Sulfur and Nitrogen in Ladle Slag

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ABSTRACT

The present work deals with some aspects of slags related to secondary metallurgy in the steelmaking process. More specifically the focus is given to sulfur and nitrogen in ladle slags. Even though slags have been fairly well–researched in the past, the available data for these elements in typical ladle slag compositions is rather scarce. In some cases the available data is in discordance. There are also inconsistencies between the literature data and what is commonly observed in the industrial processes.

Sulfide capacities were measured at steelmaking temperatures, 1823–1873 K, in ladle slags. The data was found to be in reasonable agreement with the industrial process norms. The sulfide capacity was found to increase with the basic oxides CaO and MgO; and decrease with the acidic components Al₂O₃ and SiO₂. The sulfide capacity was also found to increase with temperature.

The dependence of sulfide capacity on the oxygen partial pressure, for slags containing multivalent elements, was investigated experimentally at 1873 K with a slag containing vanadium oxide. A strong dependence of oxygen partial pressure was observed. The sulfide capacity increase by more than two orders of magnitude when the oxygen partial pressure was increased from 4.6×10⁻¹⁶ atm to 9.7×10⁻¹⁰ atm.

The nitrogen solubility and the effect of carbon was investigated in typical ladle slags and the CaO–MgO–SiO₂ system at 1873 K. Carbon increases the nitrogen solubility substantially. In the absence of carbon, the nitrogen solubility is extremely low. Low concentrations of cyanide was detected in the carbon saturated slag. This was much lower than the total nitrogen content and formation of cyanide cannot explain the large increase.

The possibility of removing sulfur with oxidation from used ladle slag was investigated experimentally at 1373–1673 K. The sulfur removal of mostly solid slag was found to be a slow process, and would not suitable for industrial practice. At 1673 K the slag was mostly liquid and more than 85% of the sulfur was removed after 60 min of oxidation in pure oxygen atmosphere.
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SUPPLEMENTS

The thesis is based on the following supplements:

**Supplement 1:** “Sulfide Capacity in Ladle Slag at Steelmaking Temperatures”

*Carl Allertz*, and *Du Sichen*


**Supplement 2:** “The Effect of Oxygen Potential on the Sulfide Capacity for Slags Containing Multivalent Species”

*Carl Allertz*, *Malin Selleby* and *Du Sichen*

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*Carl Allertz*, *Niklas Kojola*, *Wang Hui* and *Du Sichen*


**Supplement 4:** “Effect of Carbon on the Solubility of Nitrogen in Slag”

*Carl Allertz*, *Fan Li*, *Jesse F. White* and *Du Sichen*


**Supplement 5:** “Possibility of Sulfur Removal from Ladle Slag by Oxidation in the Temperature Range 1373–1673 K”

*Carl Allertz* and *Du Sichen*

The contributions by the author to the supplements included in the thesis:

**Supplement 1:** Performed literature survey, all experimental work, and most of the writing.

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1 INTRODUCTION

In today’s society steel products are used for an enormous range of applications all the way from basic constructions to highly specialized products such as surgical tools or ball bearings. In Sweden the steel production have been an important industry, and still is today. The Swedish steel industry have gone through a transition towards higher end niche products, in order to compete on the global market. This has been made possible by continuous innovation through research and process optimization. The quality of steel has been greatly improved by producing cleaner steels with less impurity elements such as sulfur, phosphorous, oxygen and hydrogen as well as harmful inclusions.

Slags plays an immensely important part in the steelmaking processes. The slag protects the steel of unwanted oxidation but is also utilized for its ability to remove impurity elements such as sulfur and phosphorous. With good slag control it is possible to achieve a steel with very low levels of these elements. One easily realizes the importance of accurate fundamental data of slag properties for the optimization of the steelmaking processes. As a result slags have been quite heavily studied. While the available data have been sufficient for the steelmaking industries in the past, more accurate data is needed for the further improvement of the processes that are used, and for the development of new processes. With the industry shifting towards more sustainable processes with less environmental impact, new research areas are created as well.

The main objective of the present work was to study sulfur and nitrogen in typical ladle slag i.e. in the high CaO–region of the Al$_2$O$_3$–CaO–MgO–SiO$_2$ system. The available data for sulfur and nitrogen are rather scarce for this kind of slags. There are also inconsistencies among the available data. In some cases the prediction by the literature is far away from the observations in the industry. In these cases a clarification is needed.

The sulfide capacity is a measurement of a slag’s affinity to sulfur, and have been widely studied for steelmaking slags. This also includes slag systems containing multivalent elements e.g. Fe, Cr. Unfortunately, the dependence of sulfide capacity on the oxygen partial pressure has not been considered for these systems. An investigation is necessary since it is uncertain whether the effect of oxygen partial pressure can be neglected. In fact, as was observed in the present work this effect is substantial. Using the available data without precaution might lead to misunderstandings.
The demand for steels containing lower concentrations of nitrogen have increased the last years. Nitrogen has been proven difficult to remove from the steel. Nitrogen in slag has been quite well–studied. In general the nitride capacity has been measured and reported. Unfortunately, the industrial observations are far away from what is predicted by most of the available data. The majority of earlier researchers used graphite crucibles for their experiments. An investigation of the effect of carbon on nitrogen in slag is thus of interest. Actually, as was discovered in the present work the effect of carbon is substantial on the nitrogen solubility of the slag. Using the earlier nitride capacity data could thus lead to great misunderstandings.
2 \hspace{1em} \textbf{BACKGROUND}

2.1 \hspace{1em} \textbf{Steel Production Process}

There are essentially two pyro metallurgical routes for producing steel, ore based production and scrap based production. Iron ore pellets are charged together with coke and lime in the top of the blast furnace. In the blast furnace the iron oxides are reduced in several steps and finally a solution of liquid metallic iron saturated with carbon is obtained, also known as hot metal. The hot metal is tapped intermittently into a torpedo car which is used to transport the hot metal to the converter furnace. In the converter the hot metal is converted into steel by removing the majority of the dissolved carbon. This is done by blowing oxygen gas at the melt surface, oxidizing the carbon to gas. After this process the liquid steel is tapped into the ladle where secondary metallurgy operations are made, which is also referred to as ladle treatment. The secondary metallurgy operations serves several purposes which includes the removal of impurity elements and inclusions, final adjusting of the chemical composition by alloying and obtaining a homogenous melt with respect to both composition and temperature. After the ladle treatment the ladle is transported to the casting station and the steel is cast by continuous casting or ingot casting.

The process in the scrap based route consists of melting steel scrap in the electric arc furnace (EAF) and then tapping the steel into a ladle. The subsequent steps follow the same route as for the ore production route.

2.2 \hspace{1em} \textbf{Slags in Steelmaking}

Slags play a very important part in the steelmaking process, in fact they are used in all the process steps mentioned above. Slag is the generic name for the ionic oxide solutions that are commonly found in metallurgical processes. The slags are both formed from elements in the raw materials and from added slag formers. In the ladle a synthetic slag is normally used. The most common components in steelmaking slags are $\text{Al}_2\text{O}_3$, $\text{CaO}$, “$\text{FeO}$”, $\text{MgO}$ and $\text{SiO}_2$ although several other may also be present.

Slags serves several purposes in the process; the slag protects the metal from unwanted oxidation, it is used for removal of impurity elements and it also works as an insulator reducing heat losses from the steel. Accurate fundamental data of slag properties is essential to control and optimize the production process.
2.2.1 Slag Refining

There are several elements that need to be precisely controlled to very low levels in the steel in order to achieve a high quality product. Slag treatment is used for removing two of the most important impurity elements, sulfur and phosphorous. The latter is usually removed from the steel in the converter or EAF processes. In the present work sulfur and nitrogen are of primary interest. Slag refining works in such a way that the liquid metal is brought in contact with the slag phase. An exchange reaction takes place where the impurity element is rejected to the slag phase. At the operational temperatures the thermodynamics favors this rejection. The exchange is principally illustrated for sulfur removal in Eq. (2.1).

\[
S_{\text{metal}} + (O^{2-})_{\text{Slag}} = (S^{2-})_{\text{Slag}} + O_{\text{metal}}
\] (2.1)

In the case of sulfur removal, or desulfurization, a low oxygen potential is favorable. That is why the final desulfurization mainly takes place in the ladle where the oxygen concentration can be lowered to very low levels. This is commonly done by “aluminum killing” the steel or by vacuum degassing. Sulfur is also removed to some extent in the blast furnace and in pretreatment in the torpedo car. However, this removal is not sufficient for meeting the requirements of higher quality steel grades.

The desulfurization is also heavily dependent on the nature of the slag that is used. Accurate data and information of the slag is vital in order to optimize the desulfurization process.

Lately, the demand for steels which also have low nitrogen content has increased. While other dissolved gases such as oxygen and hydrogen can be removed sufficiently by vacuum degassing nitrogen has been proven difficult to be removed by this technique. Although it has been proposed that nitrogen can be removed by slag refining no such process is commercially practiced in Sweden. Instead the nitrogen content is reduced by limiting the input from raw materials and use of argon purging etc. However, this is not an effective method for controlling the nitrogen content.
2.3 Scope of the Present Study

This thesis work included the study on some fundamental aspects of impurity elements in slags related to the ladle refining in the steelmaking process. The scope of the present work can be divided into the following parts:

1. Sulfur in ladle slag: A considerable amount of research have been made on the desulfurization abilities of different slag systems. This has generally been investigated by measuring the sulfide capacity. However, the data is rather scarce when it comes to typical ladle slag compositions at steelmaking temperatures i.e. 1873 K. The reported data indicate sulfide capacities which are lower compared to what has been observed in the industrial operation. In Supplement 1 the sulfide capacities for typical ladle slag compositions are investigated at 1823–1873 K.

Sulfide capacities have also been reported for several slag systems containing multivalent species such as Fe, Cr etc. These elements can adopt different valence states depending on the oxygen potential. It is reasonable to expect that the sulfide capacity of such slag would not be independent of the oxygen partial pressure, which is the general assumption when using the sulfide capacity. No conclusive study has been carried out investigating the effect of sulfide capacity on the oxygen partial pressure for these kind of slags. In Supplement 2 the sulfide capacity is measured for slags containing vanadium oxide over a large range of oxygen partial pressures.

2. Nitrogen in ladle slag: It has been proposed that nitrogen can be removed from liquid steel by a slag refining technique, similar to as sulfur is removed. A large amount of studies have been carried out measuring the nitrogen solubility in different slag systems. In many of these publications the nitride capacity is given, equivalent to the sulfide capacity. However, the available data is in considerable discordance. Some researchers have suggested that nitrogen can dissolve in slag as free nitride ions, join the slag network or form cyanide ions together with carbon. Additionally, the available data for typical ladle slag compositions is rather scarce. In the industrial operation it has been found that the nitrogen sometimes increases in the steel melt subsequent to the vacuum degassing.
In Supplement 3 the nitrogen solubility in ladle slags is measured at 1873 K. It is also investigated if the slag could be the reason for the nitrogen increase as seen in industry.

The majority of earlier measurements were made using graphite crucibles, meaning that the slag is saturated with carbon. In industry the carbon content of the slag is very low. This could explain the discordance in the available data. In Supplement 4 the effect of carbon on the nitrogen solubility in slag is investigated at 1873 K.

3.  **Sulfur removal from slag**: Subsequent to casting the remaining ladle slag is discarded. In the high quality steelmaking processes the main impurity element in the slag after use is sulfur. If sulfur could be removed, the slag could be reused in production. This would be both economically beneficial and environmentally sane since less raw materials would be needed in the production. It has been found that it is possible to oxidize CaS to CaO at elevated temperatures, thus removing sulfur to the atmosphere. It is reasonable to expect that sulfur can be removed from used slag by oxidation. In Supplement 5 the possibility of removing sulfur from used ladle slag by oxidation is investigated for both solid and liquid slag in the temperature range 1373–1673 K.

3  **THEORETICAL CONSIDERATIONS**

In this section the theoretical foundation of slag capacities for sulfur and nitrogen are given. The Ca–S–O system and the sulfur removal from solid respectively liquid slag are also briefly described.

3.1  **Slag Capacities**

The concept of slag capacity was introduced by Richardson and Fincham in 1954 where they defined the sulfide and sulfate capacities [1]. Due to its usefulness the sulfide capacity concept have been adopted by both industry and academia. The usefulness comes in the fact that direct comparison of widely different slags affinity to a certain element is possible. Capacities for several other elements have been introduced such as nitrogen, carbon and phosphorous among others. The sulfide and nitride capacities are treated below, since they are the primary interest of the present study.
3.1.1 Sulfide Capacity

The sulfide capacity is derived from the following gas ion exchange reaction:

\[
\frac{1}{2} S_2 (g) + \left( O^{2-} \right)_{\text{slag}} = \left( S^{2-} \right)_{\text{slag}} + \frac{1}{2} O_2 (g)
\]  

(3.1)

The equilibrium constant for Eq. (3.1) can be written with the activities as:

\[
K_{(3.1)} = \frac{a_{S^{2-}} \times p_{O_2}^{1/2}}{a_{O^{2-}} \times p_{S_2}^{1/2}}
\]  

(3.2)

where \( K \) is the equilibrium constant, \( a_{S^{2-}} \) and \( a_{O^{2-}} \) are the activities of sulfide and oxygen ions respectively, \( p_{S_2} \) and \( p_{O_2} \) are the partial pressures of sulfur and oxygen gas respectively. While Eq. (3.1) and (3.2) are principally correct, they are difficult to use since the activity of an ion cannot be determined. It is thus not possible to calculate \( K \) in Eq. (3.2). The sulfide capacity is a construction which partially circumvent this problem.

The activity of an element can be expressed in the infinite dilute standard state and with 1 mass% as reference according to Eq. (3.3).

\[
a_i = f_i \times (\text{mass\%}\ i)
\]  

(3.3)

Where \( f_i \) is the activity coefficient for element “i” in the infinite dilute standard state. Rearrangement of Eq. (3.2) and expressing the activity of sulfide according to Eq. (3.3) gives the sulfide capacity (\( C_S \)) defined as:

\[
C_S = (\text{mass\%}\ S)_{\text{slag}} \times \frac{p_{O_2}^{1/2}}{p_{S_2}^{1/2}} = K_{(3.1)} \times \frac{a_{O^{2-}}}{f_{S^{2-}}}
\]  

(3.4)

In Eq. (3.4) it can be seen that the \( C_S \) can easily be quantified by experiments. From the far right hand side of the equation it can be seen that \( C_S \) is only a function of temperature and slag composition. It can thus be considered a slag property.
It is also useful to express $C_S$ with the activity of sulfur dissolved in metal. This is done by considering the following reaction:

$$\frac{1}{2}S_2(g) = S(\text{1 mass\% in metal})$$ \hspace{1cm} (3.5)

where the equilibrium constant for Eq. (3.5) can be expressed as:

$$K_{(3.5)} = \frac{a_S}{p_{S_2}^{1/2}}$$ \hspace{1cm} (3.6)

If the activity of sulfur is expressed according to Eq. (3.3), and combined with Eq. (3.4) and (3.6) the following expression is obtained.

$$C_S = \frac{(\text{mass \% S})_{\text{Slag}}}{(\text{mass \% S})_{\text{Metal}}} \times K_{(3.5)} \times \frac{p_{O_2}}{f_{S_2}}$$ \hspace{1cm} (3.7)

The ratio of sulfur in slag over sulfur dissolved in metal is defined as the sulfur distribution ratio, $L_S$.

$$L_S = \frac{(\text{mass \% S})_{\text{Slag}}}{(\text{mass \% S})_{\text{Metal}}}$$ \hspace{1cm} (3.8)

The sulfide capacity can thus be used for predicting the sulfur distribution between slag and metal for some chosen conditions, if $C_S$ is known for the particular slag composition.

The underlying assumption regarding $C_S$ is that it is independent of oxygen and sulfur potential over some ranges. In other words the quantity $a_{O^{2-}}/f_{S^{2-}}$ is constant over some ranges of oxygen and sulfur partial pressures.

### 3.1.2 Nitride Capacity

Equivalent to the sulfide capacity the nitride capacity can be defined based on the following gas–ion exchange reaction:

$$\frac{1}{2}N_2(g) + \frac{3}{2}(O^{2-})_{\text{Slag}} = (N^{3-})_{\text{Slag}} + \frac{3}{4}O_2(g)$$ \hspace{1cm} (3.9)
The equilibrium constant for Eq. (3.9) can be written with the activities as:

\[ K_{(3.9)} = \frac{a_{N^{3-}} \times p_{O_2}^{3/4}}{a_{O^{2-}} \times p_{N_2}^{1/2}} \]  

(3.10)

Rearrangement of Eq. (3.10) in combination with Eq. (3.3) gives the nitride capacity as:

\[ C_N = (\text{mass}\%\ N)_{\text{Siag}} \times \frac{p_{O_2}^{3/4}}{p_{N_2}^{1/2}} = K_{(3.9)} \times \frac{a_{O^{2-}}^{3/2}}{p_{N_2}^{1/2}} \]  

(3.11)

In Eq. (3.11) it can also be seen that the nitride capacity principally is only a function of composition and temperature.

### 3.2 The Ca–S–O system

In the temperatures of interest the Ca–S–O systems contains the following condensed phases; CaO(s), CaSO_4(s), and CaS(s). The phase stability diagrams at 1473 K and 1638 K are given in Figure 3–1, the data used for producing the diagram was taken from Turkdogan [2].

![Phase stability diagram for the Ca–S–O system at 1473 K and 1638 K](image)

Figure 3–1. Phase stability diagram for the Ca–S–O system at 1473 K and 1638 K based on data from Turkdogan [2].
3.2.1 Sulfur removal from slag

Sulfur can principally be removed from slag by oxidation of the sulfur to SO$_2$ gas. In solid slag, sulfur present as CaS can be oxidized according to the following reaction:

$$\text{CaS(s)} + \frac{3}{2} \text{O}_2(\text{g}) = \text{CaO(s)} + \text{SO}_2(\text{g}) \quad (3.12)$$

Sulfur also has the possibility to form calcium sulfate according to Eq. (3.13).

$$\text{CaS(s)} + 2\text{O}_2(\text{g}) = \text{CaSO}_4(\text{s}) \quad (3.13)$$

The prevailing reaction will be dependent on the oxygen and SO$_2$ partial pressures as well as the temperature as is illustrated by Figure 3–1. If Eq. (3.13) occurs the sulfur cannot be removed by further oxidation.

In the liquid ionic slag sulfur can be removed by oxidation according to the following reaction:

$$\left(\text{S}^{2-}\right)_{\text{Slag}} + \frac{3}{2} \text{O}_2(\text{g}) = \left(\text{O}^{2-}\right)_{\text{Slag}} + \text{SO}_2(\text{g}) \quad (3.14)$$

Similar to the solid slag, sulfur can also form sulfate ions together with oxygen. This is described in the following reaction:

$$\left(\text{S}^{2-}\right)_{\text{Slag}} + 2\text{O}_2(\text{g}) = \left(\text{SO}_4^{2-}\right)_{\text{Slag}} \quad (3.15)$$

The sulfate ions will remain in the slag and cannot be removed by further oxidation.

4 EARLIER WORKS

A quite extensive investigation of previous published data was carried out during the course of the present work. Firstly the available sulfide capacity data related to ladle slags was collected and reviewed. Slags containing multivalent components were also investigated. Secondly the previous works regarding nitrogen in slag with focus on the solubility was investigated and reviewed. Lastly, earlier works considering the oxidation of sulfur from slag were reviewed.
4.1 Sulfur in Slag

An impressive amount of sulfide capacity measurements have been made for a variety of slag systems over the years [3]. This includes traditional systems that are commonly found in steelmaking processes but also some less traditional systems. Several models have also been developed in order to predict the sulfide capacities. Even though this large amount of work have been undertaken, the available data for typical ladle slag compositions at typical steelmaking temperatures (i.e. 1873 K) is rather scarce. This is especially true for slags free from CaF₂.

$C_S$ depends strongly on the slag composition as can clearly be seen in Figure 4–1 where some earlier data is plotted against the extended basicity (including $\text{Al}_2\text{O}_3$, $\text{CaO}$, $\text{MgO}$ and $\text{SiO}_2$). $C_S$ increases with basicity.

![Figure 4–1. Sulfide capacities against the extended basicity at 1873 K based on data from [4], [5] and [6].](image)

Most of the earlier studies in the quaternary $\text{Al}_2\text{O}_3$–$\text{CaO}$–$\text{MgO}$–$\text{SiO}_2$ system, which is of primary interest in this work, were carried out at much higher $\text{SiO}_2$ concentrations than what is typically found in the ladle [7–13]. It is well known that $\text{SiO}_2$ strongly affects $C_S$ [1]. It would be difficult to relate these data to ladle slag compositions without introducing considerable errors. The situation in the slag might be very different when $\text{SiO}_2$ is only a minor component.
To the author’s knowledge only Ohta et al. have measured sulfide capacities for ladle slag compositions at 1873 K [14]. It was noticed that the sulfur distribution ratio between steel and slag in industry was actually higher than what is predicted by the previous data and some models. In some cases this difference was significant. This indicates that the present available data is not sufficient for accurately predicting the industrial situation. There is thus a need for re-examining sulfide capacities in ladle slags at steelmaking temperatures.

The vast majority of earlier measurements were carried out using a gas–slag equilibration technique [3]. It is well known that the kinetics of gas–slag reactions are generally slower than liquid–liquid reactions. Long reaction times are thus required to establish the equilibrium with sulfur in the gas and the slag. These measurements are also very sensitive regarding the gas phase. If even a small leak is present during the experiment it would result in a higher oxygen and lower sulfur partial pressure, which would decrease the calculated capacity. Both of these are plausible explanations for the much lower prediction compared to the industrial situation.

Sulfide capacity measurements have also been made for some slags containing multivalent elements such as Fe, Cr etc. [10, 15–23]. These species can adopt several valence states in the slag, depending on the oxygen potential. It is well known that several ions of different valence state can co-exist in the slag. For example the fraction of $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the CaO–Al$_2$O$_3$–SiO$_2$–FeO$_x$ system is dependent on the oxygen potential [24]. The variation of $\text{Fe}^{2+}/\text{Fe}^{3+}$ will have a great impact on the slag structure since the ionic oxide solution must remain in electric charge balance. This means that the $a_{\text{O}^{2-}}$ will be a function of oxygen partial pressure in these kind of slags. As was mentioned earlier, it is generally assumed that the quantity $a_{\text{O}^{2-}}/f_{\text{S}^{2-}}$ is constant over the range of oxygen and sulfur potentials of interest when using the sulfide capacity. It is likely that this assumption does not hold for slags containing multivalent species. Unfortunately, no previous study have been carried out investigating whether the effect of oxygen potential on $C_S$ can be neglected for these kind of slags. This is needed since there is generally a large difference in oxygen potential between the laboratory situation and in the industrial processes.
4.2 Nitrogen in Slag

Solubilities of nitrogen in slags have been quite widely studied [25–47]. Measurements have been made for several different kinds of slags. Unfortunately, the available data are in considerable discordance. The nitrogen contents reported by different authors vary greatly. There are even contradictions regarding the role of SiO₂. It has been reported that SiO₂ both increases and decreases the nitrogen solubility [35, 38]. Additionally, it is not clear which species of nitrogen that are actually present in the slag.

It has been quite well established that nitrogen dissolves in the slag as free nitride ions, N₃⁻. Although, this may not be the only species of nitrogen in the slag. It has also been proposed that nitrogen joins the slag network. Martinez and Sano used a selective analysis technique for analyzing the amounts of free nitride and incorporated nitrogen [35]. They proposed that nitrogen joins the slag network and becoming either partially incorporated nitrogen, N⁻, or fully incorporated nitrogen, N⁰. Nitrogen replaces either single bonded oxygen, O⁻, fully bonded oxygen, O⁰, or a combination of the two. A possible dissolution reaction as postulated by Martinez and Sano where nitrogen joins the slag work, becoming fully incorporated nitrogen is given in Eq. (4.1).

\[
\frac{1}{2} \text{N}_2(g) + 3\left(O^-\right)_{\text{Slag}} = \left(N^0\right)_{\text{Slag}} + \frac{3}{2}\left(O^{2-}\right)_{\text{Slag}} + \frac{3}{4}\text{O}_2(g) \quad (4.1)
\]

Many authors have measured and reported nitride capacities according to Eq. (3.11). It is possible that the nitride capacity cannot be directly related to the nitrogen solubility for some conditions if species as proposed by Martinez and Sano are also present. This complicates the use of the nitride capacity. Additionally, measures in order to isolate nitrogen as nitride in the analysis are required.

It has also been proposed by several researchers that nitrogen can dissolve in the slag as cyanide ions, CN⁻ [36–40, 43–46]. This principal reaction is given in Eq. (4.2).

\[
\frac{1}{2} \text{N}_2(g) + \text{C(gr)} + \frac{1}{2}\left(O^{2-}\right)_{\text{Slag}} = \left(CN^-\right)_{\text{Slag}} + \frac{1}{4}\text{O}_2(g) \quad (4.2)
\]
The cyanide content seems to be strongly dependent on the slag composition. Schwerdtfeger et al. reported nitrogen as cyanide over the total nitrogen ratios ranging from about 1/17 to 1 in the Al$_2$O$_3$–CaO system at 1873 K [36, 37]. A general trend where the fraction of nitrogen bonded as cyanide increases with increasing fraction of calcium oxide. However, the authors mentioned that they experienced difficulties in reproducing the analytical results and the data should be taken as examples only. Shimoo et al. also studied the same system [38, 39]. They reported a fraction of about 1/4 at 1823 K and 1/7 at 1873 K. They reported considerable higher total nitrogen contents compared with Schwerdtfeger et al. The cyanide concentrations are fairly similar among the studies. Both of these research groups also measured cyanide contents in the Al$_2$O$_3$–CaO–SiO$_2$ slag system [39, 40]. Schwerdtfeger et al. measured the nitrogen solubility in a 12% Al$_2$O$_3$–48% CaO–40% SiO$_2$ slag at 1773 K and reported ratios of nitrogen as cyanide over total nitrogen of about 1/20 to 1/10 [40]. Shimoo et al. measured nitrogen solubilities in the 20%Al$_2$O$_3$–40% CaO–40% SiO$_2$ slag and reported approximate ratios of at 1/80 1773 K and 1/500 at 1823 K [39]. Cyanide have also been reported to be present in quite different slag systems containing e.g. CaF$_2$ [43–46]. These systems are not addressed in detail here due to the large difference in the nature of the ionic melts between these systems and the primary interest of this work.

It was noticed when reviewing the literature that most of the earlier experimental works were carried out using graphite crucibles [35–47]. These slags are thus saturated with carbon. The reported nitrogen contents were consistently and substantially higher compared to when an oxide or metallic crucible was used. The majority of measurements without carbon was carried out by Suito and his co–workers [25–34]. While they have conducted a large amount of measurements it should also be pointed out that there are inconsistencies in the data. This is the case even for some slags with almost identical slag composition. The authors used additions of Si$_3$N$_4$ as a source of nitrogen. There is a possibility that equilibrium was not reached in some experiments where short reaction times were employed. Nitrogen as Si$_3$N$_4$ did not have time to evaporate and establish equilibrium with the gas phase. In the experiments where longer reaction times (<10 h) were employed the nitrogen contents are significantly lower [25, 28, 30, 32].
A possible explanation for the large difference in nitrogen content would be due to the different oxygen pressures used in the studies. The studies where oxide or metallic crucible was used were generally carried out at higher oxygen partial pressures. It can be seen according to the reactions given in Eq. (3.9), (4.1) and (4.2) that the nitrogen concentration in the slag is expected to decrease with oxygen partial pressure. However, in some cases the difference in nitrogen content is about 3 orders of magnitude between slags kept in metallic compared to graphite crucible. The difference in oxygen partial pressure among these studies is around 2 orders of magnitude. This indicates that the change of nitrogen solubility is considerably greater than the change of oxygen pressure, which is less likely. Another explanation would be if nitrogen forms cyanide to a large extent at carbon saturation, when contained in graphite crucible. This would be contradictory to some of the earlier works as mentioned above, especially when SiO$_2$ is present [39, 40].

Based on the previous data it is expected that carbon somehow increases the nitrogen solubility in the slag. A clarification of this is important since the carbon contents in the slags in the later stages of steelmaking are very low. Some of the earlier data might not be applicable to slags where no carbon is present. Recently Park et al. mentioned that carbon increases the nitrogen solubility in the CaF$_2$–CaO–SiO$_2$–Al$_2$O$_3$ slag system, and proposed that this was due to formation of cyanide [44]. It would be of interest to also investigate if this is valid for ladle slags free from CaF$_2$.

### 4.3 Oxidation of Sulfur from Slag

Only a few studies have been made on the oxidation of sulfur from slag [48–51]. Earlier efforts focused on reducing the evolution of sulfur–bearing gases from disposed blast furnace slags. Pelton et al. found that sulfur can be removed from liquid blast furnace slags by reaction with oxygen in the gas phase, in the temperature range 1633–1733 K [49]. They found that the sulfur removal rate increases with oxygen partial pressure above 0.3 atm. Below 0.3 atm they reported the opposite namely the sulfur removal rate increases with decreasing oxygen partial pressure. Turkdogan and Pearce also found that sulfur can be removed from the slag to the gas phase [51]. They carried out experiments at 1823 K and reported that the desulfurization rate was noticeable slower in pure oxygen compared to if pure CO$_2$ or 1% O$_2$ – N$_2$ gas mixture was used.
Recently Hiraki et al. showed that sulfur can be sufficiently removed from used ladle slag by oxidation with an Ar–21% O$_2$ gas above 1273 K [50]. They found that more than 90% of the sulfur could be removed after 60 min of oxidation. They carried out their measurements with powdered secondary steelmaking slag containing CaF$_2$. They found that the sulfur removal rate increased with oxygen partial pressure up to 0.05 atm, and remained constant in the range 0.05–0.21 atm. To the author’s knowledge no study has been carried out investigating the possibility of removing sulfur from liquid ladle slag by oxidation. Additionally, no study has been made on the desulfurization of ladle slag free from CaF$_2$ over a wide oxygen partial pressure range. This would be of interest since the mechanism of sulfur removal from liquid slag might be very different compared to solid slag.

5 EXPERIMENTAL METHODS

5.1 Control of Oxygen Potential

In all of the experiments included in this work it was desirable to set the oxygen potential in the system. This was done by employing an “open circuit” principle where a gas with a fixed chemical potential of a species is continuously supplied to the system [52]. This way it is possible to impose a potential on the system. Any reaction products are transported away with the off gas. In this work a large range of oxygen partial pressures were required. Several techniques were employed in order to control the oxygen partial pressure at the different levels.

In the measurements where a very low oxygen partial pressure was desirable the C/CO equilibrium was used. The reaction gas consisted of either pure CO gas or a mixture with a high fraction of CO and some other gases. These were passed through a gas mixer filled with silica beads prior to entering the reaction chamber. The reaction gas was combined with the use of graphite crucibles. The gas is passed over the surplus of carbon and the following reaction takes place:

$$\text{C(gr)} + \frac{1}{2} \text{O}_2(g) = \text{CO(g)} \quad (5.1)$$

$$\Delta G^{\circ}_{(5.1)} = -114,400 - 85.8T \text{ J mole}^{-1} \quad [2] \quad (5.2)$$
The oxygen partial pressure can be altered by adjusting the fraction of CO in the inlet gas. A low gas flow of 0.1 l·min⁻¹ combined with holes in the bottom of the holding crucible ensured a long contact time between the gas and crucibles.

In some of the measurements it was desirable with a higher oxygen partial pressure. In this case the above method cannot be used. Instead the CO/CO₂ equilibria was used to set higher oxygen partial pressures. This was done by mixing an inlet gas from pure CO and CO₂ gas. At the experimental temperature the following reaction will take place:

\[ \text{CO(g)} + \frac{1}{2} \text{O}_2(g) = \text{CO}_2(g) \]  \hspace{2cm} (5.3)

\[ \Delta G^o_{(5.3)} = -280,900 + 85.2T \text{J} \times \text{mole}^{-1} \]  \hspace{2cm} (5.4)

The oxygen partial pressure can be set and altered by adjusting the ratio of CO/CO₂.

In a part of this work it was necessary to set a very low oxygen potential without having any carbon present in the system. This prevented the use of the C/CO equilibrium. Instead the Cu/Cu₂O equilibrium was used. The gas was passed over a heated mixture of Cu turnings and Cu₂O powder. The oxygen in the gas phase would react with the mixture and the equilibrium would be established according to Eq. (5.5):

\[ 2\text{Cu(s)} + \frac{1}{2} \text{O}_2(g) = \text{Cu}_2\text{O}(s) \]  \hspace{2cm} (5.5)

\[ \Delta G^o_{(5.5)} = -168,400 + 71.3T \text{J} \times \text{mole}^{-1} \]  \hspace{2cm} (5.6)

The oxygen partial pressure could be set and controlled with the temperature of the Cu+Cu₂O mixture.

In the oxidation experiments very high oxygen pressures were necessary i.e. up to 1 atm. In this case no reaction was needed to control the oxygen partial pressure, instead a gas mixture of Ar–O₂ or pure O₂ gas was used. The partial pressure of oxygen was adjusted by altering the fraction of O₂ in the gas.
5.2 Sulfide Capacity Measurements

The equipment used in these measurements is schematically depicted in Figure 5–1. The setup consisted of a graphite resistance heating element furnace together with an alumina reaction tube. The reaction tube was directly connected to the water cooled quenching chamber on top and a water cooled cap on the bottom. The reaction chamber was completely sealed off against the heating element chamber and the surroundings by the use of O–rings. The reaction gas entered the bottom of the furnace and exited on the top. An additional quenching gas inlet was located in the lower part of the quenching chamber. A suspension rod connected to a hydraulic lifting system was used to hold and position the samples in the hot zone of the furnace. The holding crucible could hold up to six samples. The furnace temperature was controlled by an Eurotherm controller together with an optical pyrometer (Raytek Thermoalert ET). An alumina sheathed thermocouple of type B (6% Rh–30%Rh) was used for precisely measuring the equilibration temperature. The tip of the thermocouple was positioned just below the bottom of the holding crucible. A gas train consisting of digital gas flow meters (Bronkhorst ±0.5%) was connected to a mixing column containing silica beads, which was connected directly to the gas inlet.
5.2.1 Materials Preparation

A detailed description of the materials preparation and experimental procedure is given in Supplement 1 and 2. Here a brief description is given. Powders of Al$_2$O$_3$, CaO, MgO and SiO$_2$ were calcined at 1173 K for 10 hours. Each slag was mixed individually from the pure oxide powders. Each sample was prepared by mixing pure Cu and Cu$_2$S powders. The mixture was placed in the bottom of the molybdenum crucible and the mixed slag was placed on top. The samples were inserted in the molybdenum holding crucible. In some measurements a graphite holding crucible was used. An alumina spacer was used to prevent direct contact between the sample crucibles from the graphite.
5.2.2 Experimental Procedure

The holding crucible was inserted in the furnace and lowered to the hot zone of the furnace. The furnace was completely sealed and the reaction chamber was evacuated for at least 30 min. The reaction chamber was refilled with the reaction gas and the furnace was heated with 1.5–2 K·min⁻¹. The samples were held at the equilibration temperature for 24 h before they were quickly withdrawn to the quenching chamber by the lifting system. Directly after, a high flow of quenching gas (Ar) was commenced (the whole procedure took less than 3 seconds). The samples were taken out after cooling and great care was taken to completely separate the slag and Cu from each other and the crucible walls prior to sending for analysis.

5.3 Nitrogen Solubility Measurements

In large the experimental equipment used for these measurements were the same as in the sulfide capacity measurements. Therefore, only a brief description is given here. An in detail description of the experimental setup can be found in Supplement 3 and 4. A schematic overview of the experimental setup is given in Figure 5–2. In this setup the furnace temperature was controlled by an Eurotherm controlled together with a Type B (6% Rh–30% Rh) thermocouple with the tip located in a gap of the heating element.

A gas train, providing the reaction gas, was directly connected to the inlet of the reaction tube. Digital gas flow meters (Bronkhorst ±0.5%) were used to control the gas flow of each gas. A gas mixer filled with silica beads was used for mixing the gases. The gas mixer was directly connected to two serially connected gas columns. Each gas column held a mixture of Cu and Cu₂O and consisted of a quartz tube wrapped in heating tape and insulation material. The temperature of the gas columns were controlled separately by PID temperature controllers together with Type K thermocouples. The thermocouple of gas column A was located externally of the tube at the top of the Cu–Cu₂O mixture. The thermocouple of gas column B was located internally of the tube with the tip just above the top of the Cu–Cu₂O mixture. Both of the tubes were sealed gas tight.

In some measurements the C/CO equilibrium was employed to control the oxygen partial pressure. In this cases it was not necessary to use the gas columns, so they were bypassed.
5.3.1 Control of Nitrogen Potential

In these measurements it was desirable to also set a nitrogen potential in the system. This was done by supplying a reaction gas containing a high fraction (>20%) of nitrogen.

5.3.2 Materials Preparation

Each slag was mixed individually from the pure oxide powders Al₂O₃, CaO, MgO and SiO₂. These oxides were calcinated at 1173 K for at least 10 h before use. The mixed slag was put in a molybdenum or graphite crucible. Three to six samples were placed in the holding crucible (of the same material as the sample crucible).
5.3.3 Experimental Procedure

The holding crucible was inserted in the furnace and lowered to the hot zone. The reaction chamber was sealed and evacuated for at least 30 min. The system was back filled with either N\textsubscript{2} or Ar gas and the columns were heated up. The gas was switched to the reaction gas mixture and the furnace was heated with a ramp speed of 2 K·min\textsuperscript{−1}. The samples were kept at the equilibration temperature (1873 K) for 48 h before they were quickly raised to the quenching chamber by the lift; and the gas flow rate was increased to 1 l·min\textsuperscript{−1}. After the experiment the slags were taken out and great care was taken in order to completely separate the slag from the crucible wall.

5.3.4 Industrial trials

The industrial trials were carried out at the SSAB plant located in Oxelösund, which is an integrated mill producing high quality slabs. After the steel is tapped into the ladle, alloying elements and a highly basic slag are added. The steel is then stirred and deoxidized at a stirring station. The slag is removed and a second synthetic slag is added. Thereafter vacuum degassing is carried out. The normal vacuum degassing time is about 25 min. Before the steel is casted, there is a waiting time of normally 20 min where argon with a low flow rate (about 60 l·min\textsuperscript{−1}) is used to stir the melt. The steel is thereafter sent for continuous casting into slabs.

Samples were taken from the steel before vacuum degassing, after vacuum degassing and after the waiting time just before the steel is sent for casting. In such a way the nitrogen content can be traced during the process. Samples of the slag were also taken after the vacuum treatment. All samples were taken using a Heraeus dual thickness sampler with an automatic sampling device.
5.4 Oxidation Measurements

A schematic drawing illustrating the experimental setup used for these measurements is depicted in Figure 5–3. The setup consisted of a resistance furnace with Kanthal heating elements together with an alumina reaction tube. The tube was directly connected to a water cooled quenching chamber on top and a water cooled cap on the bottom. The reaction chamber was completely sealed off to the surroundings by the use of O–rings. The reaction gas entered in the top of the furnace and exited from the bottom. A suspension rod was used to place and hold the samples in the hot zone. A Eurotherm controller together with a thermocouple of Type B (6% Rh–30%Rh) was used to set and maintain the furnace temperature. The even temperature hot zone of the furnace (±2 K) was 5 cm. An alumina sheathed internal thermocouple, Type B, was used for precise control of the experimental temperature. The tip of the thermocouple was placed just below the bottom of the sample. The gas flow of each gas was adjusted precisely using individual Bronkhorst (±0.5%) flow meters.

A special holding crucible was prepared in order to withstand the highly oxidizing atmosphere. An Al₂O₃ crucible was used to hold the sample crucible (see inset of Figure 5–3). In this 24 holes were drilled (3 mm in diameter) in order to ease the gas flow around the sample. This was held by platinum wires connected to the suspension rod.
5.4.1 Materials Preparation

Industrial slag taken from production was used in these measurements. A large amount of slag (around 2 kg) was collected subsequent to the vacuum degassing, after desulfurization had been made. The slag composition is given in Table 5–1. The minor components were less than 1 mass%. The slag was crushed in to powder and divided in to larger pieces (1–3) mm and powder of 180–250 μm in size. Crushed slag was placed in an alumina or magnesia crucible. Three different crucibles were used, their dimensions are listed in Table 5–2. In the case of alumina crucible 9.5 g of slag was used, in the magnesia crucible 6 g of slag was used. In the measurements where the slag was mostly liquid (1673 K) either a mixture of larger pieces and powder or only powder was used. In the lower temperature measurements (1373–1573 K) larger pieces and powder were used separately.
Table 5–1. Chemical composition of the slag taken in industry.

<table>
<thead>
<tr>
<th>Slag composition (mass%)</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SiO₂</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>29.3</td>
<td>54.0</td>
<td>7.3</td>
<td>6.9</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 5–2. Dimensions and materials of the crucibles used

<table>
<thead>
<tr>
<th>Material</th>
<th>Inner diameter (mm)</th>
<th>Inner height (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>25</td>
<td>14</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>20</td>
<td>14</td>
</tr>
<tr>
<td>MgO</td>
<td>20</td>
<td>14</td>
</tr>
</tbody>
</table>

5.4.2 Experimental Procedure

Each experiment was carried out in a similar manner. The sample was placed in the holding crucible and held in the cooling chamber. The furnace was sealed, evacuated for 30 min and refilled with Ar gas. The furnace was heated up to the experimental temperature with a ramp rate of 2 K·min⁻¹. During the heating a low flow (0.05 l·min⁻¹) of Ar was used. The sample was slowly lowered in to the hot zone, in order to avoid thermal shock of the alumina tube. This procedure took approximately 15 min. The sample was then held in the hot zone for 15 min before switching to the reaction gas. In one experiment a prolonged heating time was used (120 min) to investigate the effect of the holding time. The reaction gas consisted of O₂ or O₂–N₂ gas mixture with a total gas flow rate of 0.6–0.8 l·min⁻¹. After a reaction time of 30–120 min the sample was quickly manually raised to the quenching chamber and a high Ar gas flow rate of 0.7 l·min⁻¹ was used to quickly quench the sample. The slag was carefully removed from the crucible and sent for analysis.
5.5 Chemical Analyses

It was necessary to employ several analysis methods in the present work. The different analyses used are described below.

5.5.1 Slag Composition

Slag compositions were in some cases determined subsequent to the experiment by X–ray fluorescence (XRF). The relative uncertainty of this technique is ±5%. This analysis was carried out for all slags that were contained in graphite crucible. This was necessary since it was found in these slags that the MgO content became very low. This could be due to the reduction of MgO by carbon to gaseous Mg.

For the oxidation experiments all slags were also analyzed by this method after the experiments. This was done since the slags needed to be contained in oxide crucible (because of the very high oxygen potential) and some dissolution of the crucible wall occurred.

In the other measurements where Mo crucible was used it was not necessary to analyze each slag, since the composition changed very little. This was confirmed by analyzing a couple of slags from each set of experiments.

5.5.2 Sulfur and Carbon

Sulfur and carbon were determined by a combustion method. The sulfur content was determined with a LECO CS–600 instrument and carbon was analyzed with a LECO TCH–600 instrument.

The slag structure and sulfur distribution in some slags were investigated with a scanning electron microscope (SEM) equipped energy–dispersive X–ray spectroscopy.
5.5.3 Nitrogen

The situation of nitrogen in the slag turned out to be quite complex, and several analysis methods needed to be employed.

Nitrogen in slag, and metal, can be analyzed by combustion method similar as for sulfur and carbon. This technique was used for analyzing the total nitrogen content with a LECO TCH–600 equipment. This method was sufficient for analyzing the slags that had been contained in graphite crucibles. However, this technique was not accurate for determining the nitrogen contents in the remaining slag samples. The nitrogen content of these samples were well below the detection limit of nitrogen in slag for this technique (20 ppm). When analyzing steel the detection limit for this technique is much lower (1 ppm), which was sufficient for analyzing the steel samples.

In order to analyze the very low nitrogen content in slag a newly developed wet chemistry technique with an ultra–low detection limit (0.01 ppm) was used. This method is a combination of the “Kjeldahl” method and an Ag⁺ ion complexion method. A detailed description of the method and procedure for this analysis is included in Supplement 3.

Analysis of the cyanide content of some slags were conducted. This was done by a wet chemistry method. The full description of this method and procedure is included in Supplement 4. Due to the importance of analyzing the cyanide content and in the view of the accuracy of wet chemistry analysis some samples were checked at another laboratory using a similar technique.

6 RESULTS

6.1 Sulfide Capacity Measurements

Slags were equilibrated with liquid copper at 1823 K and 1873 K for 24 h under controlled oxygen partial pressures. According to the phase diagrams Al₂O₃–CaO–MgO–SiO₂ and the Al₂O₃–CaO–SiO₂–“V₂O₃” all compositions were completely liquid at the equilibration temperatures [53–55].
The experimental results and conditions are summarized in Table A–1 and Table A–2 in appendix A. Several oxygen partial pressures were used. In the first part of measurements, included in Table A–1, a 98.3% CO – 1.7% CO₂ mixture was used to set an oxygen partial pressure of $1.9 \times 10^{-11}$ atm at 1823 K and an 99% CO – 1% CO₂ mixture to set an oxygen partial pressure of $1.7 \times 10^{-11}$ atm at 1873 K. In the remaining measurements, included in Table A–2, three different oxygen partial pressures were used. An 93% CO – 7% CO₂ was used to set an oxygen pressure of $9.7 \times 10^{-10}$ atm, an 99.5% CO – 0.5% CO₂ to set an oxygen pressure of $4.3 \times 10^{-12}$ atm and pure CO gas in combination with a graphite sample holder was used to set an oxygen partial pressure of $4.6 \times 10^{-16}$ atm, all at 1873 K.

The equilibrium sulfur contents in the copper and slag are the directly analyzed values. The slags listed in Table A–1 are the weigh–in compositions. Some selected samples were also analyzed for their final compositions, for these samples both the initial and final compositions are listed. The analyzed compositions have been normalized. All samples included in Table A–2 were analyzed for their final slag compositions and the normalized values are listed in the table. The sulfide capacities based on the experimental data are also included in the tables.

### 6.2 Nitrogen Solubility Measurements

Nitrogen solubilities in slags were measured with a gas–slag equilibrium at 1873 K under controlled nitrogen and oxygen partial pressures. The equilibration time was 48 h. The slag compositions were completely liquid according to the CaO–MgO–SiO₂ and Al₂O₃–CaO–MgO–SiO₂ phase diagrams [53].

The measurements were both carried out with and without the presence of carbon, to investigate the effect of the same. The results of the carbon free measurements are listed in Table A–3 and Table A–4. These slags were contained in molybdenum crucibles and a pure N₂ or an N₂–Ar gas mixture was passed through the Cu/Cu₂O mixture at 760 or 770 K to set the oxygen partial pressure to $2 \times 10^{-16}$ or $4 \times 10^{-16}$ atm respectively. The compositions given in the tables are the weigh in compositions except for the nitrogen contents. Some slag samples included in Table A–3 were also analyzed by the combustion method additionally to the wet chemistry analysis. The results of this analysis indicates that the nitrogen content was below the detection limit (20 ppm) for this technique. Except for a few slags, the nitrogen contents from the wet chemistry analysis are below 1 ppm which would well explain why nitrogen could not be detected by the combustion method.
The nitride capacity was calculated based on the experimental results and is also included in Table A–3.

The samples included in Table A–4 were all analyzed for the total nitrogen content by the combustion method. The nitrogen contents in these slags were below the detection limit for this technique as well. Since the primary interest of these samples was to investigate the effect of carbon on the nitrogen solubility, no additional efforts were made in order to precisely determine the nitrogen contents.

In Table A–5 the results of the measurements with carbon are presented. Slags were contained in graphite crucibles and subjected to an atmosphere of 80% CO – 20% N₂ to set the oxygen partial pressure to 2.9×10⁻¹⁶ atm at 1873 K. The equilibrium contents of nitrogen and carbon are listed. The normalized slag compositions are also included in the table. In the Al₂O₃–CaO–MgO–SiO₂ system the MgO content became very low after the experiments. The loss could be due to the reduction of MgO by carbon.

A fairly large amount of industrial trials were carried out. The results of these trials can be divided in to three general groups. The relative change of nitrogen content in the steel is plotted against the process time in Figure 6–1a–c. The first group is plotted in Figure 6–1a, where a decrease of nitrogen is seen both during the vacuum degassing and the waiting time. The second group, presented in Figure 6–2b, shows a decrease during the vacuum treatment followed by an increase of nitrogen during the waiting time. The last group is shown in Figure 6–1c. An increase of nitrogen was observed both during the vacuum treatment and waiting time. The chemical compositions of the ladle slags are listed in Table A–6. The corresponding changes of nitrogen in the steel are also included. Only the results of the third group (Figure 6–1c) are included, since the total nitrogen content increased in these heats.
Figure 6–1. Results from industrial trials. Normalized nitrogen content in steel as function of process time before vacuum, after vacuum, and after waiting time.

Three different trends showing a) nitrogen content decreased both during vacuum period and waiting time, b) nitrogen content decreased during vacuum period but increased during waiting time, and c) nitrogen content increased both during vacuum period and waiting time.
6.3 Oxidation Measurements

Oxidation experiments were conducted with used ladle slag collected from industry. Slag samples were subjected to pure O₂ or an O₂–N₂ gas mixture at temperatures ranging 1373–1673 K. Gas flow rates of 0.6 and 0.8 l·min⁻¹ were used. The experimental conditions are listed in Table A–7 and the final slag compositions are listed in Table A–8.

In order to describe the sulfur removal, the degree of sulfur removal was defined, \( R_S \). The definition of \( R_S \) is given in Eq. (6.1). The experimentally obtained \( R_S \) are also included in Table A–7.

\[
R_S = \frac{(\text{mass\% } S)_{\text{Initial}} - (\text{mass\% } S)_{\text{Final}}}{(\text{mass\% } S)_{\text{Initial}}} \times 100
\]  

(6.1)

7 DISCUSSION

7.1 Sulfide Capacity

The sulfide capacity was calculated according to Eq. (3.7) where the following reaction was considered for the dissolution of sulfur in liquid copper:

\[
\frac{1}{2} S_2(g) = S_{(1 \text{ mass\% in Cu})}
\]  

(7.1)

\[
\Delta G^{\circ}_{(7.1)} = -120,000 + 25.2 T J \times \text{mole}^{-1} [2]
\]  

(7.2)

The activity coefficient of sulfur in liquid copper was calculated by extrapolating the data given by Sigworth and Elliott to the present experimental temperatures [56].

7.1.1 Sulfide Capacity in Ladle Slag

The sulfide capacities are plotted in the Al₂O₃(30 mass\%)–CaO–MgO–SiO₂ section in Figure 7–1 and in the Al₂O₃(35 mass\%)–CaO–MgO–SiO₂ section in Figure 7–2. Both the results at 1823 K and 1873 K are included in the figures. Some identical compositions were studied at both temperatures, the value at 1823 K is then given in parenthesis. Some compositions were also repeated which are indicated by an asterisk. In these cases the average sulfide capacity is given.
Figure 7–1. Sulfide capacities against composition in the $\text{Al}_2\text{O}_3(30 \text{ mass}\%)$–CaO–MgO–SiO$_2$ diagram. The experimental points given are $C_S \times 10^3$.

Figure 7–2. Sulfide capacities against composition in the $\text{Al}_2\text{O}_3(35 \text{ mass}\%)$–CaO–MgO–SiO$_2$ diagram. The experimental points given are $C_S \times 10^3$. Values given in parenthesis represents measurements made at 1823 K.
Both figures reveals that $C_S$ increases towards the CaO rich corner. This is expected according to Eq. (3.1) since an increase in the fraction of CaO will also increase the amount of free oxygen ions, $O^{2-}$. This will push the reaction in Eq. (3.1) to the right hand side, thus increasing the sulfur concentration in the slag. It is also noticed that MgO increases $C_S$, when replacing SiO$_2$. The effect of MgO is less profound compared to CaO, reflecting calcium’s higher affinity to sulfur. The same behavior have been found in the CaO–SiO$_2$ and MgO–SiO$_2$ systems. Sharma and Richardson reported that the $C_S$ was about half for the MgO–SiO$_2$ system compared to the CaO–SiO$_2$ system [57].

The effect of Al$_2$O$_3$ can be observed by comparing the two figures. It would be helpful to also plot the results in the hypothetical Al$_2$O$_3$–(CaO+MgO)–SiO$_2$ phase diagram. Even though CaO and MgO does not behave identically, the diagram is still useful for investigating the effect of Al$_2$O$_3$ with respect to SiO$_2$ and the basic oxides. $C_S$ is plotted in this phase diagram in Figure 7–3. When Al$_2$O$_3$ replaces SiO$_2$ and the fraction of basic components is kept constant, $C_S$ changes very little. This strongly indicates that Al$_2$O$_3$ acts as an acid for the present slag compositions.

![Figure 7–3. Sulfide capacities against composition in the hypothetical Al$_2$O$_3$–(CaO+MgO)–SiO$_2$ diagram. The experimental points given are $C_S \times 10^3$. Values given in parenthesis represents measurements made at 1823 K.](image)
From the above observations it is clear that the basic oxides increases $C_S$ while the acidic components decreases the same. The overall slag composition can roughly be expressed using the concept of slag basicity [58]. This is a convenient way of comparing slag compositions, and is frequently used in the industry. In the present work the extended basicity including the four oxides $\text{Al}_2\text{O}_3$, $\text{CaO}$, $\text{MgO}$ and $\text{SiO}_2$ was used. $C_S$ at 1873 K is plotted against the extended basicity in Figure 7–4. An approximate linear relationship is observed, where $C_S$ increases with the basicity.

![Graph showing the relationship between $C_S$ and the extended basicity](image)

Figure 7–4. Sulfide capacities against the extended basicity at 1873 K.

Ohta et al. also measured sulfide capacities in the same quaternary systems with compositions close to the present ones [14]. These authors also employed the copper–slag equilibrium. Their values are slightly lower compared to what was found in the present work. It was noticed that different sets of thermodynamical data was used for calculating $C_S$. A recalculation of the data by Ohta et al. using the same data as the present study increased the calculated $C_S$ by 10 to 20%. This brings the two studies closer together, although it does not account for the whole difference between the studies. The recalculated data of these authors are also included in Figure 7–1 and 7–2. The compositions were normalized to 30 and 35 mass% $\text{Al}_2\text{O}_3$ respectively. Although there is a difference among the studies, it can be seen that they are in reasonable agreement with each other.
The effect of temperature was also investigated. In Figure 7–2 the results at both temperatures are included. \( C_S \) is strongly dependent on temperature, the capacity is roughly increased by 50% when the temperature is increased by 50 K, from 1823 K.

It would be interesting to relate the present results with the industrial situation. This can easily be done by considering the sulfur distribution ratio (Eq. (3.8)). If the sulfide capacity is known, the theoretical \( L_S \) can be calculated according to Eq. (3.7) which can be compared with the real industrial value. Another approach is to calculate the theoretical sulfur concentration in the slag. This can be done if the sulfur concentration in the metal is also known. This approach was used to relate the present results with the industrial situation. Slag was taken right after the vacuum treatment in the OVAKO Hofors steelmaking plant. The slag composition is listed in Table 5–1, the sulfur concentration was 2.5 mass%. This slag was very close to the sample SC–6 and it can be assumed that \( C_S \) is the same for both slags. A sample of the steel was also taken at the same occasion. The sulfur concentration in the steel was 0.005 mass%.

The following reactions were considered for the dissolution of oxygen and sulfur in liquid iron respectively.

\[
\frac{1}{2} \text{O}_2(g) = \text{O}_{(\text{1 mass\% in Fe})} \quad (7.3)
\]

\[
\Delta G^{o}_{(7.3)} = 117,000 - 2.89T \text{J\times mole}^{-1} [2] \quad (7.4)
\]

\[
\frac{1}{2} \text{S}_2(g) = \text{S}_{(\text{1 mass\% in Fe})} \quad (7.5)
\]

\[
\Delta G^{o}_{(7.5)} = -135,100 + 23.4T \text{J\times mole}^{-1} [2] \quad (7.6)
\]

The equilibrium constants for Eq. (7.3) and Eq. (7.5) can be written as:

\[
K_{(7.3)} = \frac{a_{\text{O}_{(\text{Fe})}}^{1/2}}{p_{\text{O}_2}^{1/2}} = \frac{f_{\text{O}_{(\text{Fe})}} \times [\text{mass\%O}]_{\text{Fe}}^{1/2}}{p_{\text{O}_2}^{1/2}} \quad (7.7)
\]

and

\[
K_{(7.5)} = \frac{a_{\text{S}_{(\text{Fe})}}^{1/2}}{p_{\text{S}_2}^{1/2}} = \frac{f_{\text{S}_{(\text{Fe})}} \times [\text{mass\%S}]_{\text{Fe}}^{1/2}}{p_{\text{S}_2}^{1/2}} \quad (7.8)
\]
The theoretical sulfur concentration in the slag was calculated at 1873 K by combining Eq. (3.4) with the equations (7.7) and (7.8). The activity coefficient of sulfur in liquid iron was assumed to be unity due to the low sulfur concentration in the steel. After the vacuum treatment the activity of dissolved oxygen would be around 1 ppm. This gives a theoretical sulfur concentration in the slag of 1.9 mass%, which is in reasonable agreement with the actual concentration of 2.5 mass%. It should be mentioned that this is a simple calculation and it cannot fully incorporate the complexity of the industrial operation. Nevertheless, the calculation is useful for a general indication.

It would be interesting to also compare the results to other available data. As have been mentioned earlier, only the data by Ohta et al. is of interest for this comparison [14]. No identical composition could be found, instead a \( C_S \) value was obtained by interpolating the data and choosing a value for at the same extended basicity as the industrial slag (approximately 1.7). This gives a lower theoretical sulfur concentration than the present study, approximately half. This is further away from the industrial situation, approximately one third of the actual concentration.

Several models have been developed in order to predict sulfide capacities. In fact, one of those models were developed here at the Material Science Department, commonly referred to as the KTH–model [59, 60]. It is expected that the lack of data would affect the model prediction, since all models are semi–empirical in nature. A comparison with the experimental data would be of interest. Since this comparison is to illustrate lack of experimental data on the quality of model prediction, other established models will not be addressed. The sulfide capacity was calculated using the KTH model at 1873 K for a slag containing 30 mass% \( \text{Al}_2\text{O}_3 \), 55 mass% \( \text{CaO} \), 8 mass% \( \text{MgO} \) and 7 mass %\( \text{SiO}_2 \). This is close to the industrial slag and identical to the slag in sample SC–6. The predicted sulfide capacity by the model is \( 2.4\times10^{-4} \). This is much lower than the present results, about 1/20 of that of SC–6. This gives a theoretical sulfur content in the slag of 0.09 mass%, which is about 1/25 of the actual concentration. This is impossible to compare with the industrial situation.
A large amount of sulfide capacity data was measured by Nzotta and his co–workers in order to optimize the model parameters [4]. Note that no measurements were made for typical ladle slag compositions. Although, the lack of data is expected to be the main cause for the poor model prediction, experimental uncertainties could be affecting as well. It was noticed that in general, the sulfide capacity data in these studies was lower compared to other researchers. If a small leak is present during the equilibration it would be resulting in a higher oxygen pressure and lower sulfur pressure. Both of these will decrease the calculated values. This could be a contributing factor to the poor model prediction.

7.1.2 Sulfide Capacity for Slags Containing Multivalent Species

As mentioned earlier, the sulfide capacity concept have been widely adopted by industry and academia because of its usefulness and practical importance for iron–and steelmaking. Richardson and Fincham found that $C_S$ was independent of oxygen potential (below approximately $10^{-6}$ atm) in the CaO–Al$_2$O$_3$, CaO–SiO$_2$ and CaO–Al$_2$O$_3$–SiO$_2$ systems. This is of considerable convenience since it gives freedom when conducting experiments. Additionally, experiments only needs to be conducted under one controlled atmosphere since $C_S$ can be used in calculations over a large range of oxygen partial pressures. This assumption have been widely adopted and as a result experiments have been carried out over a large range of oxygen partial pressures ($10^{-14}$–$10^{-6}$ atm) [3].

From Eq. (3.4) it can be seen that the precondition when using the sulfide capacity is that the quantity $\frac{a_{O^2-}}{f_{S^{2-}}}$ is independent of the oxygen potential. When the sulfur concentration in the slag is low, the activity coefficient of sulfur, $f_{S^{2-}}$, is expected to be nearly constant. This will remain constant, or change very little, as long as the sulfur potential is not greatly increased. In slag systems where only single valence cations are present such as Al$^{3+}$, Ca$^{2+}$, Mg$^{2+}$, the dependence of $a_{O^2-}$ on the oxygen pressure could be considered negligible over some oxygen pressure range. Examples of such systems are CaO–Al$_2$O$_3$, CaO–SiO$_2$, CaO–Al$_2$O$_3$–SiO$_2$ or even higher order systems. Below a certain oxygen partial pressure one or several of the oxides will be reduced. $C_S$ is then no longer applicable. Since most of the oxide components (e.g. Al$_2$O$_3$, CaO, MgO and SiO$_2$) are stable under the prevailing oxygen partial pressures in steelmaking reactors the use of $C_S$ is very successful.
However, this assumption may not hold for all slag systems. In systems containing multivalent elements such as Fe, Cr, V etc. the situation is more complex. These elements can adopt several valence states in the slag depending on the oxygen potential. For example, in slags containing vanadium oxide it has been found that vanadium can be present as $\text{V}^{2+}$, $\text{V}^{3+}$, $\text{V}^{4+}$ and $\text{V}^{5+}$. Several of these valence states can co-exist in the slag [61, 62]. The fraction of valence states will vary with the oxygen pressure. It is likely that this also would affect $a_{O^{2-}}$.

To elaborate this aspect, a silicate slag containing vanadium oxide is taken as example (i.e. the slag used in this work). At a low oxygen pressure the majority of vanadium ions will be present as $\text{V}^{2+}$. If the oxygen pressure is increased the vanadium ions will adopt higher valence states. If the oxygen pressure is increased substantially the majority of vanadium ions will instead be present as $\text{V}^{5+}$. This will affect the surrounding slag structure, since the slag needs to retain electric charge balance. The increased charge of vanadium needs to be compensated, which can happen either by the breakage of the Si–O bonds or by dissolution of $\text{O}^{2-}$. Both of these mechanisms could occur depending on the nature of the slag. This structural change would also affect $a_{O^{2-}}$ especially if considerable amounts of $\text{O}^{2-}$ are dissolved. When $a_{O^{2-}}$ is changing with oxygen pressure, the assumption that $f_{S^{2-}}$ is constant may not be true anymore. It is expected that the quantity $a_{O^{2-}}/f_{S^{2-}}$ would be a function of oxygen pressure in this kind of slags. If this is the case, $C_S$ cannot be considered independent of the oxygen potential.

The vanadium oxide containing slag was used for experimentally investigating this aspect. $C_S$ based on the experimental data, is plotted against the oxygen partial pressure in Figure 7–5. The figure clearly shows the dependence of $C_S$ on oxygen pressure in this slag. Note that the change of $C_S$ due to the change of oxygen pressure is much greater than the effect of slag composition. The trend in Figure 7–5 viz. the increase of $C_S$ with the increasing oxygen partial pressure also make sense. A higher oxygen partial pressure is expected to increase the concentration of $\text{O}^{2-}$ ions, which would push the reaction in Eq. (3.1) to the right hand side.
Figure 7–5. Experimental obtained sulfide capacities against the oxygen partial pressure at 1873 K.

The principle as discussed above would also apply to other slag systems containing multivalent species such as Fe, Cr and Ti. Slags containing these elements are more commonly found in steelmaking operations. Unfortunately, due to the experimental difficulties it was not possible to achieve reliable results with slags containing these oxides for a comparison. It is expected that the oxygen pressure will have a great impact on the fractions of e.g. Fe\(^{2+}\) and Fe\(^{3+}\). One would further expect that \(C_S\) will vary with the oxygen potential in these systems as well. Unfortunately, none of the earlier studies brought up such discussion [1, 4, 7, 9, 10, 12, 15–23]. There is in general a large difference between the oxygen potential that were used in the measurements and what is common in steelmaking operations. In the ladle and blast furnace the oxygen level is typically 1–5 ppm (corresponding to \(p_{O_2}\) about \(10^{-15}–10^{-13.5}\) at 1873 K) and 1000 ppm in the converter (corresponding to \(p_{O_2}\) about \(10^{-9}\) atm at 1873 K). This is to be compared with the oxygen pressures (\(10^{-11}–10^{-5}\) atm) used for the earlier measurements.
To elaborate the present discussion a calculation was made for a system containing iron oxide. A CaO(27 mass%–SiO₂(40 mass%–FeO–Fe₂O₃ slag containing 0.1 mass% sulfur was used in the calculations. This composition is liquid over the whole oxygen pressure range of interest, and is close to one of the earlier works with “FeO” containing slags [16]. The calculation was made using the ThermoCalc software and the Fe-containing Slag Database [63, 64]. The calculated Fe²⁺/Fe³⁺ ratio at 1873 K is plotted against the oxygen partial pressure in Figure 7–6.

Figure 7–6. The calculated ratio of Fe²⁺/Fe³⁺ against oxygen partial pressure for a CaO(27 mass%–SiO₂(40 mass%–FeO–Fe₂O₃ slag at 1873 K.

The ratio of Fe²⁺/Fe³⁺ vary substantially in the slag over the oxygen pressure range. It is expected that this would also affect $C_S$ in this slag as well. This would indeed be of interest to study experimentally. The calculation strongly supports the present reasoning.
It is clear that the sulfide capacity is dependent on the oxygen potential when the slag contains multivalent elements. How strongly $C_S$ is affected by the oxygen partial pressure will be dependent on the multivalent element in the slag as well as the overall nature of the slag. The available data of $C_S$ for systems containing iron oxide, chromium oxide, titanium oxide etc. needs to be used with great caution. It is likely that the $C_S$ data is only valid under the conditions as was used in the laboratory measurements.

It should be mentioned that a serious attempt was made to study this aspect for a slag containing iron oxide. However, due to the experimental difficulties it was not possible to obtain reliable and reproducible results. The difficulties included finding a suitable crucible material that could hold both slag and metal over a large range of oxygen pressures; and the severe attack of iron oxide on the oxide crucibles. Instead the vanadium containing system was used, where reliable results could be achieved. The main purpose of this part of the work was to investigate the effect of oxygen potential on $C_S$, not reporting $C_S$ values for the present slag system. It should be mentioned that some crystals of vanadium sulfide was formed during the experiments. These were found in a thin layer (<300 µm) in the copper, near the copper–slag interface. This formation was found to increase with the vanadium oxide content and decreasing oxygen partial pressure. Great care was taken to completely remove this layer prior to the analysis. It is possible that a tiny fraction of sulfides were located in the bulk of the sample and could not be removed prior to the analysis. This would affect the analysis and as a consequence the calculated $C_S$ values. However, this would not change the order of magnitude of $C_S$ and not change the present discussion. To check the reproducibility a repeat run with identical conditions for one of the samples were made. In Table A–2 it can be seen by comparing SV–9 and SV–10 that the results are satisfactory reproducible.
7.2 Nitrogen Solubility

7.2.1 Effect of Carbon on Nitrogen Solubility

The nitrogen solubility was found to be extremely low in the slags free from carbon, as seen in Table A–3 and Table A–4. The wet chemistry analysis revealed that the nitrogen concentrations was below 1 ppm for the majority of the samples included in Table A–3. This is well below the detection limit of the combustion analysis technique. It is safe to assume that the nitrogen content in the slags included in Table A–4 are below the detection limit of this technique as well.

The very low nitrogen solubility was actually unexpected. The majority of previously published data reports substantially higher solubilities [35–47]. It should be pointed out that all of these measurements were carried out with graphite crucibles. Very low nitrogen concentrations, such as in Table A–3 and Table A–4, are only found in works where oxide or metallic crucibles were used [25–34]. It should be pointed out that this also correlates well with what was found in the industrial trials (Table A–6). Much higher nitrogen solubilities are observed for the slags that were contained in graphite crucibles. These results are listed in Table A–5. The same can be seen for both slag systems studied. This clearly shows that carbon increases the nitrogen solubility substantially. This was also briefly mentioned by Park et al. [44]. It is unlikely that the difference in nitrogen solubility would be due to differences in slag composition. When comparing sample NMo 5.2 in Table A–4 with NC 1.1 in Table A–5 it is seen that the nitrogen concentration is about 100 times higher in the latter, assuming a nitrogen content of 20 ppm in NMo 5.2. The actual nitrogen content may actually be much lower, as proposed by the results in Table A–3.

It is evident that carbon increases the nitrogen solubility in the slag. In order to understand the reason behind this substantial increase it is important to identify the species of nitrogen in the carbon saturated slag.
7.2.2 Investigation of Cyanide Formation

Several researchers have reported that nitrogen can form cyanide ions, \( \text{CN}^- \), in slag. This has been reported for several different slag systems \([36–40, 43–46]\). Formation of cyanide would be a plausible explanation for the increased nitrogen solubility when the slag is carbon saturated. In the present slags this would mean that virtually all nitrogen is in the form of cyanide. Although, this would be in conflict to the earlier data for the \( \text{Al}_2\text{O}_3–\text{CaO–SiO}_2 \) system \([39, 40]\). Cyanide was reported to only be a small fraction of the total nitrogen in this slag. If all nitrogen would be in the form of cyanide, a mass ratio between carbon and nitrogen of approximately 43/50 is required. If the ratio is lower than this criteria it means that there is not enough carbon present in the slag to form cyanide will all nitrogen. In Table A–5 less than one third of the slags fulfill this criteria, thus the large increase cannot be explained by cyanide formation alone.

To further investigate the presence of cyanide in the slag, wet chemistry analysis was used to selectively analyze the cyanide content. Two similar methods were used, the detailed descriptions are found in Supplement 4. These results are also included in Table A–5. Cyanide could not be detected by the first method. Low concentrations of cyanide was found by the second method, with considerable uncertainties as indicated in Table A–5. This uncertainty probably originates from the difficulty in analyzing cyanide in slags, something also encountered by Schwerdtfeger et al. \([37]\). They reported the irreproducibility of the analysis. Nevertheless, it can be concluded that cyanide is only present in very low concentrations for the present conditions. Formation of cyanide cannot account for all the dissolved nitrogen in the slags in Table A–5. Some other species containing nitrogen must be present in the slag.

The forms of nitrogen were preliminary investigated by X-ray photoelectron spectroscopy (XPS). Details of the analysis and a more in-depth discussion can be found in Supplement 4. The analysis contains considerable uncertainties and the following discussion should only be considered suggestive. Nitrogen associated with silicon and two forms of nitrogen combined with carbon were detected. One would expect that the nitrogen solubility would increase with \( \text{SiO}_2 \) fraction. As a matter of fact, this was observed as will be seen later on in this discussion. Martinez and Sano also reported of nitrogen connected to silicon \([35]\). They proposed that nitrogen joins the slag network, a possible principal reaction is given in Eq. (4.1).
Unfortunately, the mechanisms proposed by these authors does not include the role of carbon. A considerable amount of work will be needed to figure out the actual situation.

The present results are quite different than what has earlier been reported. It would be helpful to briefly discuss the differences between the present work and the previous ones. In most of the earlier works the focus is given more or less to the nitride capacity, Eq. (3.11). Nitride capacities have been reported by several researchers in different systems [25–47]. The majority of these works employed the “Kjeldahl” method or a modification of the same to analyze the nitrogen content [25–47, 39–41, 43, 45, 46]. In this method the slag is dissolved in a strong acid and the nitrogen is transferred to a solution. The nitrogen content of the solution is then determined. Actually, with this method the total nitrogen content is analyzed (cyanide escapes during the dissolution). It has been generally assumed that nitrogen dissolves as free nitride ions. As seen from the present results this might not be the case, and could lead to great misunderstandings when using Eq. (3.11).

7.2.3 Effect of Slag composition

Due to the significant difference in nitrogen solubility when the slag is free from carbon vs. saturated with carbon, the effect of slag composition will be treated separately for these two cases.

The nitrogen concentrations for the slag free from carbon (included in Table A–3) are plotted in the Al₂O₃–CaO–MgO(5 mass%)–SiO₂ section in Figure 7–7 and the Al₂O₃–CaO–MgO(10 mass%)–SiO₂ section in Figure 7–8. A general trend is observed where the nitrogen content increases towards the SiO₂–rich corner. This suggests that nitrogen is associated with silicon also when carbon is not present, however at much lower concentrations. By comparing the two figures it can be seen that nitrogen generally increases with MgO content.
Figure 7–7. Nitrogen contents against slag composition in the Al$_2$O$_3$–CaO–MgO(5 mass%)–SiO$_2$ diagram at 1873 K. Experimental points given are $10^4 \times$ mass%.

Figure 7–8. Nitrogen contents against slag composition in the Al$_2$O$_3$–CaO–MgO(10 mass%)–SiO$_2$ diagram at 1873 K. Experimental points given are $10^4 \times$ mass%.
The nitrogen contents in the carbon saturated quaternary Al₂O₃–CaO–MgO–SiO₂ system (Table A–5) are plotted against the molar fraction of SiO₂ in Figure 7–9. Due to the evaporation, the MgO content in these slags are very low. The nitrogen content increases with the fraction of SiO₂. This supports the reasoning that nitrogen would be associated with silicon in the melt. This trend also correlates with earlier data by Davies and Meherali, which are also included in the figure [42]. Even though there are differences in temperature (1823 K) and composition between the studies the trend is clear.

![Figure 7–9. Nitrogen content against the molar fraction of SiO₂ in the Al₂O₃–CaO–MgO–SiO₂ system at 1873 K. The slags were contained in graphite crucibles. Data by [42] is also included.](image)

The total nitrogen content is plotted against the molar fraction of MgO for the slags included in the CaO–MgO–SiO₂ system in Figure 7–10. This comparison is reasonable due to the narrow range of SiO₂ concentration in these slags. An overall trend where the nitrogen content is slightly increasing with MgO content is seen. Some of the data by Martinez and Sano were also included in the figure, with similar SiO₂ contents [35]. The reported data by these authors corresponds well with the present results, although their measurements were made at 1823 K.
Figure 7–10. Nitrogen content against the molar fraction of MgO in the CaO–MgO–SiO$_2$ system for two SiO$_2$ ranges. Slags were contained in graphite crucibles. Data by [35] is also included in the figure.

Interestingly, similar trends are observed both in the absence and presence of carbon, although the total contents are extremely different. Unfortunately, the trends observed cannot explain the large effect of carbon on the nitrogen solubility.

7.2.4 Nitrogen Pickup in Steel in the Ladle

In the industrial trials it was found that nitrogen sometimes increases in the melt during the waiting time (Figure 6–1b–c). A possible explanation would be that nitrogen is not completely removed from the system during the vacuum treatment, a considerable amount is captured by the slag. After the vacuum treatment when the gas flow is lowered, nitrogen is transferred back to the steel. This has been observed to be the case for hydrogen coming back to the steel [65]. The extremely low nitrogen solubility in combination with a simple mass balance evidently ruled out the slag of being the reason behind the nitrogen increase. The description of the calculation is included in Supplement 3. Another possibility would be that nitrogen enters the melt with the Ar gas. It is well known that there are often leaks present in large industrial gas distribution systems. If a leak is present some Ar would be lost, but more importantly some air would diffuse in to the Ar gas.
A carefully conducted industrial study could reveal if this is the reason for the nitrogen increases as seen in Figure 6–1b–c.

### 7.3 Oxidation of Sulfur from Slag

The degree of sulfur removal is plotted against the temperature in Figure 7–11. The sulfur removal is practically unchanged in the temperature range 1373–1573 K. However, when the temperature is increased to 1673 K the degree of sulfur removal is greatly increased. This can be explained by the fact that the slag is mostly liquid at 1673 K, while it is solid up to 1473 K and forms a two-phase mixture at 1573 K. It was found that the sulfur removal reaction is controlled by diffusion in the solid particles at these temperatures. This aspect is discussed in detail in Supplement 5. This indicate that it would be unsuitable to perform a sulfur removal process in the industry below 1573 K. This is in strong contrast compared to a recent publication by Hiraki et al. [50]. The large differences among the studies can be derived to the differences in experimental conditions.

![Figure 7–11. Degree of sulfur removal as function of temperature in the range 1373–1673 K, slags contained in Al₂O₃ crucibles.](image)
It was possible to remove the majority of sulfur at 1673 K, when the slag is mostly liquid. The sulfur in the bulk is transferred to the surface where reaction Eq. (3.14) can take place. Considering that sulfur also have the possibility to be oxidized to sulfate ions, according to Eq. (3.15), it is reasonable to expect that the desulfurization might be improved at lower oxygen partial pressures. This aspect was investigated by using an N2–O2 gas mixture. $R_S$ is plotted against the oxygen partial pressure in Figure 7–12. No substantial difference is seen among the partial pressures, the highest $R_S$ was achieved at 1 atm oxygen pressure. Since there is no large difference between the results at 1 atm compared to the lower pressures, air would be possible to be used for the sulfur removal as well. The subsequent experiments were carried out at 1 atm $O_2$ partial pressure. These results are somewhat different than the earlier works, however ladle slags have not been studied earlier [49, 51].

![Figure 7–12. Degree of sulfur removal against oxygen partial pressure at 1673 K, slags contained in $\text{Al}_2\text{O}_3$ crucible.](image)
The fact that $R_S$ increases with oxygen partial pressure indicates that sulfate is not formed in the melt under the present experimental conditions. Kobayashi et al. concluded that CaS is oxidized to CaO in air above 1223 K [66]. Pelton et al. did not detect any formation of sulfate or oxy–sulfide species within the bulk of the slag at any time [49].

The $R_S$ is plotted against reaction time in Figure 7–13. Both slags contained in Al$_2$O$_3$ and MgO crucibles are included in the figure. The sulfur removal rate decreases with the time, only a small amount of sulfur is removed when the reaction time is increased from 60 to 120 min. This decrease can be due to two factors; (i) the mass transfer of sulfur to the melt surface is decreased when the sulfur concentration is lowered, and (ii) the mass transport of SO$_2$ away from the surface is not sufficient enough. The equilibrium constant for the reaction in Eq. (3.14) can be written as:

$$K_{(3.14)} = \frac{a_{O^{2-}} \times p_{SO_2}}{a_{S^{2-}} \times p_{O_2}^{3/2}}$$

(7.9)

From the above equation it can be seen that when the sulfur concentration is decreased, a lower partial pressure of SO$_2$ is required for Eq. (3.14) to proceed to the right hand side. This would require a more efficient removal of SO$_2$ from the surface to the main gas stream. This mass transfer depends on (i) the gas flow rate, (ii) the slag surface area, and (iii) the distance from the slag surface to the edge of the crucible. The effect of gas flow rate was investigated and the results are included in Table A–7 (compare sample S–12 and S–13). No appreciable effect could be observed. Unfortunately, limitations of the experimental equipment prevented even higher gas flow rates to be used.
Figure 7–13 Indicates that long reaction times would be required for reducing the sulfur concentration to even lower levels. It is reasonable to expect that the sulfur removal rate can be greatly increased by (i) stirring the melt bath during the oxidation, and (ii) optimizing the mass transfer of SO₂ from the liquid surface to the main gas stream. In Figure 7–13 a difference in results can be seen between the two crucible materials used. The surface area of the slag in the Al₂O₃ crucible is about 50% larger than the MgO crucible. It is likely that the desulfurization would be dependent on the slag surface area since it is directly proportionate to the possible sites for Eq. (3.14) to take place. This was investigated using a smaller sized Al₂O₃ crucible (S–11) with the same inner diameter as the MgO crucibles. The final sulfur content of this samples was higher than the larger crucible size (S–8 and S–9 in Table A–8). There is evidently a large dependence on the surface area of the slag. The effect of surface area partly explains the difference seen in Figure 7–13.
It is also possible that the change of slag composition due to the dissolution of Al₂O₃ and MgO from the crucible wall would be a contributing factor to the difference in the figure. In Table A–8 it is seen that a considerable amount of Al₂O₃ was dissolved from the crucible (S–6 through S–11) wall compared to the original composition in Table 5–1. The dissolution of MgO was rather limited. The dissolution of Al₂O₃ would affect the sulfur removal in two ways. Firstly, the dissolved Al₂O₃ would dilute the slag with respect to sulfur. Secondly, the change in slag composition might affect the slag’s ability to release sulfur. The first aspect can be examined with a mass balance. The extent of the dilution and adjusted $R_S$ were calculated by assuming a constant CaO amount, the results of the calculation are listed in Table A–9. As seen in the table, the dilution does not affect $R_S$ to any large extent. The effect of Al₂O₃ on the sulfur removal was also investigated by using additions of Al₂O₃ to slags contained in MgO crucibles. The $R_S$ is plotted against the final Al₂O₃ content for these slags in Figure 7–14. It is seen that $R_S$ actually decreases with Al₂O₃ content which supports the above reasoning that the sulfur removal is greatly dependent on the surface area.

Figure 7–14. Degree of sulfur removal as a function of final Al₂O₃ content for slags contained in MgO crucibles at 1673 K.
7.3.1 Industrial Consideration

It would be of interest to briefly discuss the findings from an industrial perspective. It was possible to remove the majority of slag by oxidation at 1673 K. It is likely that the sulfur removal rate can be greatly increased if the slag is stirred simultaneously. Supplying gas with a high flow rate will also improve the sulfur removal since the produced gases are efficiently transported away. The most beneficial way to implement such an operation would be right after casting, when the slag is still in the ladle. Oxygen gas could be supplied via the porous plugs. It is likely that in some cases it would be harmful to reuse the desulfurized slag in the ladle. However, the slag can still be reused in earlier process steps such as the EAF.

It should be pointed out that during the sulfur removal from the slag sulfuriac gases, mainly SO₂, are produced. This needs also to be taken into consideration since these gases have a negative environmental impact. Measures in order to prevent emissions of such gases to the atmosphere needs to be taken.

8 SUMMARY AND CONCLUSIONS

In general the importance of well-defined experimental conditions became apparent through the course of the present work. In the nitrogen solubility measurements, the choice of crucible material had a crucial impact on the outcome of the experiments. In the case of sulfide capacity in slags containing multivalent elements, the sulfide capacity was found to be greatly affected by the oxygen partial pressure in the present slags. This effect was much greater than the effect of slag composition. Unfortunately, this aspect have been overlooked by previous researchers. The predicted sulfide capacity by the KTH-model was very far away from the industrial situation. In its current state the model cannot be used for predicting sulfide capacity data of ladle slags. The lack of data, or the possible errors in the measurements could be contributing factors for the poor prediction. Actually, it has been an important part of the present work to shine a light on some of these inconsistencies between the literature data and the industrial situation. Using the previous data without precaution might lead to considerable misunderstandings.
8.1 Sulfide Capacity

The sulfide capacity data of ladle slags were found to be in fair agreement with the industrial process norms. The sulfide capacity was found to increase with the basic components CaO and MgO, and decrease with the acidic components Al₂O₃ and SiO₂. A considerable effect of temperature was also observed. When the temperature was increased by 50 K from 1823 K, the sulfide capacity increased roughly 50%.

The dependence of sulfide capacity on oxygen potential, when the slag contains multivalent species, was investigated experimentally with a slag containing vanadium oxide. The experimental results showed a strong dependence on oxygen pressure for the present slag. This effect was found to be much stronger than the effect of slag composition. When the oxygen partial pressure was increased from $4.6 \times 10^{-16}$ atm to $9.7 \times 10^{-10}$ atm the sulfide capacity increased by more than two orders of magnitude.

This is explained by the fact that the valence of the vanadium ions will change with the oxygen partial pressure. The surrounding slag structure then needs to change, for the slag to retain electrical neutrality. The sulfide capacity cannot be assumed to be independent of oxygen potential, if the slag contains multivalent elements.

8.2 Nitrogen Solubility

Carbon was found to substantially increase the nitrogen solubility in the slags. When carbon is not present the solubility was found to be extremely low. This was also observed for the industrial slags. Chemical analysis revealed low concentrations of CN⁻ compared to the total nitrogen content in the carbon saturated slags. Formation of cyanide cannot explain the large effect of carbon, as proposed by some authors. The nitrogen solubility was found to increase with SiO₂ and MgO both when carbon was absent and present. The extremely low solubility of nitrogen ruled out the slag of being the reason for nitrogen increase in the ladle.

In general the situation of nitrogen in carbon saturated slags was found to be considerable more complex than previously known. It will take a great effort to find the actual forms of nitrogen. To find out how these species are accommodated in the slag will be an even greater endeavor.
8.3 Oxidation of Sulfur from Slag

Experiments were carried out to investigate the possibility of removing sulfur from used ladle slag by oxidation in the temperature range 1373–1573 K. The slag remained mostly solid up to 1573 K and the sulfur removal was found to be a slow process. Sulfur removal from solid slag is unsuitable for industrial practice.

At 1673 K the slag was mostly liquid, and the sulfur removal was considerably more effective. More than 85% of the sulfur was removed after 60 min of oxidation in an atmosphere of pure oxygen at 1 atm. The sulfur removal was improved with oxygen partial pressure and the highest degree of sulfur removal was achieved at 1 atm O$_2$. The sulfur removal rate was found to be dependent on the surface area, which suggest that the desulfurization can be improved by stirring the melt simultaneously and supply gas with a high gas flow rate.

The present results shows good promise on using an oxidation step for reusing slags in the industrial operation. Implementing such process would be a great improvement on reducing the necessary raw materials for producing steel.

8.4 Suggestions for Continued Research

During the course of the present work it became apparent that some areas would be interesting for further investigation, both from a scientific and industrial viewpoint. Below are some suggestions for continued research.

Sulfide capacities for steelmaking slags: Unfortunately, the prediction of $C_S$ for ladle slag with the KTH–model was poor. Implementation of complementary data for slag systems closer related to the compositions in the ladle could improve the model prediction. A detailed re–investigation of the data used for optimizing the model should be considered as well, since the data in some cases is much lower than by other authors, and could be a source of error.

Sulfide capacities for slags containing multivalent elements: It would be of interest to continue this work by experimentally investigating other systems. Systems found in steelmaking processes containing chromium oxides and iron oxides are of primary interest. This would increase the knowledge of multivalent species’ behavior in slags, and could also give some insight to the structure of oxide melts.
Nitrogen increase in the ladle: The present study ruled out the possibility of the slag being the reason for the nitrogen increase in the ladle. A plausible reason would be that nitrogen enters the melt with the Ar gas that is used for stirring. Industrial trials where this aspect is carefully investigated would be most valuable, since nitrogen is difficult to remove from the melt. If this would be the reason, it is likely that the performance of the vacuum degassing on nitrogen removal can be improved as well.

Nitrogen in slag, in the presence of carbon: As became apparent during this part of the work, the situation of nitrogen in carbon saturated slag is far more complex than was initially expected. A great effort will be required to find out which species of nitrogen that are actually present in the slag. How they are accommodated in the slag will be an even greater challenge. This would be very interesting from a scientific standpoint. Such information may primarily be of interest for other metallurgical processes where carbon is present in high concentrations, such as the metallurgical refining of silicon.

Sulfur removal from slag by oxidation: This is a rather new subject and not much research have been done. There is considerable work to implement and optimize such a process in the industry. It would be interesting to investigate the sulfur removal under simultaneous stirring as a continuing step.
REFERENCES


[64] Thermo–Calc Software Database Fe–containing Slag Database v3.2.

APPENDIX A

Tabulated Experimental Conditions and Results
Table A–1. Summarized experimental conditions with results and calculated sulfide capacities.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp. [K]</th>
<th>Slag composition (weighed in/analyzed)</th>
<th>Sulfur [mass%]</th>
<th>$C_{S} \times 10^{3}$</th>
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</thead>
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<td></td>
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<td>MgO</td>
</tr>
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<td>54</td>
<td>3</td>
</tr>
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<td>SC–3</td>
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<td>7</td>
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<td>45</td>
<td>8</td>
</tr>
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<td>55/54.0</td>
<td>8/7.5</td>
</tr>
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<td>55</td>
<td>8</td>
</tr>
<tr>
<td>SC–8</td>
<td>1873</td>
<td>30</td>
<td>55</td>
<td>8</td>
</tr>
<tr>
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<td>1873</td>
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<td>55/54.3</td>
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<td>1873</td>
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<td>SC–26</td>
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Table A–2. Summarized conditions and results from the experimental study.

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<th>Sample</th>
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<th>$p_{O_2}$ [atm]</th>
<th>Slag composition [mass%]</th>
<th>Sulfur [mass%]</th>
<th>$C_v \times 10^4$</th>
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<td>$SiO_2$</td>
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<td>25.2</td>
<td>58.6</td>
</tr>
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<td>$9.7 \times 10^{-10}$</td>
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</tr>
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<td>27.6</td>
<td>58.6</td>
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<td>9.3</td>
<td>24.2</td>
<td>58.8</td>
</tr>
<tr>
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<td>24.3</td>
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<td>25.1</td>
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Table A–3. Results from nitrogen solubility measurements in the Al₂O₃–CaO–MgO–SiO₂ at 1873 K. Mo crucibles were used.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Slag composition [mass%]</th>
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<th>Log $C_N$</th>
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<td>11</td>
<td>0.28(&lt;20)</td>
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<td>52</td>
<td>5</td>
<td>13</td>
<td>0.34(&lt;20)</td>
</tr>
<tr>
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<td>8</td>
<td>0.56(&lt;20)</td>
</tr>
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<td>6</td>
<td>5</td>
<td>0.34(&lt;20)</td>
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<td>7</td>
<td>0.43(&lt;20)</td>
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<td>12</td>
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<td>0.06(&lt;20)</td>
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<td>1</td>
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<td>5</td>
<td>0.64(&lt;20)</td>
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<td>0.32</td>
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Table A–4. Results from nitrogen solubility measurements in the CaO–MgO–SiO$_2$ at 1873 K. Mo crucibles were used.

<table>
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<tr>
<th>Sample</th>
<th>Reaction gas [atm]</th>
<th>$p_{O_2} \times 10^{16}$</th>
<th>$p_{N_2}$</th>
<th>$p_{Ar}$</th>
<th>Ingoing slag composition [mass%]</th>
<th>N×10$^4$ [mass%]</th>
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<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>CaO</td>
<td>MgO</td>
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<td></td>
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<td>9</td>
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<td>0.68</td>
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<td>0.68</td>
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<td>NMo–3.2</td>
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<td>0.8</td>
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</table>
Table A–5. Results from nitrogen solubility measurements in the CaO–MgO–SiO₂ and the Al₂O₃–CaO–MgO–SiO₂ at 1873 K. Graphite crucibles were used.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analyzed slag compositions [mass%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>NC 1.1</td>
<td>–</td>
</tr>
<tr>
<td>NC 1.2</td>
<td>–</td>
</tr>
<tr>
<td>NC 1.3</td>
<td>–</td>
</tr>
<tr>
<td>NC 2.1</td>
<td>–</td>
</tr>
<tr>
<td>NC 2.2</td>
<td>–</td>
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<tr>
<td>NC 2.3</td>
<td>–</td>
</tr>
<tr>
<td>NC 3.1</td>
<td>–</td>
</tr>
<tr>
<td>NC 3.2</td>
<td>–</td>
</tr>
<tr>
<td>NC 4.1</td>
<td>44.7</td>
</tr>
<tr>
<td>NC 4.2</td>
<td>43.2</td>
</tr>
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<td>42.7</td>
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<td>52.7</td>
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<tr>
<td>NC 6.2</td>
<td>43.2</td>
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<tr>
<td>NC 6.3</td>
<td>38.6</td>
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</tbody>
</table>

* Determined by first wet chemistry method (see experimental part).
** Determined by second wet chemistry method (see experimental part).
Table A–6. Slag composition and the change of nitrogen content in steel for the vacuum period and waiting time in the industrial trials.

<table>
<thead>
<tr>
<th>Heat</th>
<th>ΔN $10^4$x[mass%]</th>
<th>Slag composition [mass%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>During vacuum</td>
<td>During waiting</td>
</tr>
<tr>
<td>c1</td>
<td>1</td>
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<tr>
<td>c2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>c3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>c4</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>c5</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>c6</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>c7</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>c8</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>c9</td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>
Table A–7. Summary of experimental conditions and calculated degree of sulfur removal for the oxidation experiments.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>S–1</td>
<td>Al₂O₃</td>
<td>1–3</td>
<td>–</td>
<td>1373</td>
<td>60</td>
<td>1</td>
<td>0.6</td>
<td>28</td>
</tr>
<tr>
<td>S–2</td>
<td>Al₂O₃</td>
<td>1–3</td>
<td>–</td>
<td>1473</td>
<td>60</td>
<td>1</td>
<td>0.6</td>
<td>30</td>
</tr>
<tr>
<td>S–3</td>
<td>Al₂O₃</td>
<td>0.18–0.25</td>
<td>–</td>
<td>1473</td>
<td>60</td>
<td>1</td>
<td>0.6</td>
<td>30</td>
</tr>
<tr>
<td>S–4</td>
<td>MgO</td>
<td>0.18–0.25</td>
<td>–</td>
<td>1473</td>
<td>60</td>
<td>1</td>
<td>0.8</td>
<td>26</td>
</tr>
<tr>
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<td>Al₂O₃</td>
<td>1–3</td>
<td>–</td>
<td>1573</td>
<td>60</td>
<td>1</td>
<td>0.6</td>
<td>34</td>
</tr>
<tr>
<td>S–6</td>
<td>Al₂O₃</td>
<td>mix</td>
<td>–</td>
<td>1673</td>
<td>60</td>
<td>0.05b</td>
<td>0.6</td>
<td>73</td>
</tr>
<tr>
<td>S–7</td>
<td>Al₂O₃</td>
<td>mix</td>
<td>–</td>
<td>1673</td>
<td>60</td>
<td>0.21b</td>
<td>0.6</td>
<td>68</td>
</tr>
<tr>
<td>S–8</td>
<td>Al₂O₃</td>
<td>mix</td>
<td>–</td>
<td>1673</td>
<td>60</td>
<td>1</td>
<td>0.6</td>
<td>89</td>
</tr>
<tr>
<td>S–9</td>
<td>Al₂O₃</td>
<td>mix</td>
<td>–</td>
<td>1673</td>
<td>60</td>
<td>1</td>
<td>0.6</td>
<td>87</td>
</tr>
<tr>
<td>S–10</td>
<td>Al₂O₃</td>
<td>mix</td>
<td>–</td>
<td>1673</td>
<td>30</td>
<td>1</td>
<td>0.6</td>
<td>78</td>
</tr>
<tr>
<td>S–11</td>
<td>Al₂O₃</td>
<td>mix</td>
<td>–</td>
<td>1673</td>
<td>60</td>
<td>1</td>
<td>0.6</td>
<td>73</td>
</tr>
<tr>
<td>S–12</td>
<td>MgO</td>
<td>mix</td>
<td>–</td>
<td>1673</td>
<td>60</td>
<td>1</td>
<td>0.6</td>
<td>70</td>
</tr>
<tr>
<td>S–13</td>
<td>MgO</td>
<td>mix</td>
<td>–</td>
<td>1673</td>
<td>60</td>
<td>1</td>
<td>0.8</td>
<td>72</td>
</tr>
<tr>
<td>S–14</td>
<td>MgO</td>
<td>mix</td>
<td>–</td>
<td>1673</td>
<td>30</td>
<td>1</td>
<td>0.6</td>
<td>46</td>
</tr>
<tr>
<td>S–15</td>
<td>MgO</td>
<td>mix</td>
<td>–</td>
<td>1673</td>
<td>120</td>
<td>1</td>
<td>0.6</td>
<td>78</td>
</tr>
<tr>
<td>S–16</td>
<td>MgO</td>
<td>mix</td>
<td>–</td>
<td>1673</td>
<td>60</td>
<td>1</td>
<td>0.6</td>
<td>67</td>
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<tr>
<td>S–17</td>
<td>MgO</td>
<td>0.18–0.25</td>
<td>35% Al₂O₃</td>
<td>1673</td>
<td>60</td>
<td>1</td>
<td>0.6</td>
<td>74</td>
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<tr>
<td>S–18</td>
<td>MgO</td>
<td>0.18–0.25</td>
<td>40% Al₂O₃</td>
<td>1673</td>
<td>60a</td>
<td>1</td>
<td>0.6</td>
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<tr>
<td>S–19</td>
<td>Al₂O₃</td>
<td>0.18–0.25</td>
<td>40% Al₂O₃</td>
<td>1673</td>
<td>60</td>
<td>1</td>
<td>0.6</td>
<td>31</td>
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<td>S–20</td>
<td>MgO</td>
<td>0.18–0.25</td>
<td>45% Al₂O₃</td>
<td>1673</td>
<td>60</td>
<td>1</td>
<td>0.6</td>
<td>48</td>
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</tbody>
</table>

aThe additions given are the calculated total Al₂O₃ contents of the slag subsequent to melting.

bThe oxygen gas was balanced with N₂ gas to 1 atm.

cThis crucible had an inner diameter of 20 mm.
dThis sample had a prolonged heating time of 120 min.
Table A–8. Final chemical composition of the slag samples in the oxidation experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Final slag composition [mass%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>S–1</td>
<td>29.8</td>
</tr>
<tr>
<td>S–2</td>
<td>29.7</td>
</tr>
<tr>
<td>S–3</td>
<td>29.8</td>
</tr>
<tr>
<td>S–4</td>
<td>29.7</td>
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<td>S–6</td>
<td>41.5</td>
</tr>
<tr>
<td>S–7</td>
<td>40.6</td>
</tr>
<tr>
<td>S–8</td>
<td>44.2</td>
</tr>
<tr>
<td>S–9</td>
<td>42.6</td>
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<tr>
<td>S–12</td>
<td>30.4</td>
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<td>S–15</td>
<td>30.1</td>
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<td>S–16</td>
<td>33.9</td>
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<td>S–17</td>
<td>35.0</td>
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<td>S–18</td>
<td>40.9</td>
</tr>
<tr>
<td>S–19</td>
<td>46.1</td>
</tr>
<tr>
<td>S–20</td>
<td>44.8</td>
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</table>
Table A–9. Calculated final sulfur concentrations and degree of sulfur removal adjusted for dilution by Al₂O₃ for the oxidation experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analyzed S [mass%]</th>
<th>RS [%]</th>
<th>Dilution [%]</th>
<th>S (Adjusted) [mass%]</th>
<th>RS (Adjusted) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S–6</td>
<td>0.68</td>
<td>73</td>
<td>18.1</td>
<td>0.80</td>
<td>68</td>
</tr>
<tr>
<td>S–7</td>
<td>0.80</td>
<td>68</td>
<td>16.8</td>
<td>0.93</td>
<td>63</td>
</tr>
<tr>
<td>S–8</td>
<td>0.27</td>
<td>89</td>
<td>22.6</td>
<td>0.33</td>
<td>87</td>
</tr>
<tr>
<td>S–9</td>
<td>0.33</td>
<td>87</td>
<td>18.6</td>
<td>0.39</td>
<td>84</td>
</tr>
<tr>
<td>S–10</td>
<td>0.56</td>
<td>78</td>
<td>16.8</td>
<td>0.65</td>
<td>74</td>
</tr>
<tr>
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<td>37.7</td>
<td>0.92</td>
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<td>42.4</td>
<td>2.46</td>
<td>2</td>
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