A Study on Desulfurization of Hot Metal Using Different Agents

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Doctoral thesis

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Doctoral thesis in Materials Science
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Abstract

This thesis deals with desulfurization of hot metal using different agents. The aim of this study was to improve the understanding of commonly used desulfurization agents such as fluidized CaO, CaC2, commercial-CaO, Mg, and mixtures of commercial-CaO-Mg. The possibility to use ZnO for desulfurization of hot metal was also investigated. The desulfurization mechanisms and kinetics of these agents were studied. A broad comparison of the desulfurization abilities of the agents was performed under the same experimental conditions. The experimental studies were carried out in a high temperature resistance furnace at 1773 K with good quenching ability and precise control of the oxygen partial pressure.

The influence of ZnO in blast furnace slag on the sulfur removal potential was studied. It was found that ZnO does not stay in blast furnace slag under relevant oxygen potentials and consequently has no influence on its sulfur removal capacity.

The reaction mechanism of Mg was studied by adding pure Mg into hot metal. It was found that most Mg (about 90%) escaped as gas in less than two seconds, only providing a little desulfurization. MgS is not formed by homogenous nucleation, but on MgO particles originating from the surface of the added Mg metal.

The growth of CaS around CaC2, fluidized CaO and commercial-CaO were measured and compared. The parabolic rate constants were evaluated to be $2.4 \cdot 10^{-7}$ [cm s$^{-1}$] for CaC2, and $5 \cdot 10^{-7}$ [cm s$^{-1}$] for fluidized CaO particles. The bigger parabolic rate constant of fluidized CaO explains why fluidized CaO achieved a much better desulfurization of hot metal than CaC2 under the same experimental conditions. Commercial-CaO performed less satisfactory in comparison to fluidized CaO powder. This was due to both its less reactive surface and agglomeration of the particles.

Agglomerates and large CaO particles lead to 2CaO.SiO2 formation which hindered further utilization of CaO for desulfurization. The 2CaO.SiO2 formation was favored by a high oxygen potential. Since the desulfurization reaction of CaO not only produced CaS but also oxygen, the local oxygen concentration around big CaO particles was higher than around small particles.

When small CaO particles were added together with Mg they quickly transformed to CaS. The Mg-gas helped to distribute the CaO particles in the hot metal and improved the kinetic conditions.

The desulfurization abilities of some commonly used agents, namely fluidized CaO, CaC2, commercial-CaO, Mg, mixtures of commercial-CaO-Mg, and ZnO were studied and compared under the same experimental conditions. While fluidized CaO showed the best performance, commercial-CaO mixed with 20 mass % Mg achieved the second best desulfurization. Mg-granules performed slightly better than CaC2 and commercial-CaO, but somewhat less satisfactory compared to fluidized CaO and commercial-CaO-Mg mixtures. ZnO does not influence the sulfur concentration of hot metal.
Acknowledgements

First and foremost I would like to thank my supervisor Professor Du Sichen. He gave me the opportunity to perform this work and a fantastic mentorship. I deeply appreciate his guidance. I also want express my gratitude to co-supervisor Professor Patrice Nortier for all the discussions and feedback. He gave me support and inspiration.

I want to thank all the present and past colleagues in the Micro Modelling group for the nice and supportive atmosphere. You are my friends and I have enjoyed being in your company. I am very appreciative of Dr. Lars Ragnarsson who showed me the way to the Micro-Modelling group. I want to thank Dr. Bjoern Glaser for his support and magnificent work with the experimental setup and all things related to the lab.

The funding for this work was provided by Lhoist and is gratefully acknowledged. I want to thank Dr. Thierry Chopin for his valuable suggestions and the good discussions. The fine collaboration with Lhoist is much appreciated.

Most of all, I want to thank my family.
Supplements

Supplement 1: “Study on the possibility of using ZnO to increase the desulfurization potential of blast furnace slag and sulfide capacities”

David Lindström and Du Sichen

Steel research international, 2013, Vol. 84, No. 1, pp. 48-55

Supplement 2: “Study on the possibility of using ZnO for hot metal desulfurization”

David Lindström, Patrice Nortier, Bjoern Glaser and Du Sichen

Steel research international, 2013, Vol. 84, No. 5, pp. 419-425

Supplement 3: “Functions of Mg and Mg-CaO mixtures in hot metal desulfurization”

David Lindström, Patrice Nortier and Du Sichen

Steel research international, 2014, Vol. 85, No. 1, pp. 76-88

Supplement 4: “Kinetic study on desulfurization of hot metal using CaO and CaC₂”

David Lindström and Du Sichen

Submitted to Metallurgical and Materials Transactions B

Supplement 5: “Study on desulfurization abilities of some commonly used desulfurization agents”

David Lindström and Du Sichen

Submitted to Steel research international
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1. Introduction

Desulfurization of hot metal is an important step in the steel production process. Sulfur in steel negatively influences both mechanical and corrosion properties of the steel.\textsuperscript{[1,2]} A major source of sulfur in the hot metal is from the coal used in the blast furnace. As the usage of lower grade coal is being more common, more sulfur is introduced into the hot metal. Thus, there is an increasing need for efficient desulfurization of hot metal.

The desulfurization of hot metal provided by the blast furnace is not sufficient. Desulfurization of hot metal in the steelmaking converter is neither an attractive option because of the high oxygen potential.

Therefore, desulfurization of hot metal is practiced in ladles or torpedo cars to reach the low sulfur concentrations needed. The high temperature and low oxygen potential in hot metal after tapping from the blast furnace makes this a favorable position for desulfurization.\textsuperscript{[3]}

Mixing of the agent with the hot metal is usually provided by the lance injection of desulfurizing agents with inert gas or with a big refractory covered impeller in the so called KR-method.\textsuperscript{[4]}

Commonly used desulfurization agents are CaO, CaC\textsubscript{2} and Mg used individually or in combination, and sometimes together with Al or Al-ash. Na\textsubscript{2}CO\textsubscript{3} was previously a commonly used desulfurization agent but not anymore due to the associated environmental issues.\textsuperscript{[4-7]} The desulfurizing agents work by forming solid sulfide reaction products, such as CaS, that leaves the hot metal by floatation to the top slag.

There is always some blast furnace slag remaining on top of the hot metal in the ladle or torpedo car. The added agent can also work by increasing the sulfide capacity of the top slag. While hot metal desulfurization is a process, the sulfide capacity of a slag must be measured under equilibrium. However, the sulfide capacities are important for process control and are a measure to judge the usefulness of a slag used for desulfurization.

Several studies have been done to characterize sulfide capacities on slag systems ranging from two component systems of CaO-SiO\textsubscript{2} to multicomponent slag systems of e.g. Al\textsubscript{2}O\textsubscript{3}-CaO-MgO-SiO\textsubscript{2} or CaO-SiO\textsubscript{2}-CaF\textsubscript{2}-Na\textsubscript{2}O-MgO.\textsuperscript{[8-14]} It has recently been suggested that ZnO could help desulfurization of hot metal.\textsuperscript{[15-17]} This suggestion also raises the question whether ZnO might influence the sulfide capacity of remaining blast furnace slag.

Understanding the desulfurization mechanism of an agent enables more efficient usage and higher yield. Oeters et al 1973 made a fundamental study on the mechanism of CaO for desulfurization of hot metal. They reported that an outer layer of CaS was formed together with 2CaO.SiO\textsubscript{2} on the surface of CaO according to reactions (1) and (2).\textsuperscript{[18]}

\[
CaO + S = CaS + O
\] (1)
2CaO + Si + 2O = 2CaO.SiO₂ (2)

Reactivity (1) proceeds by diffusion of the reactants (S and O) through the CaS layer. On the other hand, diffusion of reactants through the di-calcium silicate layer is slow and therefore limits the desulfurization.\(^{[19]}\)

Not only di-calcium silicate has been found around lime particles used for desulfurization, but also tri-calcium silicate.\(^{[5,20]}\)

Takahashi et al. dipped lime rods in hot metal and found that CaS was only formed in the presence of slag. They reasoned that the formation of di-calcium silicate stopped the CaS formation and that solid CaO has to go into the slag in order to significantly contribute to desulfurization.\(^{[21]}\)

During desulfurization of hot metal with calcium carbide, CaS forms around the unreacted core through the following reaction (3).\(^{[19]}\)

\[ CaC_2 + S = CaS + 2C \] (3)

A graphite layer between the CaS layer and CaC₂ was observed by Talballa et al.\(^{[22]}\) Coudure and Irons investigated the influence of particle size on the kinetics of hot metal desulfurization with CaC₂.\(^{[23]}\) They described the reaction between CaC₂ and dissolved sulfur as a reaction controlled by diffusion and found that decreasing the particle size increased the desulfurization rate.

Even though magnesium and mixtures of magnesium with lime have been used successfully in steel plants, the mechanisms of these agents are still not well known. Studies on industrial performance of Mg have shown various results with reported end sulfur concentrations varying between several hundred ppm to below ten ppm.\(^{[24-28]}\) The kinetics of desulfurization with Mg was investigated by Nakanishi who injected Mg-granules with carrier gas into a 15 kg hot metal bath.\(^{[29]}\) Irons and Guthrie added vaporized Mg into a hot metal bath of 60 kg.\(^{[30]}\) A significant reduction of the sulfur concentrations were noted in both studies after treatment times ranging between 30-60 minutes. It was argued by Nakanishi that mass transfer of sulfur in the metal was the rate controlling step and that the desulfurization took place on the Mg bubble surface. Irons and Guthrie believed that dissolution of Mg-bubbles in the hot metal determined the rate of desulfurization. They proposed that dissolved Mg desulfurize hot metal by nucleation of MgS on particles in the melt through the following reaction (4).

\[ Mg + S = MgS \] (4)

Irons and Celik developed the model further with studies in a 400 kg furnace and compared the desulfurization behavior between CaC₂ and CaO-30mass%Mg.\(^{[31]}\) They found the rate of desulfurization was superior with the CaO-Mg mixture. The good performance of CaO-Mg mixtures have also been documented in industrial studies.\(^{[7,27,31]}\)
Recently, Kumar and Liu\textsuperscript{[15]} suggested that ZnO in the dust from the iron and steel industry could be recycled and used as a desulfurizing agent through reaction (5).

\[ \text{ZnO} + \text{S} = \text{ZnS} + \text{O} \]  

ZnS would leave the hot metal as gas, and the authors’ claim that ZnO would bring the sulfur concentration in hot metal down to levels below that of the capability of CaO.\textsuperscript{[15-17]}

Due to the scattered and even poor-defined experimental conditions in the literature, it is difficult to compare the performance of different desulfurizing agents. Most studies are done under different experimental conditions in terms of treatment time, temperature, and duration of treatment, top slag, and oxygen potential in the system, etc. Thus, there is a need for a comparative study of the commonly used desulfurization agents under relevant and well controlled conditions.

The focus of the work is to improve the understanding of desulfurization of hot metal using different agents. The possibility to use ZnO for desulfurization of hot metal was investigated. The reaction mechanisms and kinetics using the following agents were studied: fluidized CaO, commercial-CaO, CaC\textsubscript{2}, Mg, and mixtures of commercial-CaO with Mg. The abilities of these agents to desulfurize hot metal were also studied and compared.
2. Experimental

2.1 Materials

The materials and gases used for studying the sulfide capacities of ZnO enriched blast furnace slag are listed in Table 1. The slag components: Al$_2$O$_3$, CaO, MgO and SiO$_2$ were calcinated in a muffle furnace for at least 8 hours at 1373 K before being mixed and weighed to prepare the different sample mixtures for master slag.

Table 1. Materials used for sulfide capacity measurement.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Purity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum oxide</td>
<td>99.997</td>
</tr>
<tr>
<td>Calcium oxide</td>
<td>99.95</td>
</tr>
<tr>
<td>Magnesium oxide</td>
<td>99.95</td>
</tr>
<tr>
<td>Silicon oxide</td>
<td>99.8</td>
</tr>
<tr>
<td>Calcium sulfide</td>
<td>99.9</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>99.99</td>
</tr>
<tr>
<td>Copper metal powder</td>
<td>99.99</td>
</tr>
<tr>
<td>Silver metal powder</td>
<td>99.99</td>
</tr>
<tr>
<td>CO gas</td>
<td>99.97</td>
</tr>
<tr>
<td>0.4%CO$_2$-CO gas</td>
<td>99.97</td>
</tr>
<tr>
<td>2.3%CO$_2$-CO gas</td>
<td>99.97</td>
</tr>
</tbody>
</table>

Six master Al$_2$O$_3$-CaO-MgO-SiO$_2$ slag compositions were chosen. For each master composition, two slags with different ZnO contents were produced, one with low ZnO addition about 1 mass % and the second one with a higher ZnO addition about 6 mass %. The slags were prepared in a three-step procedure described in supplement 1.$^{[32]}$ The individual target slag compositions of each sample is found in Table 3a-c.

All graphite parts (crucible, stirrer and holder) were made from high purity grade graphite IG 110. The hot metal used in this study was pig iron from a Swedish steel industry with an initial sulfur concentration of 460±10 ppm. The zinc concentration in hot metal was less than 100 ppm. The main composition of the hot metal is listed in Table 2.

Table 2. Main components of hot metal.

<table>
<thead>
<tr>
<th>Mass [%]</th>
<th>C</th>
<th>Si</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.9</td>
<td>0.21</td>
<td>0.046</td>
</tr>
</tbody>
</table>
Fluidized lime, named as Flucal was supplied by Lhoist. The powder was delivered in small vacuum sealed packages. The majority of the particles were in the size range of 50-100 μm, as revealed by light optical microscope examination.

Commercial lime of reagent grade from Alfa Aesar was also used. It was calcinated at 1173 K and then stored in a desiccator before the experiments. Samples of this type are referred to as commercial-CaO to distinguish them from Flucal lime. Examination with light optical microscope showed that most particles were below 300 μm, while some agglomerates were observed in the powder after storage.

Calcium carbide was obtained from SKW metallurgie group and 80 % of the particles were smaller than 63 μm according to the manufacturer. It was stored in tightly sealed cans and kept in a desiccator.

The Mg-granules were supplied by Lhoist and had a size below 0.5 mm.

2.2 Setup

An experimental setup was developed to study the reaction mechanisms and abilities of commonly used agents to desulfurize hot metal. For this purpose, the setup needed following functions.

(1) The agent should be kept at low temperature before addition to avoid premature reaction. The addition should be very rapid to ensure all agents being added into the hot metal.

(2) The hot metal should be stirred to enhance the contact between agent and dissolved sulfur.

(3) The sample along with the crucible should be quenched to maintain the composition of the hot metal at high temperature.

The experiment setup is schematically presented in Figure 1. The high temperature furnace with super Kanthal heating elements was controlled with a proportional integral differential (PID) controller using a B-type thermocouple (Pt-6%Rh / Pt-30%Rh). Another B-type thermocouple is placed just beneath the holding graphite crucible and allowed the sample temperature to be followed. The temperature variation in the even temperature zone was ±3 K.

The reaction tube made of alumina was connected to a water cooled quenching unit made of brass. The whole reaction chamber is gas tight by sealing with high temperature resistant rubber O-rings. The quenching unit is equipped with two gas inlets. Argon gas with high flow rate can be injected onto the sample when it is in the quenching position. The use of argon gas would ensure efficient quenching of the sample.
The hot metal is kept in a graphite crucible, which is held by a graphite holder. A graphite connector connects the graphite holder to a long steel tube. The steel tube is placed in the central axial position and connected to the lift (Lift 1, driven by motor) above the reaction chamber. It is possible to slide the steel tube while at the same time ensuring good sealing by using a system of rubber O-rings. Fast quenching is enabled by moving the sample from the hot zone of the furnace to the water cooled quenching unit in less than one second using the Lift 1.

Figure 1. The experimental setup.

A graphite stirrer was used for both adding the agent powder and mixing the bath of hot metal. The details of the stirrers can be seen in Figures 3 and 4. The graphite rod of the stirrer unit was connected to a steel rod, which went all way through the graphite sample holder and the outer steel tube.

O-rings were used to seal the outer steel tube and the steel rod. The rod was connected to a stirring motor sitting on the second lifting system (Lift 2). The second lifting system could move the stirrer and the stirring motor vertically, both down and up relative to the first lifting system. This movement would allow the insertion of the agent and the stirrer into the hot metal and removal of the stirrer from the liquid. The stirring motor was a Eurostar Digital supplied by Ika-Werke. Single layer of thin cellophane foil was wrapped around the stirrer to hold the agent power.
Three different types of experiments were performed and referred to as: sulfide capacity measurements, mechanism study, and study of desulfurization abilities. The setup was modified for each type of experiment. A detailed description of the modifications of the different types of experiments follows.

2.3 Procedure

Prior to heating of samples in any of the three different experiment types, the reaction tube was evacuated using a vacuum pump. Thereafter, the reaction tube was flushed with Ar-gas before filling it with the reaction gas. Reaction gas (pure CO-gas or CO/CO\textsubscript{2} gas mixtures) was flushed through the system during heating-up of the furnace and throughout the whole experiment at a constant gas flow rate. All the experiments were conducted at 1773 K. The experimental procedures were different in the three types of experiments. The details of the different experiments are explained below.

2.3.1 Control of oxygen potential

The sulfide capacity measurements were carried out at three different oxygen partial pressures: 4.2\cdot10^{-16}, 3.5\cdot10^{-13}, and 1.2\cdot10^{-11} atm. using: pure CO, 0.4% CO\textsubscript{2}-CO, and 2.3% CO\textsubscript{2}-CO, respectively. Both the experiments for the mechanism study and the desulfurization abilities were carried out at the oxygen partial pressures of 4.2\cdot10^{-16} atm.

The pure CO gas was equilibrated with graphite crucibles to obtain a constant oxygen partial pressure. The C(s)/CO(g) equilibrium is expressed by reactions (6)-(7).

\[
C(s) + \frac{1}{2}O_2(g) = CO(g) \quad (6)
\]

\[
\Delta G_6^O = -112877 - 86.514 \cdot T \quad [33]
\]

\[
\Delta G_6^O = -112877 - 86.514 \cdot T \quad [33]
\]

The oxygen partial pressures in the CO-CO\textsubscript{2} mixtures could be calculated by the following reactions,

\[
CO(g) + \frac{1}{2}O_2(g) = CO_2(g) \quad (8)
\]

\[
\Delta G_8^O = -281885 + 85.678 \cdot T \quad [33]
\]

Molybdenum crucibles were used in the experiments having CO-CO\textsubscript{2} mixtures.
2.3.2 Sulfide capacity measurements

The sample was held by either graphite or Mo crucible, Figure 2. The samples were connected to a sample holder according to Figure 2. This sample holder run through the gas tight O-ring sealing and connects to Lift 1. In these experiments, no stirrer, Lift 2, or stirring motor was used as indicated by Figure 1. In the case of silver-slag equilibrium, graphite crucible and C-CO equilibrium were employed. On the other hand, Mo crucible and CO-CO₂ gas mixture were used when copper-slag equilibrium was studied.

![Crucibles and base metals at different oxygen potentials.](image)

In a general run, the crucible (graphite or molybdenum) was filled with 7 g of the base metal (silver or copper). 0.45 g of CaS was put on the top of the base metal. On the top of CaS, 7 g of the prepared slag was added. The sample was kept at the target temperature for 72 hours. Thereafter, it was quenched. Lift 1 (Figure 1) lifted the sample to the quenching chamber within one second. The sample was flushed with Ar-gas at a very high flow rate. The sample was expected to be solidified within a few seconds.
2.3.3 Mechanism study

250 g of hot metal with an initial sulfur concentration 460±10 ppm (0.046 mass %) was used. It was kept in a graphite crucible which was attached by a sample holder connected to the steel tube according to Figure 3.

A graphite push rod with a graphite stirrer at the end is used for both adding the agent to the hot metal and stirring the metal bath.

A small cylindrical cavity (4 mm in depth and 8 mm in diameter) was made at the bottom of the stirrer. The addition of agent was kept in the cavity by a single layer of thin cellophane foil. In most experiments, an amount of 0.021 g powder was used, while in a few experiments with CaC$_2$ addition, a small cube of 0.023 g was used. All the CaC$_2$ samples were prepared in a dry box filled with argon. The calcium carbide cube was sized about 2.1x2.1x2.1 mm$^3$ and grinded out of a bigger piece using 240# grit paper. Keeping the addition agent in the cavity would ascertain the reaction time and easy location of the reacted particles.

![Figure 3. Stirrer design for the mechanism study.](image)
In a typical run for the mechanism study, the stirrer along with the desulfurization agent was positioned in the cold zone of the reaction chamber, 1.4 m above the hot metal sample. The hot metal was heated up to target temperature and kept there for 30 minutes for stabilization. Then, the stirrer with the agent was quickly pushed down into the liquid metal; and stirring was started immediately. A stirring speed of 100 rpm was utilized for all experiments with CaO and CaC$_2$. No stirring was used in the experiments for studying the mechanism of Mg and mixtures of CaO and Mg. After a predetermined reaction time, the sample along with the stirrer was quickly moved to the quenching chamber (less than 1 second) by the lift and quenched by argon with high flow rate.

### 2.3.4 Study of desulfurization abilities

In the experiments to study the desulfurization abilities of commonly used agents (Flucal, commercial-CaO, CaC$_2$, Mg-granules, commercial-CaO-Mg, and ZnO), the same setup as in the mechanism study was used except that the stirrer had a slightly different design as seen in Figure 4. The agent was attached under the stirrer using thin foil of cellophane.

![Figure 4. Stirrer design in experiments for studying different agent’s desulfurization abilities.](image-url)
The following procedure was used in the experiments to study the agents desulfurization abilities:

1. Heating up the hot metal held in graphite crucible to 1773 K in a controlled oxygen atmosphere ($P_{O_2} = 4 \cdot 10^{-16}$ atm).
2. Fast insertion of the desulfurization agent.
3. Stirring the hot metal sample at 400 rpm for 5 minutes.
4. Lifting stirrer out of hot metal, followed by 5 minutes of waiting time for particle floatation.
5. Lifting the sample rapidly to the quenching chamber (in less than 1 second) and quenching the sample with Ar-gas stream of high flow rate.

Once the sample was quenched, a piece of it was cut out and sent for sulfur analysis.

### 2.4 Analysis

Sulfur analysis of the quenched hot metal samples were performed with LECO combustion technique (ASTM E1019). The detection limit of sulfur in hot metal is 10 ppm. X-ray fluorescence was used to analyze the zinc concentration. It had a detection limit of 100 ppm for zinc. The Mg concentration was analyzed with optical emission spectroscopy (ASTM E1999) and had a detection limit of 10 ppm.

The slags were analyzed by atomic absorption spectroscopy (AAS) using a Perkin-Elmer AAnalyst 300. The elements in the silver bulk metal were also analyzed with AAS. The elements in the copper bulk metal were analyzed with inductively coupled plasma optical emission spectrometry using a Perkin-Elmer Optima 5300 DV. Both techniques have relative uncertainties of ±5 %. Sulfur analysis in both slags and base metals were performed with LECO combustion technique. The sulfur detection limit in the slags was 100 ppm. The detection limits of sulfur in copper and silver are 50 ppm and 100 ppm, respectively.

A cutting machine was used to prepare cross-sections of the sample from the mechanism study. Special effort was taken to get the cross-section through the lime or calcium carbide particles. High purity ethanol (99.8 %) was used to clean the surface directly after cutting. Ethanol was also used as cooling agent during grinding and polishing of the surface of the cross-section. Great care was taken to minimize influence of the preparation procedure on the reacted particles. To study the reaction, the particles were examined using a Hitachi S-3700 scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS).
3 Results

3.1 Possibility to use ZnO in blast furnace slag to increase desulfurization potential

One way that ZnO could possibly help desulfurization of hot metal is if it increases the desulfurization potential of the blast furnace slag. To investigate if there is such an effect, synthetic blast furnace slag with ZnO was prepared and equilibrated with copper or silver at 1773 K at three different oxygen partial pressures.

Tables 3a-3c shows the equilibrium compositions of the slags and metals for three oxygen partial pressures, respectively. By comparing the target composition to the analysis of the slag compositions after equilibrium in Tables 3a–3c, it is clearly seen that the concentrations of Al$_2$O$_3$, CaO, MgO, and SiO$_2$ in the slag after the experiments are in good accordance with the target slag composition while a great amount of the ZnO has escaped from the slag. The target compositions of ZnO in the different slags varied between 1–6 mass %. Only between 0.001 and 0.067 mass % ZnO remains in the slag after the experiments. Moreover, very low levels of Zn were detected in the base metals.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Mass %</th>
<th>Copper solution</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>SiO$_2$</th>
<th>S</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn</td>
<td>S</td>
<td>Target / Analysis</td>
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</tr>
<tr>
<td>a</td>
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<td>40.7</td>
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</tr>
<tr>
<td>c</td>
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<td>35.4</td>
<td>8.8</td>
<td>7.9</td>
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<td>0.93</td>
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<td>10.1</td>
<td>30.6</td>
<td>35.8</td>
<td>8.8</td>
<td>7.0</td>
</tr>
<tr>
<td>e</td>
<td>0.247</td>
<td>1.04</td>
<td>14.4</td>
<td>14.6</td>
<td>26.0</td>
<td>30.7</td>
<td>17.3</td>
<td>16.1</td>
</tr>
<tr>
<td>f</td>
<td>0.303</td>
<td>0.63</td>
<td>14.4</td>
<td>13.2</td>
<td>24.0</td>
<td>28.4</td>
<td>13.5</td>
<td>12.2</td>
</tr>
<tr>
<td>g</td>
<td>0.224</td>
<td>1.05</td>
<td>14.4</td>
<td>13.2</td>
<td>18.3</td>
<td>23.2</td>
<td>17.3</td>
<td>16.5</td>
</tr>
<tr>
<td>h</td>
<td>0.57</td>
<td>1.06</td>
<td>14.2</td>
<td>15.3</td>
<td>18.1</td>
<td>22.0</td>
<td>17.1</td>
<td>14.3</td>
</tr>
</tbody>
</table>

Table 3a. Target compositions of the Al$_2$O$_3$-CaO-MgO-SiO$_2$-ZnO slags and the analyzed compositions after equilibrating with Cu at $P_{O_2} = 1.2\cdot10^{-11}$ atm.
Table 3b. Target compositions of the Al$_2$O$_3$-CaO-MgO-SiO$_2$-ZnO slags and the analyzed compositions after equilibrating with Cu at $P_2O_5 = 3.5 \times 10^{-13}$ atm.

<table>
<thead>
<tr>
<th>Mass %</th>
<th>Copper solution</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>SiO$_2$</th>
<th>S</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample name</td>
<td>Zn</td>
<td>S</td>
<td>Target / Analysis</td>
<td>Target / Analysis</td>
<td>Target / Analysis</td>
<td>Target / Analysis</td>
<td>Analysis</td>
</tr>
<tr>
<td>i</td>
<td>0.321</td>
<td>1.04</td>
<td>14.5</td>
<td>13.1</td>
<td>34.9</td>
<td>37.8</td>
<td>12.6</td>
</tr>
<tr>
<td>j</td>
<td>1.050</td>
<td>1.04</td>
<td>14.4</td>
<td>14.2</td>
<td>30.6</td>
<td>34.8</td>
<td>8.8</td>
</tr>
<tr>
<td>k</td>
<td>1.190</td>
<td>0.79</td>
<td>14.2</td>
<td>16.4</td>
<td>25.5</td>
<td>32.1</td>
<td>17.1</td>
</tr>
<tr>
<td>l</td>
<td>0.463</td>
<td>0.84</td>
<td>14.5</td>
<td>14.0</td>
<td>24.2</td>
<td>28.4</td>
<td>13.6</td>
</tr>
<tr>
<td>m</td>
<td>1.670</td>
<td>0.90</td>
<td>14.2</td>
<td>15.6</td>
<td>23.5</td>
<td>24.8</td>
<td>13.4</td>
</tr>
</tbody>
</table>

Table 3c. Target compositions of the Al$_2$O$_3$-CaO-MgO-SiO$_2$-ZnO slags and the analyzed compositions after equilibrating with Ag at $P_2O_5 = 4 \times 10^{-16}$ atm.

<table>
<thead>
<tr>
<th>Mass %</th>
<th>Silver solution</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>SiO$_2$</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample name</td>
<td>Mg</td>
<td>Zn</td>
<td>Target / Analysis</td>
<td>Target / Analysis</td>
<td>Target / Analysis</td>
<td>Target / Analysis</td>
</tr>
<tr>
<td>n</td>
<td>0.019</td>
<td>0.008</td>
<td>14.7</td>
<td>15.1</td>
<td>37.3</td>
<td>37.9</td>
</tr>
<tr>
<td>o</td>
<td>0.011</td>
<td>0.024</td>
<td>14.6</td>
<td>14.4</td>
<td>37.1</td>
<td>40.4</td>
</tr>
<tr>
<td>p</td>
<td>0.029</td>
<td>0.007</td>
<td>14.5</td>
<td>14.7</td>
<td>34.9</td>
<td>37.5</td>
</tr>
<tr>
<td>q</td>
<td>0.028</td>
<td>0.023</td>
<td>14.4</td>
<td>14.0</td>
<td>34.6</td>
<td>38.2</td>
</tr>
<tr>
<td>r</td>
<td>0.009</td>
<td>0.028</td>
<td>14.6</td>
<td>14.8</td>
<td>31.1</td>
<td>35.5</td>
</tr>
<tr>
<td>s</td>
<td>0.010</td>
<td>0.008</td>
<td>14.8</td>
<td>14.7</td>
<td>24.7</td>
<td>28.2</td>
</tr>
<tr>
<td>t</td>
<td>0.025</td>
<td>0.005</td>
<td>14.7</td>
<td>15.2</td>
<td>18.6</td>
<td>24.0</td>
</tr>
<tr>
<td>u</td>
<td>0.013</td>
<td>0.002</td>
<td>14.8</td>
<td>14.9</td>
<td>18.8</td>
<td>23.1</td>
</tr>
</tbody>
</table>

Only the sulfur concentrations in the copper metal samples can be determined, because the sulfur concentrations in silver samples are lower than the detection limit. Table 3a and 3b shows these results together with the sulfur contents in the equilibrated slags. The contents of elements Al, Ca, and Mg in all copper samples are below their detection limits; 100, 50, and 50 ppm, respectively. Hence only the S and Zn contents are given in Tables 3a and 3b.
The contents of both Zn and Mg can be analyzed in the silver samples run at $P_{O_2} = 4 \cdot 10^{-16}$ atm. The results are seen in Table 3c. The contents of S, Al and Ca are below the detection limits.

### 3.2 Mechanisms of the reactions

#### 3.2.1 Pure Mg addition

To study the function of Mg in hot metal desulfurization, pure Mg-chips were quickly added into the hot metal. The added amount was 0.42 g in all cases and corresponded to 4.8 times the amount of Mg needed to remove all sulfur. There were strong vibrations in the pushrod from the moment the Mg was added into the hot metal. There was a noise due to bubbling of Mg gas simultaneous with the vibrations in the push rod. The duration of the bubbling process (as indicated by the rod vibration and bubbling noise) was less than 2 seconds. Hot metal samples were quenched directly after the bubbling period (2 seconds after Mg addition), and 10 as well as 20 seconds after the Mg addition.

The appearances of the samples with and without Mg addition are compared in Figure 5. The left sample, which was quenched directly after the bubbling period (2 seconds), shows that splashing and bubbling have been going on. This is in contrast with the reference sample without Mg addition shown to the right which has a quite different appearance.

![Figure 5](image)

Figure 5. The left sample was quenched 2 sec. after Mg-addition and the right reference sample has no Mg-addition.

The cross sections of the hot metal samples which were quenched 2, 10 and 20 seconds after Mg addition are shown in Figure 6. The three samples after Mg addition have similar appearances. In
all the three cases (samples quenched at 2, 10 and 20 seconds), cluster of reaction products were mostly found in the upper part of the sample close to the top surface.

Figure 6. Cross-sections of samples quenched 2, 10 and 20 sec. after Mg-addition. Reaction products were found above the black line.

The heights of the region where the clusters are observed are given in Table 4 in order to compare the results with the results of CaO-Mg mixtures.

Table 4. Distance from the surface of the metal above which reaction products are found

<table>
<thead>
<tr>
<th>Sample</th>
<th>Quenched after</th>
<th>Distance from surface [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>2 sec</td>
<td>10-15</td>
</tr>
<tr>
<td>Mg</td>
<td>10 sec</td>
<td>10-15</td>
</tr>
<tr>
<td>Mg</td>
<td>20 sec</td>
<td>10-15</td>
</tr>
<tr>
<td>Mg-4% CaO</td>
<td>2 sec</td>
<td>10-15</td>
</tr>
<tr>
<td>Mg-4% CaO</td>
<td>20 sec</td>
<td>10-15</td>
</tr>
<tr>
<td>Mg-30% CaO</td>
<td>20 sec</td>
<td>15-20</td>
</tr>
<tr>
<td>Mg-50% CaO</td>
<td>20 sec</td>
<td>15-20</td>
</tr>
<tr>
<td>Mg-70% CaO</td>
<td>20 sec</td>
<td>35-40</td>
</tr>
<tr>
<td>Mg-80% CaO</td>
<td>20 sec</td>
<td>35-40</td>
</tr>
</tbody>
</table>

Note: The height of the hot metal is 45mm
The element mappings of the clusters found in the top regions of the sample quenched at 2 seconds is seen in Figures 7. The same observations are made in the samples quenched after 20 seconds. The micrographs clearly show the co-existence of MgS and MgO. There is no pure MgO particle (or cluster) detected in the two samples. Neither pure MgS particle was found in the samples. A few particles of MgS with small amount of MgO were occasionally seen.

Figure 7. Element mappings show the Co-existence of MgO and MgS in the upper region of the sample quenched 2 sec. after addition of pure Mg.

Combustion analysis (LECO) was used to analyze the sulfur contents of the metal after the experiments. The sulfur contents were 360 ppm for all the three samples quenched 2, 10 and 20 second after pure Mg addition. This value is only slightly lower than the initial concentration of 460 ppm, which indicates that the efficiency of using pure Mg for desulfurization of hot metal is very low.

The Mg concentration in the sample quenched after 2 seconds was analyzed with OES and it showed a result of 180 ppm. This indicates that about 90% of the added Mg escaped as gas.
3.2.2 CaO (Flucal)

Different reactions times were used in the experiments for studying the reaction mechanism of Flucal. Most of the single Flucal particles are transformed to CaS when the reaction time is long enough (most particles were measured in the range between 50-100 μm). The element mappings over a cross-section of the sample quenched 5 minutes after the Flucal addition is shown in Figure 8. Most of the CaO (Flucal) particles have been completely transformed into CaS.

Figure 8. CaO particles transformed to CaS in hot metal after 5 minutes of reaction.
A small CaO particle completely transformed to CaS is shown with high magnification in Figure 9. No silicon is present around the particle, thereby indicating the absence of any calcium silicate layer.

Figure 9. Small CaO (Flucal) particles completely transformed to CaS.
At short reaction times, a layer of CaS is formed on the surface of the CaO particle. Figure 10 shows the element mappings of a particle reacted for 30 seconds. The CaS layer is clearly shown by the mappings. This particle is about 100 μm, while the CaS layer is about 30 μm. The absence of any calcium silicate layer is evident, similar as with the particles shown in Figure 9.

Figure 10. CaO particle transitioning to CaS after 30 seconds of reaction time.
The thickness of the CaS layer formed around single Flucal particles is measured as a function of reaction time and showed in Figure 11. All the CaS-layer measurements using the SEM were done on single particle and not agglomerate.

Figure 11. CaS-layer thickness as a function of reaction time for Flucal and CaC₂.
3.2.3 Calcium carbide

Figure 12 shows the element mappings of a calcium carbide particle with a diameter of approximately 25 μm after reaction of 25 seconds. An outer layer (about 10 μm in thickness) of CaS is formed around the unreacted carbide. The carbon mapping is not presented in the figure due to the great uncertainties associate with carbon analysis using EDS. The absence of calcium silicate phase is also evidently shown.

![Figure 12. Partial transformation of CaC2 particle into CaS after 25 seconds.](image)

Figure 13 presents the element mappings over the cross-section of the calcium carbide cube quenched after 8 minutes of reaction. A thick layer of CaS about 120 μm in thickness was formed around the calcium carbide cube. Between the CaS layer and the remaining CaC2 cube, a thin graphite layer is detected. Although the carbon analysis using EDS involves great uncertainty, the absence of Ca in this layer is a strong evidence of the layer of graphite phase. The graphite layer was also reported by Talballa et. al.\cite{122} The CaS outer layer grows inwards from the original
interface between hot metal and calcium carbide. It is worthwhile to mention that the silicon mapping evidently indicates the absence of any calcium silicate phase.

Figure 13. CaS growth on CaC₂ cube after 8 minutes of reaction time.

The thickness of CaS layer as a function of reaction time in the case of CaC₂ is also presented in Figure 11. In view that the layer thickness measured in the CaC₂ particle compares well with the measurements in cubes at lower reaction times, the layer thickness at longer reaction times are measured using cubes (The CaC₂ particles are smaller than 100 μm).
3.2.4 Commercial CaO

The reaction mechanism of commercial-CaO was also investigated. The element mappings of a commercial-CaO particle after 30 seconds of reaction in hot metal are shown in Figure 14. The layer of CaS on the particle (about 50 μm in size) of commercial-CaO is only about 10-15 μm. This can be compared with the 30 μm thick CaS layer formed around a Flucal particle (about 100 μm in size) after the same reaction time 30 seconds.

Figure 14. Element mappings showing CaS growth on commercial-CaO particle after 30 seconds reaction time.
The prevalence of agglomerates is much higher with commercial-CaO than the ordinary Flucal. The element mappings of a sample quenched after 5 minutes of reaction time is presented in Figure 15. It shows the presence of calcium silicate around an agglomerate of commercial lime. EDS analysis indicated the presence of both $3\text{CaO} \cdot \text{SiO}_2$ and $2\text{CaO} \cdot \text{SiO}_2$. The formation of calcium silicate phases is only observed in big agglomerates. The agglomerate in Figure 15 is about 500-600 μm and it is evident that both CaS and calcium silicate is present. Calcium silicate formation will be discussed in detail later in the discussion part.

Figure 15. Agglomerate of commercial-CaO surrounded by calcium silicate and calcium sulfide.
3.2.5 Commercial-CaO-Mg addition

Distribution of commercial-CaO particles in the hot metal is improved when a small amount of Mg is added together with lime. Since Mg vaporizes at 1363K, most of it quickly rushes out of the hot metal bath as gas when added at 1773 K. When an optimized amount of Mg is added together with lime, the Mg-gas is actually helpful in distributing the lime particles. This aspect is evidently shown by the experimental results. Figure 16 shows the SEM microphotograph of a sample quenched 20 seconds after the addition of commercial-CaO-20mass%Mg mixture. It is seen that the lime particles (sized <100μm) spread out by Mg-gas in a cross-section of a hot metal sample. A detailed discussion will be given later in the discussion part.

Figure 16. Commercial-CaO particles spread out in hot metal by Mg-vapor.
3.3 Study of desulfurization abilities

Different amounts of desulfurization agents were added into the hot metal to study their performances in desulfurization. The added amount of agent is expressed by eq. 10

\[ N_{\text{add}}^i = \frac{n_i}{n_S} \]  

\( n_S \) in equation (1) stands for the initial moles of sulfur in the hot metal whereas \( n_i \) represents the added moles of agent \( i \). The subscript, \( i \), in \( n_i \) denotes CaO, CaC\(_2\), Mg or CaO-Mg mixtures.

Figure 17. Comparison of desulfurization abilities of CaO (Flucal), commercial-CaO, CaC\(_2\), Mg-granules, ZnO, and mixtures of commercial-CaO and Mg.
Figure 17 shows the results of desulfurizing hot metal with the different agents. The added quantities of agents varied between \( N_{add} = 1 \) - 7. All the experiments were conducted under identical conditions. The temperature was 1773 K. The stirring speed was 400 rpm for 5 minutes and the subsequent floatation was 5 minutes. The particle sizes of the agents are given in Table 5 together with the added quantities and the end sulfur levels.

Table 5. Sulfur concentration after desulfurization, added quantities of desulfurization agents and particle sizes.

<table>
<thead>
<tr>
<th>Desulfurization agent</th>
<th>( S_{after} ) [ppm]</th>
<th>( N_{add} )</th>
<th>Particle size [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flucal</td>
<td>200</td>
<td>1.00</td>
<td>50-100</td>
</tr>
<tr>
<td>Flucal</td>
<td>40</td>
<td>3.51</td>
<td>50-100</td>
</tr>
<tr>
<td>Flucal</td>
<td>20</td>
<td>6.99</td>
<td>50-100</td>
</tr>
<tr>
<td>Flucal</td>
<td>20</td>
<td>7.00</td>
<td>50-100</td>
</tr>
<tr>
<td>Commercial-CaO</td>
<td>240</td>
<td>2.44</td>
<td>&lt;300</td>
</tr>
<tr>
<td>Commercial-CaO</td>
<td>200</td>
<td>3.50</td>
<td>&lt;300</td>
</tr>
<tr>
<td>Commercial-CaO</td>
<td>160</td>
<td>5.00</td>
<td>&lt;300</td>
</tr>
<tr>
<td>Commercial-CaO</td>
<td>130</td>
<td>6.99</td>
<td>&lt;300</td>
</tr>
<tr>
<td>CaC(_2) powder</td>
<td>240</td>
<td>3.06</td>
<td>&lt;63</td>
</tr>
<tr>
<td>CaC(_2) powder</td>
<td>230</td>
<td>3.51</td>
<td>&lt;63</td>
</tr>
<tr>
<td>CaC(_2) powder</td>
<td>330</td>
<td>1.01</td>
<td>&lt;63</td>
</tr>
<tr>
<td>CaC(_2) powder</td>
<td>130</td>
<td>7.01</td>
<td>&lt;63</td>
</tr>
<tr>
<td>ZnO</td>
<td>460</td>
<td>5.00</td>
<td>&lt;200</td>
</tr>
<tr>
<td>ZnO</td>
<td>450</td>
<td>5.00</td>
<td>&lt;200</td>
</tr>
<tr>
<td>Mg-granules</td>
<td>330</td>
<td>2.32</td>
<td>&lt;500</td>
</tr>
<tr>
<td>Mg-granules</td>
<td>120</td>
<td>4.82</td>
<td>&lt;500</td>
</tr>
<tr>
<td>Mg-granules</td>
<td>110</td>
<td>7.00</td>
<td>&lt;500</td>
</tr>
<tr>
<td>Commercial-CaO-10 mass%Mg</td>
<td>190</td>
<td>3.96</td>
<td>&lt;300</td>
</tr>
<tr>
<td>Commercial-CaO-20 mass%Mg</td>
<td>80</td>
<td>4.42</td>
<td>&lt;300</td>
</tr>
</tbody>
</table>

Figure 17 shows clearly that an increasing amount of addition leads to lower sulfur concentration for all agents except for ZnO, which has no influence at all. Obviously, the use of Flucal results in the best desulfurization over the whole range of quantities added. As an example, an end sulfur concentration of 20 ppm is reached when the Flucal addition is \( N_{add}^{CaO} = 7 \).
From Figure 17 it is seen that the ability of desulfurization of commercial-CaO powder is considerably less. For example, adding \( N_{\text{add}}^{\text{CaO}} = 7 \) of commercial-CaO leads to the end sulfur content of 130 ppm. The final sulfur concentrations are much higher than the ones obtained using Flucal.

In the figure, it is also seen that the performance of CaC\(_2\) powder is very similar as the commercial-CaO, over the whole range of added amounts of agents.

The Mg addition resulted in splashing of the hot metal and vibration in the push rod. The escape of the Mg gas was reported in supplement number 3.\(^{[34]}\) The addition of Mg-granules (\( N_{\text{add}}^{\text{Mg}} = 4.82 \)) leads to an end sulphur concentration of 120 ppm, lower than the case of calcium carbide as well as commercial-CaO, but still higher than the case of Flucal powder.

When commercial-CaO-20mass\%Mg (\( N_{\text{add}}^{\text{CaO-Mg}} = 4.42 \)) are used, the final sulfur concentration reached 80 ppm. This is the second best performance of the agents compared, but not as good as the performance of Flucal.
4. Discussion

4.1 Influence of ZnO on sulfur removal from hot metal

There are two possibilities that ZnO could help remove sulfur from hot metal. (1) by influencing the remnant blast furnace slag that resides on top of the hot metal so that its sulfide capacity is increased. Or (2) if ZnO meets sulfur dissolved in the hot metal and forms ZnS.

4.1.1 Influence of ZnO on sulfur removal capacity in blast furnace slag

It is expected that the oxygen partial pressure at the interface between hot metal and slag in the ladle or torpedo car is at the level of C-CO equilibrium or even lower. However, the slag layer is exposed to higher oxygen partial pressure at its upper surface. The results (see Tables 3a-3c) clearly show that the slag phase contains very low concentration of ZnO in the range of oxygen partial pressure from 4∙10⁻¹⁶ atm to 1∙10⁻¹¹ atm. This evidently rules out the possibility that ZnO helps the slag to capture sulfur during the hot metal treatment. Even at an oxygen pressure of 1∙10⁻¹¹ atm, the ZnO contents in the slag are only 0.1-0.2 mass%. This low level could hardly help in increasing the sulfide capacity.

4.1.2 Sulfide capacities

The experimental data are still useful for the hot metal desulfurization, even though ZnO did not stay in the slag. There is always some blast furnace slag on the surface of the ladle or torpedo car. It is always useful to determine the sulfide capacities of the slags in the relevant region with consideration of CaO addition for optimization of the process. The data in Tables 3a-b along with the oxygen partial pressure can be used to calculate the sulfide capacities of the slags equilibrated with copper.

Richardson and Fincham[35] defined the sulfide capacity as,

\[
C_S = (mass\%S)_{slag} \cdot \frac{P_{O_2}}{P_{S_2}}
\]  

(11)

It is based on measurable parameters. The oxygen partial pressure is known since it is controlled. The sulfur concentration in the slag is measured and found in table 3a and 3b.

By using the thermodynamic data for the equilibrium between sulfur gas and sulfur dissolved into the copper metal[36], the sulfur partial pressure can be calculated:

\[
\frac{1}{2}S_2(g) = [S]^{Cu}
\]  

(12)
\[ \Delta G_{12}^O = -R \cdot T \cdot \ln \frac{a_{S}^{Cu}}{P_{S_2}^{f}} = -119662.4 + 25.23 \cdot T [J/mol] \]  

(13)

where \( a_{S}^{Cu} \) stands for the activity of sulfur in copper with composition in mass\% and the infinitely dilute solution as the reference state and the hypothetical 1 mass\% S as the standard state:

\[ a_{S}^{Cu} = \text{(mass\%S)} f_{S}^{Cu} \]  

(14)

The activity coefficient of sulfur is taken from Sigworth and Elliot.\textsuperscript{[36]}

\[ \log f_{S}^{Cu} = (\frac{-179}{1773} - 0.004 \cdot \text{(mass\%S)} + \frac{18}{1773} \cdot \text{(mass\%S)}^2) \]  

(15)

From this, the partial pressure \( P_{S_2} \) is calculated with the data listed in Tables 3a and 3b. Using the \( P_{S_2}, P_{O_2} \) and the sulfur content in the slag, the sulfide capacity can be evaluated.

The calculated sulfide capacities of the different slags are shown in Table 6 whereas the corresponding slag compositions are given in Tables 3a and 3b.

Table 6. The calculated sulfide capacities.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>( C_S )</th>
<th>Sample name</th>
<th>( C_S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>2.8\cdot10^{-4}</td>
<td>h</td>
<td>1.1\cdot10^{-4}</td>
</tr>
<tr>
<td>b</td>
<td>4.3\cdot10^{-4}</td>
<td>i</td>
<td>1.9\cdot10^{-4}</td>
</tr>
<tr>
<td>c</td>
<td>8.4\cdot10^{-5}</td>
<td>j</td>
<td>3.6\cdot10^{-5}</td>
</tr>
<tr>
<td>d</td>
<td>6.1\cdot10^{-5}</td>
<td>k</td>
<td>7.3\cdot10^{-5}</td>
</tr>
<tr>
<td>e</td>
<td>1.2\cdot10^{-4}</td>
<td>l</td>
<td>4.0\cdot10^{-5}</td>
</tr>
<tr>
<td>f</td>
<td>8.4\cdot10^{-5}</td>
<td>m</td>
<td>1.3\cdot10^{-4}</td>
</tr>
<tr>
<td>g</td>
<td>1.0\cdot10^{-4}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In Figure 18, the sulfide capacity values for slags with 15±2 mass\% \( Al_2O_3 \) are shown as solid dots. Only the slags with 15±2 mass\% \( Al_2O_3 \) are included in the figure and they have been normalized to 15 mass\% \( Al_2O_3 \). The exact compositions can be found in Table 3.
Literature data on sulfide capacities obtained at 1773 K are given as open squares in Figure 18. The present experimental values are designated with letters whereas the literature data with numbers.

Figure 18 shows that Point j (C₅=3.6·10⁻⁵) and point 5 (C₅=4.4·10⁻⁵), which are very close in composition, compare very well. Point k (C₅=5.4·10⁻⁵) and point 6 (C₅=7.3·10⁻⁵) are also very close in both composition and sulfide capacities. Point 8 and point 9 which is the experimental data reported by Nzotta et. al.[12], seem to suggest lower sulfide capacities than the present work and Abraham et. al. [13] as well as Kalyanram et. al.[14] The present experimental data are generally in good agreement with the sulfide capacity data by Abraham et. al.[12] as well as Kalyanram et. al.[14]

It was not possible to evaluate the sulfide capacities of the slag in equilibrium with the silver samples because the sulfur levels are below the detection limit. The calculated sulfide capacities from the present experiments are generally in line with those found in the literature.
4.1.3 ZnO as an agent for desulfurization of hot metal

The result of adding ZnO as a desulfurizing agent is in strong contrast to the other tested agents which all show an influence on the end sulfur level, Figure 17. By analyzing the zinc concentration before and after the ZnO addition it was verified that the ZnO was successfully added. The results in Figure 17 clearly show that ZnO has no function in desulfurization (see Table 5). This conclusion is in great contradiction with the publications by Kumar et. al.[15-17] This discrepancy necessitates a theoretical consideration of the data of Kumar et al.

There are three papers published by Kumar et al. on using ZnO for desulfurization of hot metal.[15-17] Their work is based on reaction (5).

\[
\text{ZnO} + S = \text{ZnS} (g) + O
\]  

\[
\Delta G^0_S = -368987 - 173.61 \cdot T [J/mole]
\]  

Surprisingly, the three papers give three different values for the standard Gibbs energy for reaction (5). No effort is made to clarify this situation. However, it seems reasonable to make theoretical calculation assuming the data, equation (16), in their most recent publication is valid.[15] Kumar et al. used this data and calculated the equilibrium sulfur concentration at 1700 K. They arrive at value of 1.86 ppm. Unfortunately, a calculation using the same data employed by Kumar et al.[15] leads to a sulphur level of 18.6 ppm (but not 1.86 ppm).

Furthermore, Kumar’s calculation is based on the assumption that the oxygen content in hot metal is 0.1 ppm. However, it is reported[37,38] that the oxygen contents in carbon saturated hot metal ranges between 1-4 ppm. Hence, Kumar and his co-workers have used too low oxygen activity in their calculation.

A new calculation using 1 ppm oxygen content in hot metal and the rest of data used by Kumar and his co-workers[15], results in sulfur content of 186 ppm. This result is 100 times more than the value reported by Kumar et. al.[15]

The standard Gibbs energy for reaction (5) is evaluated based on the galvanic cell study by Kumar et. al.[15-17] The authors use the following solid electrolyte cell,

\[
\text{Pt, Mo, MoO}_2 / \text{Yttria Stabilised zirconia / ZnO, ZnS, SO}_2, \text{Pt}
\]  

A close review of this galvanic cell shows that it is unstable at the temperature of interest. It cannot be used for any thermodynamic consideration.

The results show that ZnO does not contribute to the removal of sulfur from hot metal. These results along with the re-evaluation of the thermodynamic data reported in the literature leads to an evident conclusion that the use of ZnO to desulfurize hot metal by the formation of ZnS gas is
not possible to any extent. It was found that ZnO cannot help the slag to increase its desulfurization power. Hence, a conclusion that ZnO cannot be used as desulfurization agent can be drawn.

4.2 CaO (Flucal) particles and calcium carbide

The tiny, dispersed Flucal particles as well as calcium carbide particles both work for hot metal desulfurization. Studying the reaction mechanisms of single particles of CaO (Flucal) or CaC₂ shows the formation of CaS

Figure 11 show that the Flucal particles have much higher desulfurization efficiency than CaC₂ particles. As seen in the SEM microphotographs (Figures 8-10, 14) the desulfurization proceeds by diffusion through the CaS phase in the case of CaO and by diffusion through both CaS layer and graphite layer in the case of CaC₂ (Figures 12-13).

In the experiments for studying the reaction mechanisms of CaO and CaC₂, less than 10% of the amount of reactant needed for complete desulfurization is used. The hot metal bath is constantly stirred at 100 RPM. The mass transfer in the liquid phase is not expected to be the limiting kinetic factor.

Therefore, the reaction rate can be considered inversely proportional to the instantaneous reaction product layer thickness according to equation (18)

\[
\frac{dx}{dt} = \frac{K}{x}
\]  

(18)

where t is the reaction time, x is the CaS layer thickness, and K is the parabolic rate constant. On integration, eq.(18) gives eq.(19).

\[
x = \sqrt{2Kt}
\]  

(19)

An evaluation of the parabolic rate constants for these two cases gives some illumination to the performances of the two types of materials. The parabolic rate constants, K, for CaO and CaC₂ are calculated by using eq. (19) based on the data in Figure 11. The parabolic rate constant is calculated to be \(5\times10^{-7} \text{[cm s}^{-1}\)] for Flucal and \(2.4\times10^{-7} \text{[cm s}^{-1}\)] for calcium carbide. The experimental data for CaC₂ include both particle and cube data, since they are comparable. It is not proper to make cube for Flucal, as the product utilizes the advantage of surface treatment. The use of cube for Flucal would give misleading results.

The doubled K value of Flucal in comparison with CaC₂ well explains the high efficiency of the Flucal particles in desulfurization as shown in Figure 17. At \(N_{\text{add}}^{\text{CaO}} = 7\), Flucal brings the sulfur
concentration down to 20 ppm. The corresponding addition, $N_{\text{add}}^{\text{CaC}_2} = 7$, of calcium carbide takes the sulfur concentration to 130 ppm.

The present results reveal that Flucal CaO particles are very efficient in desulfurization in comparison with CaC$_2$. This is because the lower diffusion resistance of CaS layer formed on the particle surface.

### 4.3 Commercial-CaO and formation of di-calcium silicate

It is common knowledge that CaO easily forms calcium hydroxide upon interaction with water. The commercial-CaO was stored in a desiccator, but it is still likely that the surface of CaO particles are subjected to some degree of calcium hydroxide formation and possibly other processes, e.g. adsorption of CO$_2$ when the particles meet the humidity and carbon dioxide during the delivery.

It is seen that the layer thickness (30 μm) on Flucal is about twice the thickness on the commercial-CaO by comparing the CaS layer thicknesses on the single particles of the Flucal powder and commercial-CaO powder (Figure 10 and Figure 14) after 30 seconds of reaction time.

It could be that Flucal particles have better surface properties, but the change of the surface of the commercial-CaO particles could also be responsible for the lower growth rate of CaS layer. However, the surfaces of commercial-CaO particles are less reactive.

In Figure 15, it is shown that commercial-CaO particles form agglomerates. The agglomeration formation does not only reduce the total surface area, but also lead to formation of calcium silicates.$^{[39]}$ Calcium silicate formation on lime agglomerates are in accordance with the observations by both Oeters et al. and Takahashi et.al, who used CaO rods.$^{[18,21]}$ The silicate formation in the case of agglomerates and big CaO particles and not with small CaO particles are related to the local oxygen concentration around the particle.

The low concentration of dissolved Ca in the metal (<1 ppm) makes mass transfer of Ca extremely slow. The low local calcium activity practically rules out the possibility for reaction (20) to take place.

$$4\text{CaO} + \text{Si} = 2\text{CaO.SiO}_2 + 2\text{Ca}$$ (20)

Thus, it is likely that di-calcium silicate is formed by the following reaction.

$$2\text{CaO} + \text{Si} + 2\text{O} = 2\text{CaO.SiO}_2$$ (21)
When CaO desulfurization agent is added into hot metal with high Si concentration, the limiting factor for the formation of calcium silicate through reaction (21) would be the oxygen supply. It is well known that the oxygen level in hot metal is at ppm level. It is not enough to generate calcium silicate. This argument is supported by the absence of calcium silicate in the case of single small Flucal particles (Figures 9,10) and CaC₂ (Figures 12,13).[39] The desulfurization reaction,

\[
\text{CaO} + S = \text{CaS} + O
\]

leads to the formation of oxygen. A tiny CaO particle (usually < 50 μm) would not generate sufficient oxygen locally for reaction (20) to take place. On the other hand, big CaO agglomerate can generate sufficient oxygen through reaction (1), and thereby increasing the local oxygen potential, which would result in the formation of calcium silicate through reaction (21) (see Figure 15).

Figure 17 shows that an amount of commercial-CaO of \( N_{\text{add}}^{\text{CaO}} = 7 \) brings down the sulfur content to 130 ppm, whereas the same amount of Flucal takes the sulfur concentration down to 20 ppm.

The desulfurization ability is decreased due to three factors: (1) the surfaces of commercial-CaO particles is less reactive (the growth of CaS becomes slow), (2) the reduced surface area due to formation of agglomerates, and (3) the agglomerates leading to the formation of calcium silicate layer which increases the resistance to mass transfer.

Maintaining good surface properties of the powder is essential to maintain high reactivity of lime in desulfurization. To add the powder in an optimized manner will help the dispersion of the particle in the liquid metal. Decreasing the local oxygen potential by addition of other agents would help even commercial-CaO to improve its performance.

4.4 Mg and commercial-CaO-Mg mixtures

One of the alternatives of additives into CaO for desulfurization is Mg granules. To gain an insight of the function of lime-Mg mixtures, it is essential to understand how the two agents work individually. The function of Mg in hot metal desulfurization has been studied and discussed in detail in supplement 3.[34] The study shows that when Mg is added into hot metal, most of it rushes out as Mg-gas in less than 2 seconds. MgS is not formed by homogeneous nucleation but on MgO particles which originate from the surface of the added Mg-granules. The co-existence of MgO and MgS is shown in the element mappings in Figure 6.

The study[34] indicates that 180 ppm of magnesium is dissolved in the sample during the Mg addition. It corresponds to 10 % of the total addition. Thus, 90 % of the Mg-addition escaped as gas during the initial 2 seconds after addition. The use of Mg is not efficient because of the
escape of large amount of Mg vapor. The sulfur content is lowered from 460 ppm to 360 ppm by the formation of MgS on MgO micro particles during the initial 2 seconds after addition.

It was suggested by Irons and Guthrie\textsuperscript{30} that MgS formation in hot metal takes place at the surface of inclusions by dissolved Mg through reaction (4).

\[ \text{Mg + S} = \text{MgS} \quad (4) \]

Their finding agrees well with our previous publication.\textsuperscript{34} The addition of $N_{\text{add}}^{\text{Mg}} = 4.8$ of Mg granules followed by stirring bring down the sulfur content to 120 ppm, as shown in Figure 17.

As mentioned above, the sulfur content is brought down to 360 ppm after 2 seconds, and 180 ppm of magnesium is dissolved in the sample after this time period. It is reasonable that reaction (4) continues on the surface of solid particles in the hot metal after the initial period of 2 seconds.

A simple calculation reveals that the dissolved Mg quantity (180 ppm) can theoretically remove 237 ppm of sulfur according to reaction (4). Hence, the reaction (4) will bring the sulfur level down further from 360 ppm to 123 ppm. This prediction agrees excellently well with the experimental result in Figure 17, viz. 120 ppm.

A lower oxygen potential in the hot metal favors the reaction,

\[ \text{CaO + S} = \text{CaS + O} \quad (1) \]

It is well understood that mixing Mg with CaO will have the same effect, since the following reaction (22) takes place parallel to reaction (1)

\[ \text{Mg + O} = \text{MgS} \quad (22) \]

Lowering the oxygen potential does not only promote CaS formation through reaction (3), but also helps to avoid formation of di-calcium silicate around the lime particles according to reaction (21).\textsuperscript{39}

The generation of huge amount of Mg gas stirs the metal bath violently, as reported in the third supplement.\textsuperscript{34} The Mg gas helps in spreading the lime particles, see Table 4.

Though the spreading effect depends very much on the reactor and addition position, Table 4 still indicates there is an optimal ratio between CaO and Mg, at which the CaO particles are distributed well in the liquid metal. As the Mg part reduced and the lime part increased, particles are found over a larger area of the sample. A mixture of 20-30 mass% of Mg seems to be optimal under the present laboratory conditions. This optimal agrees very well with the results of desulfurization presented in Table 4 and Figure 17. When the commercial-CaO is mixed with 20 mass% Mg ($N_{\text{add}}^{\text{CaO-Mg}} = 4.4$), the desulfurization reached 80 ppm. The small Mg addition helps
the commercial-CaO to perform better. But is still not as good as the Flucal which reached 40 ppm at $N_{\text{add}}^{\text{CaO}} = 3.5$. The violent local stirring of the metal bath by Mg gas could even shatter the agglomerates formed during storage. This would further enhance the sulfur pickup by the CaO particles.

The present results and reasoning is in good accordance with the industrial study by Visser and Boom.\textsuperscript{[7]} They desulfurized 283 tons of hot metal at 1673 K from 250 ppm sulfur to 7 ppm in 10 minutes by injecting CaO-15mass%Mg as agent mixture (3.1 kg/ton steel).

Good results of desulfurization of hot metal by combining CaO and Mg are reported also by other researchers.\textsuperscript{[27,28,40]} On the other hand, their explanation of the results is somehow different from the present reasoning.

4.5 Comparison of desulfurization abilities

The abilities to desulfurize hot metal were tested and compared under similar experimental conditions for the following agents: fluidized lime (Flucal), Commercial-CaO, CaC\textsubscript{2}-powder, Mg-granules, and Commercial-CaO-Mg mixtures. ZnO as a desulfurization agent was also tested.

Figure 17 shows that the desulfurization of hot metal increased as larger quantities of the agents were added. This was true for all the tested agents, except for ZnO which showed no influence at all on the sulfur concentration in the hot metal.

The zinc concentrations in the hot metal samples were below the detection limit (100 ppm) before the experiments. Analysis of zinc in the hot metal samples after the ZnO addition experiments showed that the zinc concentrations reached between 130 and 370 ppm. Since the partial pressure of zinc is almost zero, the dissolved zinc would eventually escape to the gas. However, it is evidently seen that ZnO has been successfully added into the hot metal. A comparison of sulfur contents before and after the experiment shows evidently that the addition of ZnO into hot metal has no effect on the sulfur content in the hot metal.

No formation of ZnS was observed in or on the top of the hot metal. Neither was condensed ZnS found in the reaction chamber. On the other hand, condensed Zn could be detected on the steel push-rod above the stirrer.

In Figure 17 it is seen that the Flucal performs the best. For example, an addition of Flucal of $N_{\text{add}}^{\text{CaO}} = 7$ takes the sulfur concentration down to 20 ppm. The performance of commercial-CaO is considerably less. The use of commercial-CaO at $N_{\text{add}}^{\text{CaO}} = 7$ gave an end sulfur concentration of 130 ppm. When CaC\textsubscript{2}-powder of the quantity $N_{\text{add}}^{\text{CaC}_2} = 7$ was added, the same concentration (130 ppm) was also reached. In fact, the commercial-CaO and the CaC\textsubscript{2}-powder actually performed very similar over the whole range tested as seen in Figure 17.
The addition of Mg to hot metal resulted in splashing, bubbling sound and vibrations in the push rod during the first 2 seconds after addition. These are due to the escape of Mg gas, which has been reported in supplement 3. This study reveals also that only a small amount of dissolved Mg remains in the hot metal. The addition of Mg-granules ($N_{Mg}^{add} = 4.82$) leads to an end sulphur concentration of 120 ppm, lower than the case of calcium carbide as well as commercial-CaO, but still higher than the case of Flucal powder.

When a small part of the commercial-CaO was replaced by Mg-granules, a significant reduction of the final sulfur concentration could be achieved. When commercial-CaO-20mass%Mg ($N_{CaO:Mg}^{add} = 4.42$) are used, the final sulfur concentration reached 80 ppm. Note that the total mass of the additions in the case of commercial-CaO-Mg additions are all the same as the mass of $N_{CaO}^{add} = 3.5$. It seems that mixing a certain amount of Mg granules with the commercial-CaO make the lime powder more efficient.
5. Summary

Lower sulfur concentration in hot metal and a more efficient desulfurization process is always the interest of steel producers. By studying the process of desulfurization of hot metal with agents commonly used, an understanding was gained on these agents’ reaction mechanisms, kinetics and desulfurization abilities. Fluidized lime, commercial-CaO, calcium carbide, Mg-granules, and mixtures of commercial-CaO with Mg are commonly used agents that were studied. The possibility to use ZnO as a desulfurization agent was also investigated. All experiments were carried out in a high temperature furnace with good control of the oxygen potential at a temperature of 1773 K.

ZnO was recently suggested as an alternative desulfurization agent. The present study showed that ZnO does not influence the sulfide capacity of ZnO enriched blast furnace slag. ZnO does not stay in the slag at oxygen potentials relevant to the industry. Neither does ZnO function as a desulfurization agent.

To study the reaction mechanisms of Mg for desulfurization of hot metal, pure Mg was quickly added into hot metal. Most of the Mg rushed out of the hot metal in less than two seconds. It was found that MgS was not formed by homogenous nucleation but on particles of MgO originating from the surface of the added Mg. Most of the added Mg (90 %) escaped the sample quickly as gas. However, the fraction that dissolved into the hot metal continues to form MgS on the surface of micro particles. Adding mixtures of lime and Mg showed that there is an optimum mixture at which the quickly expanding Mg-gas helps distribute the lime particles in the hot metal. Mg improves the kinetic conditions for desulfurization with CaO.

The reaction mechanisms of CaO and CaC₂ were also studied. Small amounts of fluidized CaO, commercial-CaO, or CaC₂ were pushed into the hot metal and kept there for different periods of time to study the development of reaction products of the agents. Single CaO particles desulfurize hot metal by forming CaS. With CaC₂, an outer layer of CaS grew around an inner layer of graphite.

The growth of CaS as a function of time, in both the case of CaO and CaC₂, are diffusion limited. The parabolic rate constant was evaluated to be 5\cdot10^{-7} [cm s^{-1}] on fluidized CaO particles, and 2.4\cdot10^{-7} [cm s^{-1}] on CaC₂. The bigger parabolic rate constant of fluidized CaO explains it’s much better ability to desulfurize hot metal compared to CaC₂. The CaS growth was significantly less on particles of commercial-CaO than on fluidized lime. The surface properties of CaO particles plays important role in desulphurization. Poor CaO surface makes the CaS growth on single particles slower and the particles becomes sensitive for agglomeration.

Large CaO particles and agglomerates of CaO led to the formation of 2CaO.SiO₂. It hindered the further utilization of CaO for desulfurization. Formation of 2CaO.SiO₂ was favored by a high oxygen potential. The desulfurization reaction with CaO does not only produce CaS but also
dissolved oxygen. This makes the local oxygen concentration higher around big CaO-particles than small CaO-particles.

Mixing 20 mass % Mg with the commercial-CaO makes it perform better, but still not as well as Flucal. The Mg improves the functionality of commercial-CaO by distributing the lime particles and reducing the local oxygen potential.

The agent’s abilities to desulfurize hot metal under the same experimental conditions were compared. They performed in the following order: fluidized lime (Flucal), commercial-CaO mixed with 20 mass % Mg, Mg granules, CaC₂ powder, and commercial-CaO. ZnO has no function at all for desulfurization of hot metal.
6. References


[34] D. Lindström, P. Nortier, D. Sichen: Steel research international, 85 (2014), No. 1, 76.


