1. Also, the lime dissolution rate was higher in liquid ilmentite-containing mineral than in fluorspar.

2.5 Metal droplets formation

In steel production, the molten metal is usually covered by a molten slag. In an earlier study of metal droplets entrained into slag by rising gas bubbles, two mechanisms of metal droplets formation were proposed: large metal droplets are formed by a jet formation mechanism and fine metal droplets are formed when the metal film covering the gas bubble is ruptured when the gas bubble passing through the metal/slag interface (7). The experiment consisted of a vertical electrical resistant
furnace, an X-ray imaging system and a gas supply and a control system.

Both entrainments caused by single bubbles and multi-bubbles were studied. For the single bubble experiments, droplets formed by jet could be observed clearly. Here the bubble had a size of about 13mm in diameter. When a bubble entering from a liquid to another liquid with a lower density, it is possible that there is a film of the formed liquid covered the bubble. This can be explained by the interaction between the interfacial tension between two liquids and the buoyancy force. If the buoyancy force is much higher than the interfacial tension, then the bubble can pass the interface so quick that there is no time for the film to drain and rupture. But in this paper \(^7\), the interfacial tension between metal and slag is high enough so that the metal film can drain and rupture.

In this study \(^7\), it was observed that the metal firm ruptured first and then the jet was formed. The author proposed that this observation explains that the jet formation was driven by both the bubble wake and the cavity collapse together. In Figure 6, metal droplet formation steps are described. When the bubbles rising from iron melt into slag (a), the metal film drains and there is a hole formed on the top of the bubble (b). In (b) the arrows pointed downwards show the surface tension of iron and the interfacial tension of iron/slag on the inner film surface and outer film surface respectively. There is a local stress because of different values of the interfacial tension on the metal film, which leads to a rupture of a bubble (c). In this way, fine metal droplets are formed when the metal film is ruptured. Thereafter, a jet is formed inside the bubble (c). When a jet is high enough, it becomes unstable and will form a jet droplet (d).

Figure 6 Metal entrainment into slag due to one single bubble \(^7\)
Metal droplets formed by the jet formation can be observed by an X-ray unit, but the small metal droplets formed by a film rupture can’t be observed by the X-ray unit used in the paper (7). So the observation of a fine metal droplet formation was done in an indirect way. Two concepts were used in the paper (7): a “film coefficient” \( \Phi = \sigma_s - \sigma_m - \sigma_{s-m} \) and a “flotation coefficient” \( \Delta = \sigma_s - \sigma_m + \sigma_{s-m} \). Here \( \Phi \) is used to describe the bubble film stability and \( \sigma \) is the flotation ability of droplet. Here \( \Phi \) is negative in the molten metal/slag system. It means that a bubble can’t carry an intact film from molten metal to slag. So the film will rupture and form small metal droplets. In the study (7) most small droplets had a size smaller than 10 \( \mu \)m.

2.6 Analyzing methods

2.6.1 Scanning electron microscope (SEM) equipped with energy dispersive spectrometry (EDS)

A SEM is using a beam of electrons to scan samples to obtain an image. The electrons interact with the atoms that consists the sample producing signals, which contains information of the sample: such as composition and topography.

The interaction cross-section is used to specify the probability of beam electrons interacting with the sample. In a SEM, the cross-section is very small (8). The penetration depth of electrons and the interaction volume depend on factors such as: the angle of incidence, the magnitude of current, the accelerating voltage and the average atomic number (Z) of the sample. The accelerating voltage and the atomic number play most important roles in deciding the depth, as shown in Figure 7.

![Figure 7 Schematic shapes of the interaction volume, where the accelerating voltage and the density are the](image)
most important factors\textsuperscript{(8)}.

The penetration depth $x$ can be calculated approximately according to the formula below\textsuperscript{(8)}:

$$x(\mu m) = \frac{0.1E_0^{1.5}}{\rho}$$

(19)

where, $E_0$ is the accelerating voltage (keV) and $\rho$ the density of sample (g/cm\textsuperscript{3}).

Backscattered electron (BSE) is one of the common signals that a SEM can produce. They are beam electrons reflected from the sample by elastic scattering and the intensity of signals depends on the average atomic number ($Z$) of the sample. Images produced by a BSE detector show a composition map of areas with different average atomic numbers by different shades of grey. So BSE images are useful in analyzing samples with multiphase samples. A comparison of a BSE image and a secondary electron (SE) image is shown in \textbf{Appendix 1}.

Another important signals produced by the interaction between beam electrons and samples is X-rays. The number and energy of emitted x-rays can be measured by an energy dispersive spectrometer. The x-ray detector converts the emitted x-rays into voltage signals, which are sent to a pulse processor. Usually, a software can be used to identify the x-ray lines in the resulting energy spectra quickly. In general, EDS peaks from elements of concentration of 0.5wt % are distinctly identifiable\textsuperscript{(9)}.

\textbf{2.6.2 Petrography}

Petrography is the knowledge to study rocks, minerals and ores using a microscope. Now this method is also used to analyze other materials, such as polymers, biomaterials, ceramics and steels. The concept of petrography analysis began with an English scientist, Sir Henry Clifton Sorby. His way to prepare specimens so that the true structure of materials can be observed made him to the father of both petrography and metallography.

There are two ways to prepare specimens for a petrography analysis: thin sections and polished bulk specimens. Polished bulk specimens are prepared for examination with a reflected light microscope. Specimens for thin sections are thinner than 30 $\mu$m.
and need a transmitted polarized light microscope.

There are several steps for preparing specimens, such as sectioning, impregnation and encapsulation, grinding and polishing. In order to get the true structure of materials, minimizing influence from specimen preparation as much as possible is important. The grinding can remove the deformation remained after the sectioning step and make a surface as flat as possible. The polishing is performed to remove the deformation caused by grinding and to obtain a high finish surface. Thin sections have more preparation steps than polished bulk sections and it requires a longer time. However thin sections provide more micro structural information.

2.6.3 Electrolytic extraction

Electrolytic extraction is one method to dissolve the matrix of sample using different electrolytes. By filtration of the electrolytes after extraction, materials that are not dissolvable such as inclusions in steels will remain on the filter. Then, the filter will be cut and taped on conductive holder for observation in SEM. Figure 8 shows a schematic principle of electrolytic extraction.

![Figure 8 Schematic principle of electrolytic extraction](image)

This method is suggested to test if it is possible to study titanium compounds (Ti(C,N) inside metal droplets. The advantage of this method is that it gives a three-dimensional information such as the real size, as shown in Figure 9.
2.6.4 X-ray Fluorescence (XRF) Spectrometry

The XRF technique is widely used to determine the elemental composition in the steel industry. This method can analyze both metallic and oxidic materials. Samples can be compact or in a powder form. In addition, even liquid materials can be analyzed using a special sample container. One advantage of the XRF technique is that samples are not destroyed during analysis. In this way, consumption of calibration samples can be reduced. The biggest disadvantage with the XRF technique is the difficulty to determine light elements with atomic numbers lower than 12 (Z<12)\(^{(10)}\).

2.6.5 Combustion Infrared Detection

In order to analyze carbon and sulfur, a combustion infrared detection technique is a common method to use. Metals can burn in oxygen if a high enough temperature is achieved. A weighed sample is melted in a ceramic crucible in a high frequency induction furnace, which is in contact with an oxygen stream. The oxygen works as a combustion fuel and as a carrier gas. The impurities in the oxygen gas can influence the result, especially for samples with ultralow carbon and sulfur contents. Tungsten is usually used to facilitate the melting. Also, an accelerator is usually added on the top of the sample before analysis in order to ignite the sample. There are different accelerators for different samples. Carbon released from the melted sample reacts with the oxygen to form CO and CO\(_2\). Therefore CO will be converted into CO\(_2\) and an
infrared detector can measure the amount of CO\textsubscript{2}. In this way, the content of carbon can be calculated. Sulfur from the melted sample will also react with oxygen to form SO\textsubscript{2} and an infrared detector measures the amount of SO\textsubscript{2}. In this way, the content of sulfur can be calculated. Both carbon and sulfur are calculated in weight percent.

2.7 Metal- and slag samples from desulphurization in SSAB Luleå

The laboratory in SSAB Luleå has an automatic system to analyze metal samples from the production lines. The most common elements in the metal samples are Si, Mn, P, Cr, Ni, Cu, Mo, Ti and V. Most elements in the samples, except light elements such as C and S, can be analyzed with the standard XRF method. Carbon and sulfur can be analyzed with the LECO CS200 Carbon Sulfur Determinator. Carbon and sulfur in slag samples are analyzed in the same way.

2.7.1 Slag sample preparation

The slag sample should be totally dry before sample preparation. If it contains moisture, it should be dried in a thermal furnace at 105 ºC for two hours. Thereafter, the slag sample is crushed in a jaw crusher. A 30 g sample is taken and ground with 30 ml acetone in a vibrating cup mill for 2 minutes. Thereafter, a 5 g sample is put in a glass crucible and tempered in a furnace at 950 ºC for 4 hours. After tempering, the crucible is weighed and a parameter of mass change (in %, called GLF) after tempering is calculated. The mass change can be positive or negative. During tempering, the metallic elements in the slag combine with oxygen and form oxides, leading to a positive mass change. While carbon and sulfur form gases which can result in a negative mass change. The GLF-parameter is a result of these mass changes. It is important to oxidize metallic compounds in the slag sample. Otherwise, the metallic compounds will react with the platinum crucible and destroy the platinum crucible later in the sample preparation process.

The next step for sample preparation before an XRF analysis is done using a method called a bused beads preparation. In this fusion technique, the slag is dissolved in a flux at high temperatures (>1000 ºC) in a platinum crucible. The temperature is high enough to melt the flux and dissolve oxides efficiently. Usually lithium
tetraborate \((\text{Li}_2\text{B}_4\text{O}_7)\) is used as flux. The melt is later cast in a casting-dish of platinum, where after a homogenous glass disk is formed after cooling of the sample. Here, a 1.6 g slag sample is used. The relationship between the amount of slag and flux is 1:4. The glass dish after cooling is ready for an XRF analysis, which is done using an ARL 9900 or an ARL 9800 XRF instrument. Figure 10 shows a sketch of the fusion technique.

Figure 10 A sketch of the fusion technique

The XRF analysis can determine the composition of the following elements and compounds: Fe, CaO, SiO\(_2\), MnO, P\(_2\)O\(_5\), Al\(_2\)O\(_3\), Na\(_2\)O, K\(_2\)O, V\(_2\)O\(_5\), TiO\(_2\) and Cr\(_2\)O\(_3\).

As mentioned before, XRF can’t be used for determination of carbon and sulfur. A small amount of slag from the same slag sample before tempering is weighed before being analyzed using combustion infrared detection. A 0.1 g slag sample is put in a glass crucible with a high purity iron chips as an accelerator. The equipment for analysis is called a LECO CS444 instrument.

2.8 Titanium compounds

In an earlier study\(^{(12)}\), \textit{in situ} observations of the formation of TiC and Ti(C,N) from hot metal was done in a confocal scanning laser microscope (CSLM) equipped with an infrared image furnace. The metal sample contained carbon-saturated iron together with a Fe-4 wt\% Ti master alloy. The sample was held in an alumina crucible and heated up to a predetermined temperature. During heating, a high purity Ar gas was used to prevent the formation of titanium compounds during heating. When the predetermined temperature was reached the gas was switched to N\(_2\) gas and the sample
was held during 30 min so the melt became saturated with nitrogen. For observation of the TiC formation, Ar gas was used. Thereafter, the sample was cooled slowly at a rate of 0.1K/s. The images of the metal surface were shown in a monitor and recorded in tape.

In Figure 11, two kinds of observed crystals are shown, one with smooth surface and the other with rough surface. According to the observations, the crystals with a rough surface tended to connect. However, the bond was not strong, i.e. they separated when the metal bath moved. Crystals with a smooth surface didn’t tend to stick to each other. Overall, the crystals had square or rectangular forms.

![Confocal scanning laser microscope image showing precipitates on the surface of Fe-Csat-0.2 wt%Ti](image.png)

**Figure 11** Confocal scanning laser microscope image showing precipitates on the surface of Fe-Csat-0.2 wt%Ti (12)

Two samples with different Ti-contents were compared in the paper (12): one containing 0.37 wt% Ti and the other containing 0.22 wt% Ti. The element mappings result showed that the sample with a higher Ti-content tended to form TiN. However, the sample with a lower Ti-content tended to form Ti(C,N) instead.

In the paper (12), the precipitation temperature of the first observed crystal of Ti(C,N) compound were determined with varied Ti-contents in the metal melt, as shown in Table 1. When the precipitation temperature for a Ti-content is decided,
more experiments were repeated when using the same Ti-content. It shows that the precipitation temperature of Ti(C,N) decreases with a decreased Ti-content.

Table 1 Precipitation temperature of Ti(C,N) in Fe-Csat-Ti $^{12}$

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ti, mass%</th>
<th>Precipitation Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.24</td>
<td>1773, 1788, 1785</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>1773, 1770, 1775</td>
</tr>
<tr>
<td>3</td>
<td>0.18</td>
<td>1767, 1764</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
<td>1762, 1758</td>
</tr>
<tr>
<td>5</td>
<td>0.12</td>
<td>1747, 1738, 1740</td>
</tr>
<tr>
<td>6</td>
<td>0.11</td>
<td>1694, 1696</td>
</tr>
<tr>
<td>7</td>
<td>0.07</td>
<td>1645, 1648</td>
</tr>
</tbody>
</table>
3 EXPERIMENT

In this thesis work, both metal and slag samples were taken from eight heats: a) four reference heats and b) four heats with a reduced calcium carbide content with 150kg. For each heat, three metal and slag samples were taken: i) before injection, ii) after injection of half of the amount and iii) after injection. Slag sampling was carried out manually using a long steel scoop. All slag samples were cooled in air on a metal floor. Hot metal samples were taken using a normal production sampler. Fig 12 shows a metal sample and the slag sample is shown later in the report. The body of the iron sample is used to determine the chemical composition for all elements except for C. The small ears of the iron sample are used to determine the C-content.

Figure 12 An example of hot metal sample

3.1 Composition of hot metal samples

Table 2 shows the chemical composition of the most important elements in the hot metal. The analysis of these elements will usually not differ a lot before and after the desulphurization process. Table 3 shows the sulfur content in the hot metal before
and after desulphurization. At SSAB, the maximum sulfur content is typically below 0.005% after desulphurization. The analysis was done at SSAB Oxelösund.

Table 2 Composition (wt%) of hot metal samples before desulphurization (10529-10532: reference; 11073-11076: reduced carbide addition)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>V</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>10529</td>
<td>4.640</td>
<td>0.633</td>
<td>0.267</td>
<td>0.036</td>
<td>0.259</td>
<td>0.159</td>
</tr>
<tr>
<td>10530</td>
<td>4.570</td>
<td>0.603</td>
<td>0.269</td>
<td>0.036</td>
<td>0.265</td>
<td>0.124</td>
</tr>
<tr>
<td>10531</td>
<td>4.670</td>
<td>0.765</td>
<td>0.286</td>
<td>0.036</td>
<td>0.269</td>
<td>0.192</td>
</tr>
<tr>
<td>10532</td>
<td>4.550</td>
<td>0.599</td>
<td>0.271</td>
<td>0.035</td>
<td>0.265</td>
<td>0.130</td>
</tr>
<tr>
<td>11073</td>
<td>4.550</td>
<td>0.884</td>
<td>0.320</td>
<td>0.041</td>
<td>0.272</td>
<td>0.173</td>
</tr>
<tr>
<td>11074</td>
<td>4.550</td>
<td>0.852</td>
<td>0.315</td>
<td>0.040</td>
<td>0.276</td>
<td>0.177</td>
</tr>
<tr>
<td>11075</td>
<td>4.470</td>
<td>0.904</td>
<td>0.317</td>
<td>0.040</td>
<td>0.276</td>
<td>0.192</td>
</tr>
<tr>
<td>11076</td>
<td>4.520</td>
<td>0.721</td>
<td>0.297</td>
<td>0.039</td>
<td>0.265</td>
<td>0.152</td>
</tr>
</tbody>
</table>

Table 3 Sulfur content in hot metal before and after desulphurization with carbides

<table>
<thead>
<tr>
<th></th>
<th>Before DeS</th>
<th>After DeS</th>
</tr>
</thead>
<tbody>
<tr>
<td>10529</td>
<td>0.062</td>
<td>0.002</td>
</tr>
<tr>
<td>10530</td>
<td>0.067</td>
<td>0.003</td>
</tr>
<tr>
<td>10531</td>
<td>0.064</td>
<td>0.003</td>
</tr>
<tr>
<td>10532</td>
<td>0.070</td>
<td>0.002</td>
</tr>
<tr>
<td>11073</td>
<td>0.075</td>
<td>0.004</td>
</tr>
<tr>
<td>11074</td>
<td>0.071</td>
<td>0.003</td>
</tr>
</tbody>
</table>
The composition of hot metal after desulphurization is very similar to the composition before desulphurization, except with respect to the S-, Si- and Ti-contents.

### 3.2 General sample preparation

A small piece is cut from the hot metal sample before mounting it in a conductive filled phenolic mounting compound for SEM analysis. After mounting, the sample is ground in four steps with grinding papers of different roughnesses. The grain size is organized from rough to fine and is shown as following: 240, 320, 640 and 1200. When one step is finished, the sample is turned 90º before the next grinding. When the grinding marks from earlier steps disappear totally, the current step can be terminated. The hot metal sample can be washed by water during grinding. It is important to get a surface which is as flat as possible. After grinding, the sample is washed by water and dried before polishing.

During polishing, a diamond paste with lubrication is used. The sample is polished in the opposite direction of the turning machine. The polishing cloth has a particle size of 3 µm. The process continues until a high shine mirror surface is obtained. After polishing, the sample will be washed with water and dried carefully for observation.

The samples are kept in a vacuum container to avoid oxidation of samples by the air and moisture. The samples can be used in both an SEM and a LOM.
The slag sample is treated in the same way as the metal sample, but the only difference is that the slag sample is washed with methanol instead of water. This is done to avoid the oxidation of the slag sample.

3.3 Slag samples

Before slag samples could be mounted in SEM powder, they were crushed with a hammer in a holder, shown in Figure 13. Big slag lumps fell apart as is shown in Figure 14.

![Figure 13 The holder used to punch slag samples](image1)

![Figure 14 Slag sample before punching to the left and slag sample after punching to the right](image2)

As seen in Figure 14, the size of the slag after punching is different. Most of the
samples analyzed in SEM were large size samples; only one sample of finer powders was studied as shown in Table 4.

Table 4 Different size of slag particles used in SEM samples

<table>
<thead>
<tr>
<th>Trial 1</th>
<th>Trial 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>S10532-3</td>
<td>S11076-3</td>
</tr>
<tr>
<td>S10529-3</td>
<td>S11073-3</td>
</tr>
<tr>
<td>S10530-3</td>
<td>S11074-3</td>
</tr>
<tr>
<td>S10531-3</td>
<td>S11075-3</td>
</tr>
</tbody>
</table>

Figure 15 shows one slag sample containing of large slag pieces and one slag sample of fine slag pieces after mounting in a SEM powder. In (b), the bright dots are the fine slag pieces. As can see in (a) several slag pieces were not surrounded by slags, i.e. they were pure iron.

Figure 15 SEM samples with large slag pieces (a) and fine slag pieces (b)

3.4 SEM

In the SEM, three analyses were tested: point-, line-, surface analysis and mapping
of a surface. A point analysis and surface analysis give the composition information in wt-% and at-%. Moreover, a line analysis gives variation of elements along a chosen line. Mapping of a surface gives a clear picture of where the elements exist within the sample. The example of these analyses result can be seen in Appendix 2.

4 RESULTS & DISCUSSION

4.1 SEM image

From the chemical composition results, it can be seen that the slag from the desulphurization of the hot metal mainly consists of metal droplets, CaS, Ti-compounds and calcium silicate. The metal droplets will be discussed in detail later.

Figure 16 shows a typical slag image which consists of big metal droplet and other slag compounds. In the metal droplet, there are many graphite precipitations as well as a layer of Ti-compound around the metal droplet. There is a square Ti-compound marked with number 4 beside the droplet. Also, the spherical phase marked with number 9 is CaS. Most of the CaS particles in the slag have more or less spherical shapes. Moreover, several CaS particles are merged together. Areas with the same shade of grey indicate that these areas have a similar chemical composition. The remaining area which is darker grey consists mainly of calcium silicate.
4.2 Metal droplets

Metal droplets contain Si, Mn, P, V, Ti, S, Fe and C. Note, that the C-content is not included in the EDS analysis. The content of the other elements vary a lot. Therefore it is difficult to find a difference between two trials with respect to the chemical composition.

The metal droplets studied in this paper have different sizes. Plots of all elements’ content to the size of droplets have been done. Generally, the content of the elements is higher the smaller the size of the metal droplet is. The plots can be seen in Appendix 3.

In the composition analysis, it is observed that calcium is dissolved in the metal
droplets. One plot of the calcium content as a function of the size of the metal droplets is shown in Figure 17. The size of metal droplets varies from 1 µm up to 133 µm.

![Graph showing calcium content vs size of metal droplets.](image)

Figure 17 the Ca-content varies with the size of metal droplets

A trend line is plotted and a prediction equation is shown in the plot. Here, the calcium content decreases with an increasing size of the metal droplets. When a droplet is as small as 1 µm, the content of calcium can be as high as 23 wt%. According to the Fe-Ca phase diagram, the maximum solubility of Ca in iron is reported to be 0.032 at% (about 0.023wt%) at a temperature of 1538°C. When hot metal solidifies, the solubility of Ca is almost 0 wt% according to the phase diagram.

The S-content shows a similar trend as illustrated in Figure 18.
The S-content increases dramatically when the size of the metal droplets are close to 1.

In this report, the analysis is a kind of two-dimensional (2D) cross section analysis, which has some limitations as mentioned in the theory part. So it is difficult to tell what exists under the metal droplets’ surfaces. This result can likely be obtained when the electron beam reaches a layer under the metal droplets, i.e. it gives a mixed result of metal droplets and slag under the surfaces. In this case, when analyzing metal droplets using the SEM equipment, it is important to choose metal droplets with a large enough size to get reliable SEM results.

All metal droplets in Figure 17 contain higher Ca-contents than the maximum solubility allowed in the hot metal. This indicates that all analyses of metal droplets in this paper actually are a mixed results of metal droplets and possible slag layers below the metal droplets.
4.3 Study of CaS compounds in slag

When analyzing the slag, different phases can be observed. One of the phases consists mainly of Ca and S, with different O contents. Figure 19 shows a comparison of the ratio of Ca/S for the two trials. From Figure 19, we can see that both trials have a ratio of Ca/S around 1.2, except for the three points marked within the circle. These three points are from sample S11076-3 in Table 4. After punching with hammer, the slag has different size: some are bigger and some are very small like fine powder. The sample with a fine slag powder shows a higher value of the Ca/S ratio. If these three points are disregarded, there is no significant difference between the Ca/S ratio between the two trials. The ratio of 1.2 indicates that this phase does not only consist of CaS, but also of some amount of CaO.
If the ratio of Ca/(S+O) is 1, all Ca is combined with S or with O. Four points in Figure 20 has the ratio close to 1, while three points within the circles contain a very high O content. Also, these three points differ more from the ratio of Ca/S compared to the remaining points. The two points in the left circle are from one image, which did not have a flat surface. This could have disturbed the measurements.

The Ca/(S+O) ratio in Figure 21 is around 1 except for the points marked within
the circle. These points are from the same sample as discussed in Figure 19. Because the high content of detected Ca, the Ca/(S+O) is still higher than 1 for these three points, which indicates an exceeded Ca-content.

In studying CaS in slag, samples using large slag pieces show more or less similar results, if disregarding those three points in Figure 20. Whereas the sample using a fine slag powder shows a exceeded Ca-content than could be expected.

4.4 Study of Ca-O-Si compounds in slag

CaS in slag has been discussed. Another important part of the slag consisted of Ca, O and Si together. These three elements can form different compounds according to a phase diagram between CaO and SiO$_2$. A phase diagram is shown later in Figure 24.

In order to understand which compounds that exist in slag, the ratio of Ca/Si for different points was plotted in Figure 22.

![Figure 22 The ratio Ca/Si for the two trials: trial 1 has 9 points and trial 2 has 7 points](image)

For both trials, most of the points lie inside the lines. The lower line has a ratio of 2 and the upper line has a ratio of 3, which indicates $2\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot \text{SiO}_2$. 
respectively. The points between these two lines can be said to be a mixture of 2CaO·SiO$_2$ and 3CaO·SiO$_2$. Most points in trial 1 are closer to the lower line except for the three points within the two circles. More specifically, these points are more likely to be 2CaO·SiO$_2$. The two points in the upper red circle come from the same sample. They have a special appearance than the other points, as seen in the upper picture in Figure 23 marked as number 17 and number 20. These two points have a ratio of around 3. This indicates that they probably only consist of 3CaO·SiO$_2$. The point in the lower red circle come from an area which is not conducted enough. This is seen in the lower picture in Figure 23, which is marked as number 5.

In trial 2, only 7 points were obtained from the composition results. Except one point outside the region, all the other points are close to the upper line. This means that compared to trial 1, the content of 3CaO·SiO$_2$ in trial 2 is higher than in trial 1. These points still represent a mixture of the compounds 2CaO·SiO$_2$ and 3CaO·SiO$_2$, but trial 2 has a higher content of 3CaO·SiO$_2$ than trial 1.
The two broken lines in Figure 24 represent the two horizontal lines in Figure 22. The average temperature at the sampling time is around 1400 °C, which is shown as the vertical broken line in Figure 24. According to the phase diagram, the slag compound of Ca, O and Si exist as a mixture of 3CaO·SiO₂ and 2CaO·SiO₂ at a temperature of 1400 °C. At a lower temperature, the slag compound of Ca, O and Si exist as a mixture of CaO and 2CaO·SiO₂.
In the slag phase with Ca, O and Si as the main elements, the O content is calculated according to the Ca and Si content from the composition results. This is done using the following formula (20).

\[
O_{\text{calc}} = \frac{n(Ca)}{2} + 2 \times \frac{n(Si)}{2}
\]  

(20)

where \(O_{\text{calc}}\) is the calculated oxygen content, \(n(Ca)\) and \(n(Si)\) are the calcium content and the silicon content from the chemical analysis. This calculated oxygen content is called \(O_{\text{calc}}\) and the ratio of \(O_{\text{calc}}\) to the analyzed O content is calculated and plotted in Figure 25 for the two trials.

Figure 24 Phase diagram of CaO and SiO₂
The Ocalc/O ratio for the two trials
Trial 1 Trial 2

![Graph showing the Ocalc/O ratio for two trials.]

**Figure 25** the ratio Ocalc/O for the two trials, same points as in Figure 22

Almost all points are below the line of value 1, which indicate that the calculated oxygen content is always lower than the analyzed value. The two trials show no significant difference, except for the two points marked within the circle. These two points are the same points as in the upper red circle in **Figure 22**.

There is another kind of slag phase which is very similar to the one containing mainly Ca, O and Si. The only difference is that it contains Al of different contents. In **Figure 26**, the Ca/Si ratio is also plotted for both trials, three points from trial 1 and four points from trial 2. All of the points are inside the two lines marking a ratio of 2 and a ratio of 1. The upper line with a ratio of 2 corresponds to 2CaO·SiO₂ and the lower line with a ratio of 1 corresponds to CaO·SiO₂. In this case, all these points represent a mixture of the two compounds, with a low amount of Al₂O₃.
The Ca/Si ratio for the slag phase containing four elements

Figure 26 the ratio Ca/Si for the two trials (slag phase with Ca, O, Si and Al as main elements): trial 1 has 3 points and trial 2 has 4 points

4.5 Particles inside metal droplets

When studying the metal droplets, some grey particles were found inside the droplets. According to their compositions, most of them consist of Fe and O, while the rest contain some Ca. All SEM images of metal droplets containing oxide particles can be seen in Appendix 4.

Figure 27 shows the Fe/O ratio for the particles. Most of the particles are within the two lines, which indicate FeO (the upper line) and Fe₂O₃ (the lower line), respectively. For those points outside the area of the two lines, a strong influence from metal droplet matrix is obtained in the composition results.

The points in Figure 27 come from samples from 3 heats only. Oxide particles were not observed in other samples. This may depend on the sample preparation. No explanation to the influence of those oxide particles on the metal droplets could be found. However, one consideration is if it is possible that these oxide particles can
influence metal droplets viscosity.

![Graph showing the Fe/O ratio of particles inside metal droplets](image)

**Figure 27** The Fe/O ratio of particles inside metal droplets

### 4.6 Carbide efficiency

The parameter $\eta$ (%) is used to describe the carbide efficiency and it is defined according to the following formula (21):

$$\eta = \left( \frac{\left[ S\right]_{in} - \left[ S\right]_{out}}{m_{hot\ metal}} \right) \cdot \frac{m_{CaC_2}}{M_{CaC_2}} \cdot 100 \quad (21)$$

where $\left[ S\right]_{in}$ and $\left[ S\right]_{out}$ is the sulfur contents before and after desulphurization respectively, $m_{hot\ metal}$ is the initial mass of hot metal, $m_{CaC_2}$ is the total mass of carbides used during the process, $M_s$ and $M_{CaC_2}$ is the molar mass of sulfur and carbide respectively. **Table 5** shows the carbide efficiency for the two trials.

**Table 5** Carbide efficiency in trial 1 and trial 2

<table>
<thead>
<tr>
<th>Trial</th>
<th>Carbide efficiency (%)</th>
<th>Trial 2</th>
<th>Carbide efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>
The carbide efficiency is used to compare the two trials with respect to the desulphurization effect. More specifically, how desulphurization is influenced when using smaller amounts of carbides. From Table 5, we can see that trial 2 has a higher carbide efficiency than trial 1. The average efficiency of carbides reaches 21.3% in trial 1 and 25.99% in trail 2. These values are not high, which indicates that most of the calcium in the carbides is combined with other element such as O to form slag or they are dissolved in the hot metal.

The calcium content is not included in the hot metal composition analysis at SSAB. This is because the calcium content is too low to be detected by the XRF instrument, while the other elements are analyzed by this method. So most of the calcium in carbides actually combines with O and forms CaO, which is one important component in slag.
5 CONCLUSIONS

In this pre-study of desulphurization of hot metal, both a literature study and experiments have been carried out. Some conclusions can be drawn as follows:

1. In metal droplets, the content of elements varies a lot with the size of metal droplets. The variation is different from element to element. The calcium and sulfur contents increase with a decreased size of the metal droplets. But the chemical composition for calcium and sulfur is a mixed result of the metal droplets and the slag under the metal droplets. So it is very important to choose metal droplets with large enough size to ensure correct SEM results, without influence from the slag.

2. One of the important phases in slag is CaS with a low content of CaO. Large slag sample give better results when studying CaS compared to the sample from a fine powder.

3. Another important part of the slag consists of Ca, O and Si. Most of the chemical composition determinations in the slags show that they contain a mixture of 2CaO·SiO$_2$ and 3CaO·SiO$_2$.

4. Besides Ti-compounds, iron oxides are found inside the metal droplets in three of the eight samples. The oxides can exist alone or as a mixture of FeO and Fe$_2$O$_3$.

5. The carbide efficiency is higher for the samples of trial 2 than trial 1. More specifically, the efficiency is 26.0% in trial 2 and 21.3% in trial 1. Overall, the carbide efficiency is very low.
6 FUTURE WORK

In the future, the focus will be to study metal droplets in slag samples. Some suggestions about future work are listed below.

1. Ti-compounds were thought to be one reason that metal droplets stay in the slag phase. Also iron oxides were found in this work, so it is interesting to dissolve metal droplets by electrolytic extraction to study what compounds could be found inside the metal droplets.

2. More SEM analysis can be done on metal droplets to obtain more data in order to study if there is composition gradient for elements within the sample. Here large droplets need to be the focus to avoid influence from the slag in the analysis.

3. Thermo-Calc can be used to study the stability of different phases containing Ti when the slags are cooled to room temperature.

4. In order to study metal droplets with electrolytic extraction, better slag/metal droplets separation is necessary. Because electrolytic extraction requires the sample should be conductive, while the slag contain oxides which are not conductive. The oxides make the electrolytic extraction more difficult.

5. It is interesting to study the thermodynamic relationship between the dissolved oxygen and sulfur in order to understand the reason for the low carbide efficiency.
REFERENCES


APPENDIX 1 Comparison of BSE (upper) and SE (lower) images

These figures show an area inside a metal droplet. The grey squares represents iron oxides.
APPENDIX 2 Examples of analyzing results from SEM
Point analysis marked with “+” and numbers (a), line analysis marked with a green line (b), surface analysis marked with yellow rectangular and number (c) and element mappings (d).
APPENDIX 3 Plots of elements content as a function of the size of droplets

Mn

P

V

Ti

Si
APPENDIX 4 Images of metal droplets with oxide particles

Areas marked with a number in a circle are oxide particles.

Images are from sample 10529-3. (b) is an enlarged figure of the area in (a).
Images are from sample 10531-3.
The above three images are from sample 11076-3 containing fine slag powders.