The effect of $\text{Al}_2\text{O}_3$, $\text{CaO}$ and $\text{SiO}_2$ on the phase relations in vanadium containing slags

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ABSTRACT

Today, the main raw material for vanadium production is vanadium containing steelmaking slags. The yield of the vanadium extraction process is affected by the composition of the slag, which in turn determines the phases present, the fractions of the phases and the distribution of the elements between the phases. The aim of this thesis was to experimentally investigate the effect of Al$_2$O$_3$, CaO and SiO$_2$ on the phase relations in vanadium containing slags at 1673 K.

Synthetic slags, in which the contents of Al$_2$O$_3$, CaO and SiO$_2$ were varied individually, were equilibrated at 1673 K in a vertical resistance furnace. Closed molybdenum crucibles were used to set the oxygen potential of the individual samples. The phases present, the phase compositions and the phase fractions of the samples were studied using SEM-EDS and LOM combined with an image analysis software.

The results indicate that the samples consisted of a mixture of a vanadium and iron rich spinel phase and an iron and silicon rich liquid phase at 1673 K. Practically all the vanadium was concentrated into the spinel phase while no free silica or solid phases into which both calcium and vanadium concentrate to a significant extent were observed. The effect of Al$_2$O$_3$ on the phase compositions and the phase fractions was seen to be limited in the range studied. CaO primarily affected the composition of the liquid phases, while the effect on the phase fractions was small. SiO$_2$ affected both the composition and fraction of the phases. The main effect was a decreased fraction of spinel phase, with an increasing vanadium content in the spinel phase as consequence.
ACKNOWLEDGMENTS

I would like to express my gratitude towards Swerea MEFOS for funding this thesis work. I would also like to thank my supervisors, Mikael Lindwall at Swerea MEFOS and professor Sichen Du at KTH, for the guidance, support and helpful discussions during the course of this work. Finally, I would like to thank my fellow group members for all the support and good times.
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1 INTRODUCTION

Vanadium a transition metal which is used primarily as an alloying element in steelmaking. Approximately 80% of the vanadium produced is used for this purpose [1]. It is the 22nd most abundant element in the earth’s crust and found in a large variety of compounds [2]. However, due to the relatively low concentrations of vanadium in the available sources, the majority of the vanadium bearing products are produced from raw materials which are by-products in other metal or energy processes [3]. Today, the main raw material for production of vanadium bearing products is titaniferous magnetite ores [4]. In the major route for recovering vanadium from titaniferous magnetite ores, the ore is reduced in a blast furnace, producing a vanadium containing hot metal. The hot metal is pre-oxidized in a converter process in order to produce a vanadium rich slag. The remaining hot metal has a carbon content of approximately 3% and returned to the steelmaking process [5]. During the pre-oxidation of the hot metal, the vanadium is primarily concentrated in solid spinel phases in the slag. The vanadium is thereafter extracted from the slag in a hydrometallurgical process route. To begin with, the slag is ground and separated from any metallic iron. The slag is then salt roasted and leached followed by precipitation of vanadium pentoxide. Commonly, a soda roasting-water leaching process is employed [6]. The extraction of the vanadium from the slag is affected by the slag composition, which in turn determines the phases present, the fraction of the phases and how the elements are distributed between the phases. High silica and lime contents have been reported to have negative effects on the vanadium extraction process. A high silica content can lead to the formation of free silica in the slag. During roasting, free silica can form low-melting point sodium iron silicates. A high lime content can lead to the formation of calcium vanadates during roasting. These reactions leads to part of the vanadium being retained in a water insoluble form, thus decreasing the yield during water leaching [6]. Furthermore, an increasing vanadium content in the slag causes an increasing fraction of solid spinel phase, resulting in an increased slag viscosity.

Previous studies of vanadium containing slags have shown that they mainly consist of spinel phase and different silicate phases [5, 7, 8, 9]. The spinel phase is iron and vanadium rich and can be described as (Fe²⁺, Mg²⁺, Mn²⁺)(Fe³⁺, V³⁺, Ti³⁺, Cr³⁺, Al³⁺)O₄ [7]. The silicate phases have primarily been reported to be olivine phases and pyroxene phases in which Fe, Mn, Mg, and Ca exist [5, 7, 8, 9]. The spinel phase is considered to be the main vanadium concentrating phase in the slags. However, goldmanite, described as Ca₃V₂(SiO₄)₃, has been reported to form at high CaO contents [5]. Some authors also claim that calcium might exist in the spinel phase, increasing the risk of formation of calcium vanadates during roasting [7]. The reported contents were, however, low. Also, these findings are not in accordance with what has been reported for high CaO contents [5].
The aim of this thesis is to experimentally investigate the effect of the $\text{Al}_2\text{O}_3$, $\text{CaO}$ and $\text{SiO}_2$ contents on the phase relations in vanadium containing slags at 1673 K. The effect on phases present, phase compositions and phase fractions is considered. The results could provide fundamental knowledge for better understanding of the production of vanadium containing slags and its impact on the following extraction processes.
2 BACKGROUND

2.1 Vanadium

Vanadium (V) was first discovered by Andrés Manuel del Rio in 1801. However, the element was erroneously identified as a form of chromium and vanadium was therefore rediscovered by Nils Gabriel Sefström in 1830 who named the element after the Norse goddess Vanadis [2]. Vanadium is a grey to white metal with atomic number 23, belonging to group 5 of the periodic table of elements together with elements like niobium and tantalum [6]. Some selected properties of vanadium are presented in Table 1.

Table 1. Properties of vanadium [6]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic mass</td>
<td>50.9415</td>
</tr>
<tr>
<td>Density</td>
<td>6110 kg/m³</td>
</tr>
<tr>
<td>Melting point</td>
<td>1910 °C</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>BCC</td>
</tr>
</tbody>
</table>

Vanadium can adopt multiple oxidation states, ranging from -1 to +5 and forms a large variety of compounds [10]. The oxidation states commonly found in chemical compounds are +2 to +5 [6]. Vanadium and its compounds are toxic and have been proposed to have a range of effects, e.g. hematological changes, neurobehavioral injury, embryotoxicity and respiratory injury [11]. The toxicity is related to the oxidation state of vanadium and its chemical form, i.e. organic or inorganic form, with pentavalent vanadium as the most toxic and mobile form [1].

The main application of vanadium is as an alloying element in the iron and steelmaking process, primarily in the form of ferrovanadium (FeV). It has been estimated that approximately 80% of the vanadium bearing products are used for this application [1]. Vanadium is used as an alloying elements in a number of different steels, e.g. low alloy steels, tools steel, carbon steels and HSLA steels. Depending on the steel the vanadium content typically varies from 0.03 to 5 %. The main effects of vanadium addition in steels are

- Improved hardness and toughness at elevated temperatures due to carbide formation
- Improved strength and toughness due to formation of nitrides and carbides which inhibit grain growth
- Increased hardenability due to delayed formation of pearlite and bainite

Vanadium is also used in the production of titanium alloys, catalysts and in advanced research and industry [6].
Vanadium does not occur in nature in its native form but in compounds, generally divided into oxides, phosphates, silicates, sulfates, sulfides, titanates and vanadates [6]. The resources of vanadium, defined as concentrations of vanadium in such form and amount that economic extraction of vanadium from the concentration is currently or potentially feasible, are estimated to exceed 63 million tons in 2015. Of these, 15 million tons are identified as vanadium reserves, defined as the part of the resources which meets the specified minimum physical and chemical criteria related to current mining and production practices [12]. The geographical distribution of the vanadium reserves is shown in Fig. 1.

![Geographical distribution of vanadium reserves. Based on data from U.S. Geological Survey](image)

Despite vanadium being found in a large variety of compounds, the majority is found in four major types of deposits [6]

- Titaniferous magnetite
- Phosphorite and phosphatic shale
- Crude petroleum and tar sands
- Minette type iron ores

### 2.2 Overview of the vanadium production process

As mentioned, the main part of the vanadium is produced from titaniferous magnetite, either in the form of vanadium containing slags as a by-product of iron and steelmaking processes or, to a lesser degree, in the form of mineral concentrates [4]. Other raw materials include other types of vanadium containing ores, spent catalysts and vanadium containing fly ashes from power plants [13]. A schematic overview of the vanadium production process is presented in Fig. 2.
Fig. 2. Schematic overview of the vanadium production process

As can be seen from Fig. 2, the main route for vanadium production is an extraction process in which vanadium pentoxide is produced. The vanadium pentoxide can be further processed into the final vanadium bearing products [6]. The main vanadium bearing products are ferrovanadium, aluminium-vanadium master alloy, vanadium metal and alloys and vanadium chemicals and catalysts [2].

2.3 Vanadium extraction from iron and steelmaking slags

As mentioned, the vanadium in the slag is extracted and purified in a hydrometallurgical process route [6]. A schematic overview of the vanadium extraction process is shown in Fig. 3.
The purpose of the salt roasting process is to convert the vanadium into a water-soluble form. By roasting the raw materials under oxidizing conditions with sodium salts added, vanadium is oxidized to its highest valence state, $V^{+5}$, and water-soluble sodium vanadate salts are formed. Commonly sodium is added in the form of soda (Na$_2$CO$_3$) and the roasting is performed at 900-1200°C. The reaction during soda roasting can be described as

$$Na_2CO_3(s) + V_2O_5(s) = NaVO_3(s) + CO_2(g)$$

During the leaching process the vanadium compounds in the roasted slag are dissolved, producing a vanadium rich solution. Water leaching of salt roasted material typically results in a vanadium extraction of 65-85%. In order to obtain a pure vanadium solution the leaching solution can be purified using e.g. solvent extraction, ion exchange separation or carbon adsorption and desorption [6].

Precipitation of the vanadium from the purified leaching solution is the final step in the vanadium pentoxide production route. Many different precipitation processes exist depending on the target vanadium pentoxide grade and the properties of the leaching solution. Traditionally, so-called red cake precipitation has been used to precipitate the vanadium from a boiling solution to which sulfuric acid is added to lower the pH to 2-3. This process results in the formation of a red-brown precipitate (“red cake”) which can fused to fused black oxide (86-92% V$_2$O$_5$) or air dried to technical grade vanadium pentoxide (83-86% V$_2$O$_5$). Another possibility is to produce ammonium metavanadate which, when thermally decomposed, can form V$_2$O$_5$ of a purity ≥99.5% [6].
As stated, the composition of the vanadium containing slag affects the vanadium extraction process. A first step in understanding the effect of the slag composition on the vanadium extraction process is to study its effect on the phase relations in the slag.
3 EXPERIMENTAL

3.1 Principle

The approach for the experimental investigation was to equilibrate synthetic slag samples at 1673 K, quench them and study the effect the Al\textsubscript{2}O\textsubscript{3}, CaO and SiO\textsubscript{2} contents on the phases present, the phase compositions and the phase fractions in the slag. A simplified slag system, compared to industrial slags, with a composition range of interest was provided by Swerea MEFOS, see Table 2. It should be noted that the vanadium content of the slag studied is approximately twice as high compared to the slags usually used in the industry today.

Table 2. Slag system and composition range of interest

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>4-6</td>
</tr>
<tr>
<td>CaO</td>
<td>1-5</td>
</tr>
<tr>
<td>FeO</td>
<td>Bal.</td>
</tr>
<tr>
<td>MnO</td>
<td>5.5</td>
</tr>
<tr>
<td>SiO\textsubscript{2}</td>
<td>1-17</td>
</tr>
<tr>
<td>V\textsubscript{2}O\textsubscript{3}</td>
<td>30</td>
</tr>
</tbody>
</table>

The use of synthetic slag allowed for a possibility to vary the Al\textsubscript{2}O\textsubscript{3}, CaO and SiO\textsubscript{2} contents individually in a controlled manner. The resulting changes in composition in the samples were balanced with FeO while keeping the MnO and V\textsubscript{2}O\textsubscript{3} contents constant in all samples.

As mentioned, vanadium can exist in multiple oxidation states. It is thus important to control the oxygen potential of the system in order to obtain results representative of the industrial conditions. The aim of the experimental approach was to set the oxygen potential during the experiments by using closed crucibles. Due to the varying FeO content in the samples, this allowed for individual oxygen potentials according to the composition of the sample.

In order to decrease the time required to reach equilibrium at 1673 K, the samples were first held for 6 h at 1873 K followed by 48 h at 1673 K.
3.2 Materials
The materials used for the experiments, along with suppliers and purities, are presented in Table 3.

**Table 3. Materials used in the experiments**

<table>
<thead>
<tr>
<th>Material</th>
<th>Purity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>99.5</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>CaO</td>
<td>99.95 (metals basis)</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Fe</td>
<td>99.9+ (metals basis)</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>99.5 (metals basis)</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>MnO</td>
<td>99.5</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>SiO₂</td>
<td>99.5</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>V₂O₃</td>
<td>98</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Ar gas</td>
<td>5.0 (99.999%)</td>
<td>AGA</td>
</tr>
</tbody>
</table>

Iron and molybdenum crucibles respectively were used to hold the material during the experiments.

3.3 Sample preparation

3.3.1 Calcination and drying of oxide powders
Prior to the experiments, the Al₂O₃, CaO and SiO₂ were calcinated at 1173K for 10 h to remove moisture and CO₂. The Fe₂O₃ and MnO were dried at 373 K for 12 h. In order to avoid oxidation, the V₂O₃ was not dried. The powders were stored in a desiccator until used.

3.3.2 Preparation of FeO
FeO was synthesized individually prior to the mixing of the slag samples. The principle of the FeO preparation was to heat a mixture of Fe₂O₃ and Fe to a temperature at which FeO is stable, see Fig. 4.
FeO and Fe powders in a ratio equivalent to 51 mol% O and 49 mol% Fe were mixed in an agate mortar for 20 minutes to ensure a homogenous material. The mixture was packed tightly into an iron crucible (OD 40 mm, ID 36 mm, H 80 mm) using a steel rod. The crucible was closed using a conical iron lid. According to Fig. 4 the resulting system corresponds to a Fe-FeO equilibrium when heated to 1163 K.

A schematic overview of the setup used for the FeO production is shown in Fig. 5.
A vertical resistance furnace with an alumina reaction tube (OD 62 mm, ID 51 mm, H 780 mm) was used. Water cooled brass pipes were used to cool the ends of the reaction tube, where the furnace was sealed with rubber stoppers. Argon gas was introduced into the reaction tube through the gas inlet in the upper rubber stopper in order to prevent oxidation of the iron crucible. A gas outlet in the lower rubber stopper allowed the gas to leave the furnace. In order to support the iron crucible and place it in the hot zone of the furnace, a smaller alumina tube (OD 39 mm, ID 31 mm, H 340 mm) was used. Small holes were drilled in the alumina tube to enable the gas to flow freely to the gas outlet. A type K thermocouple (Chromel - Alumel) was used to measure the temperature of the sample. The thermocouple was inserted through the upper rubber stopper and placed with its tip between the iron crucible and the reaction tube, level with the center of the sample.

In order to insert the sample into the furnace, the iron crucible was placed on the supporting alumina tube. The crucible and the alumina tube was inserted from the bottom of the furnace, making sure that the sample was centered in the reaction tube. The furnace was sealed with the rubber stoppers, carefully placing the thermocouple in the correct position without disturbing the iron crucible. Before starting heating the furnace, the argon gas was turned on and the furnace was flushed. The sample was heated to 1163 K and held for 60 h to allow the solid-solid reaction between the Fe$_2$O$_3$ and Fe to occur. After letting the furnace cool down, the iron crucible was removed. The sintered “FeO” pellet was gradually crushed into a powder.

3.3.3 Preparation of slag samples

A total of twenty-two slag samples, divided into three different series, were studied.

- Samples 1-12: Twelve samples divided into three subgroups, for studying the effect of each of the components Al$_2$O$_3$, CaO and SiO$_2$. In each subgroup, two of the components were fixed to compositions in the middle of the range studied while the remaining component was varied. The samples were used to study the effect of the individual components on the phases present, the phase compositions and the phase fractions in the slag.

- Samples 13-16: Four additional samples in which the maximum and minimum contents of CaO and SiO$_2$ respectively were combined. The samples, together with samples 9 and 12 with the minimum and maximum amounts of Al$_2$O$_3$, were used to investigate the extremes of the range studied, focusing on the phases present in the slag.

- Samples 17-22: Six samples with the same compositions as samples 9, 12 and 13-16 which were not quenched but allowed to cool slowly in the furnace. The samples were used to investigate the effect of cooling rate on the phases present in the slag.
The target slag compositions for samples 1-22 are presented in Table 4. Apart from the variations in the $\text{Al}_2\text{O}_3$, CaO and $\text{SiO}_2$ contents, it can be noted that the FeO content in the samples varies between 48.5 and 37.5 mass%.

**Table 4. Target slag compositions**

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>$\text{Al}_2\text{O}_3$</th>
<th>CaO</th>
<th>FeO</th>
<th>MnO</th>
<th>$\text{SiO}_2$</th>
<th>$\text{V}_2\text{O}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>1</td>
<td>45</td>
<td>5.5</td>
<td>13.5</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
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<td>43.7</td>
<td>5.5</td>
<td>13.5</td>
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<tr>
<td>3</td>
<td>5</td>
<td>3.6</td>
<td>42.4</td>
<td>5.5</td>
<td>13.5</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>5</td>
<td>41</td>
<td>5.5</td>
<td>13.5</td>
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</tr>
<tr>
<td>5</td>
<td>5</td>
<td>3</td>
<td>46.5</td>
<td>5.5</td>
<td>10</td>
<td>30</td>
</tr>
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<td>6</td>
<td>5</td>
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<td>5.5</td>
<td>12.3</td>
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</tr>
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<td>7</td>
<td>5</td>
<td>3</td>
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<td>14.6</td>
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<tr>
<td>8</td>
<td>5</td>
<td>3</td>
<td>39.5</td>
<td>5.5</td>
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</tr>
<tr>
<td>9</td>
<td>4</td>
<td>3</td>
<td>44</td>
<td>5.5</td>
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<tr>
<td>10</td>
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<tr>
<td>11</td>
<td>5.4</td>
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<td>42.6</td>
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<tr>
<td>12</td>
<td>6</td>
<td>3</td>
<td>42</td>
<td>5.5</td>
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<tr>
<td>13</td>
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<td>14</td>
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<td>15</td>
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<td>16</td>
<td>5</td>
<td>5</td>
<td>37.5</td>
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<td>17</td>
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</tr>
<tr>
<td>17</td>
<td>5</td>
<td>1</td>
<td>48.5</td>
<td>5.5</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>18</td>
<td>5</td>
<td>5</td>
<td>44.5</td>
<td>5.5</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>19</td>
<td>5</td>
<td>1</td>
<td>41.5</td>
<td>5.5</td>
<td>17</td>
<td>30</td>
</tr>
<tr>
<td>20</td>
<td>5</td>
<td>5</td>
<td>37.5</td>
<td>5.5</td>
<td>17</td>
<td>30</td>
</tr>
<tr>
<td>21</td>
<td>4</td>
<td>3</td>
<td>44</td>
<td>5.5</td>
<td>13.5</td>
<td>30</td>
</tr>
<tr>
<td>22</td>
<td>6</td>
<td>3</td>
<td>42</td>
<td>5.5</td>
<td>13.5</td>
<td>30</td>
</tr>
</tbody>
</table>
The samples were prepared individually, aiming at a sample weight of 5 g. The appropriate amounts of each oxide powder were mixed in an agate mortar for 10 minutes to ensure a homogenous material. Pellets (Ø 11 mm) were prepared by uniaxially pressing the mixture in a steel die, applying a pressure of 10 MPa. The pellets were placed in molybdenum crucibles (OD 14 mm, ID 13 mm, H 40 mm) and stored in a desiccator until used in the experiments. Each sample was weighed in order to monitor any weight change.

3.4 Setup

A schematic overview of the setup used for the equilibrium experiments is shown in Fig. 6.

![Schematic overview of the furnace setup used for the equilibrium experiments](image_url)

Fig. 6. Schematic overview of the furnace setup used for the equilibrium experiments

A vertical resistance furnace with Kanthal heating elements and an alumina reaction tube (OD 80 mm, ID 70 mm, H 1000 mm) was used. At the top of the furnace the reaction tube was connected to a water cooled aluminium quenching chamber. This allowed for quick cooling of the samples without withdrawing them from the furnace. A smaller water cooled aluminium cooling chamber was connected to the bottom of the reaction tube. Argon gas was introduced into the furnace to avoid oxidation of the molybdenum parts. Two gas inlets, one in the lower cooling chamber and one in the upper quenching chamber, were used. The upper gas inlet was used during quenching to enhance the cooling of the samples. A gas outlet in the quenching chamber allowed the gas to leave the furnace. In order to control the argon gas flow during the experiments a Bronkhorst flow meter was used. The samples were held using a molybdenum sample holder (OD 54 mm, ID 48 mm, H 120 mm) connected to a computer controlled lifting system via a steel rod with a molybdenum extension. The samples
could thus be lowered and raised in the furnace in a controlled manner. A type B thermocouple (70%Pt/30%Rh – 94%Pt/6%Rh) with its tip placed just below the sample holder was used to measure the sample temperature. The reaction chamber was sealed from the surrounding atmosphere using O-rings and radial seals.

### 3.5 Procedure
The samples, between three and six for each run, were placed in the sample holder. In order to keep the crucibles from moving or tipping over during the experiments molybdenum wire was used to hold them together. For each run a lid was made from molybdenum sheet. The lid was placed on the crucibles and pressed down using a molybdenum disc (Ø 30 mm, H 5 mm). The sample holder was connected to the lifting rod using two molybdenum screws. It was thereafter lowered into the quenching chamber, in which the samples were held during heating of the furnace. Special care was made to ensure the reaction chamber was vacuum tight. Using a vacuum pump, the furnace was evacuated for 60 minutes before being filled with argon gas. During the experiments the argon flow rate was set to 0.1 l/min. The furnace was heated up to 1873 K with a heating rate of 1.7-2 K/min. When the target temperature was reached, the samples were slowly lowered into the hot zone to avoid cracking the reaction tube due to thermal shock. Lowering of the samples took approximately 30 minutes. The samples were held at 1873 K for 6 h before lowering the temperature to 1673 K at a rate of 2 K/min. After the temperature had stabilized the samples were held at 1673 K for 48 h. The samples were raised to the quenching chamber in a few seconds in order to quench the samples. During quenching argon gas was introduced into the quenching chamber with a flow rate of 0.8 l/min. Samples 19-24, which were not quenched, were left in the hot zone as the furnace cooled down at a rate of 2 K/min. Each sample was weighed in order to monitor any weight change. The crucibles were cracked and the slag and crucible were separated. The collected slag was stored in a desiccator until prepared for analysis.

### 3.6 Analysis
In order to investigate the phases present and their composition scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDS) was used. A piece of each slag sample was hot mounted in conductive resin (Struers PolyFast). The mounted samples were ground and polished in ethanol to avoid oxidation. A diamond paste with a particle size of 3 µm (MTI Corporation) was used during polishing. Before analysis, each sample was gold coated using a JEOL JFC-1300 to ensure a conductive surface. A Hitachi S-3700N SEM with a Bruker EDS analyzer was used for the analysis. The phase fractions were estimated using light optical microscopy (LOM) in combination with an image analysis software. In order to decrease the mounting induced cracks in the samples, a piece of each sample was cold mounted in an epoxy resin (Struers EpoFix). The mounted samples were then ground and polished as described above. An Olympus PMG3 LOM with the image analysis software Leica QWin was used for the analysis.
4 RESULTS
4.1 Morphology

From the SEM investigation of the slag samples it was seen that the general microstructure consisted of angular particles embedded in a multiphase matrix. Typical examples of the microstructures of the quenched samples are presented in Fig. 7.

![SEM micrographs at 500x magnification of (a) sample 8; (b) sample 15](image)

**Fig. 7.** SEM (BSE) micrographs at 500x magnification of (a) sample 8; (b) sample 15

From Fig. 7 it can be seen that the matrices had a dendritic structure. It can also be seen that the coarseness of, primarily, the matrices varied between the samples.

A uneven phase distribution was seen in the samples, see Fig. 8 for an illustration.

![SEM micrographs at 150x magnification of sample 1](image)

**Fig. 8.** SEM (BSE) micrographs at 150x magnification of sample 1

The structures shown in Fig. 8 represent what was typically observed. Larger areas of matrix, with no particles present, could be seen in practically all samples. This uneven phase distribution was seen locally. The structure showed no signs of an overall uneven phase distribution in the samples. Fig. 8 (b) also shows some porosity, which was commonly found in the samples.

The effect of slow cooling on the sample morphology was mainly a coarser matrix structure. The coarseness of the particles was not affected significantly by slow cooling. For some samples slow cooling resulted in a larger number of matrix phases compared to the corresponding quenched sample.
For a comparison of the structure between a quenched and slow cooled sample see Fig. 9. Note that the samples shown have the same composition.

![Fig. 9. SEM (BSE) micrographs at 150x magnification of (a) sample 12; (b) sample 22](image)

**4.2 Phase compositions**

The EDS analyses showed that the angular particles consisted of a vanadium and iron rich phase. The matrices were shown to consist of mainly iron and silicon rich phases. No free silica or solid phases in which both calcium and vanadium concentrate to a significant extent were found in any sample. This applies to the quenched as well as the slow cooled samples. The major phases observed are marked A - C in Fig. 10. Note that this division of the observed phases is based on morphology and composition.

![Fig. 10. SEM (BSE) micrograph at 500x magnification of sample 1. The major phases observed are marked A-C](image)

The composition ranges for phases A-C, obtained by EDS analysis, are presented in Table 5. The dashes in Table 5 do not necessarily indicate that the element in question was not detected at all but that the analyzed contents were very low. Note that all compositions obtained from EDS analysis are given as normalized compositions with molybdenum excluded unless otherwise stated.
Table 5. Composition ranges for phases A-C

<table>
<thead>
<tr>
<th>Phase</th>
<th>Comp. [mass%]</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>FeO</th>
<th>MnO</th>
<th>SiO₂</th>
<th>V₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td>&lt;6</td>
<td>-</td>
<td>38-44</td>
<td>3-5</td>
<td>-</td>
<td>47-57</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>-</td>
<td>&lt;16</td>
<td>48-65</td>
<td>10-13</td>
<td>21-27</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>11-18</td>
<td>6-22</td>
<td>26-34</td>
<td>4-6</td>
<td>28-45</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

From Table 5 it can be seen that phase A mostly consisted of iron and vanadium, with low amounts of aluminium and manganese. It is also clear that vanadium was almost exclusively concentrated to phase A. The matrix phases, phases B and C, were iron and silicon rich phases into which practically all of the silicon and calcium concentrated. It can be noted that there was practically no aluminium in phase B.

Area scans of the matrices using EDS analysis were made in order to determine their average compositions. The composition range obtained by EDS analysis of the matrices is presented in Table 6.

Table 6. Composition range for the matrices

<table>
<thead>
<tr>
<th>Comp. [mass%]</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>FeO</th>
<th>MnO</th>
<th>SiO₂</th>
<th>V₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6-8</td>
<td>3-18</td>
<td>41-58</td>
<td>8-9</td>
<td>23-31</td>
<td>-</td>
</tr>
</tbody>
</table>

From Table 6 it can be seen that the matrices consisted of mainly iron and silicon. The analyses showed that these components, presented as FeO and SiO₂, made up approximately 65-80 mass% of the matrices. It can also be seen that only calcium, iron and silicon varied to a large extent in the matrices. The aluminium and manganese contents were relatively constant.

The effect of the contents of Al₂O₃, CaO and SiO₂ on the compositions of the matrix and phase A was investigated using EDS analysis. The composition of the matrix was analyzed using area scans. At least four measurements for each sample and phase/area were made and an average was calculated. It should be remembered that all changes in composition made regarding Al₂O₃, CaO and SiO₂ were balanced with FeO.
4.2.1 Effect of Al$_2$O$_3$

The effect of Al$_2$O$_3$ on the phase compositions was investigated over the range 4-6 mass% Al$_2$O$_3$. The CaO and SiO$_2$ contents were kept constant at 3 and 13.5 mass% respectively. The contents of the components in the matrix and phase A plotted as a function of total Al$_2$O$_3$ content are presented in Fig. 11.

![Graphs showing the content of components as a function of total Al$_2$O$_3$ content in samples 1-4](image)

**Fig. 11.** Contents of the components in (a) the matrix; (b) phase A plotted as function of total Al$_2$O$_3$ content in samples 1-4
4.2.2 Effect of CaO

The effect of CaO on the phase compositions was investigated over the range 1-5 mass% CaO. The Al₂O₃ and SiO₂ contents were kept constant at 5 and 13.5 mass% respectively. The contents of the components in the matrix and phase A plotted as a function of total CaO content are presented in Fig. 12.

![Graphs of component contents vs. total CaO content for matrix and phase A in samples 5-8](image)

**Fig. 12.** Contents of the components in (a) the matrix; (b) phase A plotted as function of total CaO content in samples 5-8
4.2.3 Effect of SiO$_2$

The effect of SiO$_2$ on the phase compositions was investigated over the range 10-17 mass% SiO$_2$. The Al$_2$O$_3$ and CaO contents were kept constant at 5 and 3 mass% respectively. The contents of the components in the matrix and phase A plotted as a function of total SiO$_2$ content are presented in Fig. 13.

![Graph depicting the effect of SiO$_2$ on phase compositions][1]

**Fig. 13.** Contents of the components in (a) the matrix; (b) phase A plotted as function of total SiO$_2$ content in samples 9-12.
4.3  Phase fractions
The effect of the composition on the fraction of phase A was analyzed using a LOM in combination with an image analysis software. The fraction of phase A was estimated from the two-dimensional area fraction obtained from the LOM images. Ten images per sample were used to calculate an average fraction.

4.3.1  Effect of Al₂O₃
The effect of Al₂O₃ on the fraction of phase A was investigated over the composition range stated in section 4.2.1. The estimated fraction of phase A plotted as a function of total Al₂O₃ content is presented in Fig. 14.

![Graph: Fraction of phase A plotted as function of total Al₂O₃ content in samples 1-4]

**Fig. 14.** Fraction of phase A plotted as function of total Al₂O₃ content in samples 1-4

4.3.2  Effect of CaO
The effect of CaO on the fraction of phase A was investigated over the composition range stated in section 4.2.2. The estimated fraction of phase A plotted as a function of total CaO content is presented in Fig. 15.
4.3.3 Effect of SiO$_2$

The effect of SiO$_2$ on the fraction of phase A was investigated over the composition range stated in section 4.2.3. The estimated fraction of phase A plotted as a function of total SiO$_2$ content is presented in Fig. 16.

**Fig. 15.** Fraction of phase A plotted as function of total CaO content in samples 5-8

**Fig. 16.** Fraction of phase A plotted as function of total SiO$_2$ content in samples 9-12
5 DISCUSSION

5.1 Phases

The composition and morphology of phase A indicate that it is an iron-vanadium spinel phase. This is in accordance with what is usually observed in vanadium containing slags of similar type. The calcium content in the spinel phase was very low for all CaO contents in the slag. This supports that CaO does not dissolve significantly in the spinel phase. The varying iron and vanadium contents, along with the presence of aluminium and manganese, indicate that it is not a stoichiometric phase. Instead, it is more probable that it is a solid solution phase in which some of the constituent elements are present in multiple oxidation states occupying different lattice sites. Phase A being an iron vanadium spinel phase suggest that the phase was present at 1673 K, see Fig. 17 for the FeO-V₂O₃ phase diagram. The morphology, along with the limited change in spinel particle size with a change in the cooling rate support that the spinel phase was present at 1673 K.

![FeO-V₂O₃ phase diagram](image)

**Fig. 17.** FeO-V₂O₃ phase diagram [8]

The structure of the matrices suggests that phase B was precipitated during cooling of the samples and thus that the matrix was liquid at 1673 K. This is also supported by the matrix structure becoming coarser with a decreasing cooling rate. The area analyses of the matrices were used to further investigate this possibility. The matrix compositions acquired were reduced to the three ternary systems, Al₂O₃-FeO-SiO₂, CaO-FeO-SiO₂ and FeO-MnO-SiO₂, and the normalized compositions were plotted in the corresponding phase diagrams, see Fig. 18-Fig. 20.
Fig. 18. Liquidus surface of the ternary system Al₂O₃-FeO-SiO₂ [14]. The marked area corresponds to the composition range of interest.

Fig. 19. Liquidus surface of the ternary system CaO-FeO-SiO₂ [14]. The marked area corresponds to the composition range of interest.
Fig. 20. Liquidus surface of the ternary system FeO-MnO-SiO$_2$ [14]. The marked area corresponds to the composition range of interest.

Fig. 18-Fig. 20 show that the compositions plotted would all be liquid at 1673 K. It should, however, be remembered that this approach is based on simplified versions of the matrices. The matrices being liquid means that the quenching was not fast enough too “freeze” the state of the slag samples at 1673 K. Further experiments with more efficient quenching are required to verify if the matrices were actually liquid.

The matrix phases, phases B and C, are, based on the analyzed compositions, probably iron rich silicates. The varying compositions once again imply that these are not stoichiometric phases. Based on its composition, phase B could be an olivine phase. From Fig. 18-Fig. 20 it can be seen that, for the compositions marked, it is not unlikely that an olivine phase, containing iron, manganese, calcium and silicon, would precipitate from the liquid phase during cooling. This is also in accordance with previous observations in vanadium containing slags of similar type. Phase C is an even more complex phase which includes all slag components except vanadium. A possibility, apart from phase C being a silicate phase, is that it is a glassy phase. This is supported by the observation that more phases were present in the matrix in slow cooled samples compared to quenched samples. In order to further characterize the observed phases, a crystallographic investigation using e.g. XRD could be conducted.

Finally, Fig. 18-Fig. 20 might also give an indication of why no free silica was found. It can be seen that the FeO-SiO$_2$ ratios of the marked compositions are such that no silica should precipitate from the liquid at 1673 K.
5.2 Effect of Al$_2$O$_3$, CaO and SiO$_2$ on the phase compositions and phase fractions

It has been concluded that the slag samples most likely consisted of a mixture of spinel particles and a liquid phase at 1673 K. The matrix and phase A will hereafter be referred to as “liquid phase” and “spinel phase”.

5.2.1 Effect of Al$_2$O$_3$

The results showed that the effect of an increasing Al$_2$O$_3$ on the compositions of the liquid phase and the spinel phase were small. Al$_2$O$_3$ distributed between both phases and a slight increase in the Al$_2$O$_3$ contents in both the liquid phase and the spinel phase could be seen as the overall content increased. No big effect on the FeO contents could be seen. The contents of the components which only concentrate to one phase, i.e. CaO, SiO$_2$, and V$_2$O$_5$, were practically constant. This indicates that the effect of Al$_2$O$_3$ on the phase fractions is also small. This is, to some extent, supported by the results from the investigation of the effect of the overall Al$_2$O$_3$ content on the fraction of spinel, where no clear change could be observed. The variations seen are likely within the uncertainty of the analysis method used. The very limited effects of an increasing Al$_2$O$_3$ content observed could be a consequence of the range over which the Al$_2$O$_3$ was varied being narrow. This could lead to any actual effects being smaller than the errors of the analysis methods used.

5.2.2 Effect of CaO

An increasing overall CaO content was seen to almost exclusively affect the composition of the liquid phase. Due to the very low contents of CaO in the spinel phase, practically all CaO added went to the liquid phase. This resulted in, approximately, a five times increase of the CaO content in the liquid phase, as the overall content increased from 1 to 5 mass%. At the same time, a decrease in the FeO content of the liquid phase almost corresponding to the increase in CaO content in the liquid phase, could be seen. A very small change could be seen in the remaining components. It thus seems as if CaO and FeO can substitute in the liquid phase. Regarding the spinel phase, the composition remained virtually unaffected by the change in overall CaO content. It is notable that observed change in the FeO content in the liquid phase did not seem to have any effect on the FeO content in the spinel phase. The almost complete compensation of the increase of the CaO content in the liquid phase by a decrease of the FeO content in the liquid phase, along with the unaffected composition of the spinel phase, indicates that CaO has a small effect on the phase fractions. This is, once again, supported by the results from the investigation of the effect of the overall CaO content on the fraction of spinel, where no clear change could be observed.

5.2.3 Effect of SiO$_2$

The results indicate that a change of overall SiO$_2$ content affects the composition of both the liquid phase and the spinel phase in several ways. First of all, the SiO$_2$ content in the liquid phase increased as the overall content increased. However, this was only approximately a 20% increase while the overall content increased with 70%. It should be noted here that SiO$_2$ was only found in the liquid
phase. Furthermore, moderate decreases in the CaO and FeO contents in the liquid phase with increasing overall SiO$_2$ content could be seen. No change in the Al$_2$O$_3$ and MnO contents could be seen. Regarding the spinel phase, an increase of the V$_2$O$_3$ content was seen with an overall increase in the SiO$_2$ content. At the same time the FeO content decreased. Also in the spinel phase, the contents of Al$_2$O$_3$ and MnO remained constant. These compositional changes suggest that the fraction of spinel phase decreases, i.e. the fraction of liquid increases, with increasing overall SiO$_2$ content. This is supported by the results from the investigation of the fraction of spinel, where a decreasing fraction of spinel phase is seen with an increasing overall SiO$_2$ content. The small decrease in FeO content in the liquid phase along with the decrease in FeO content in the spinel phase would, based on a decreasing fraction of spinel phase, require a redistribution of FeO from spinel phase to liquid phase. The same principle applies to the Al$_2$O$_3$ and MnO contents. Assuming a decreasing fraction of spinel phase, practically constant Al$_2$O$_3$ and MnO contents in both phases would require a redistribution of these components from spinel phase to liquid phase. It should, however, be remembered that the contents of Al$_2$O$_3$ and MnO were low and that small changes in these components are within the uncertainty of the analysis method.

5.3 Experimental uncertainties
The average sample weight before the experiments, the average total sample and crucible weight before the experiments and the weight change during the experiments are presented in Table 7. The observed weight change was negative for all samples, meaning a weight loss.

Table 7. Weight data, averaged

<table>
<thead>
<tr>
<th>Sample weight [g]</th>
<th>Sample + crucible weight [g]</th>
<th>Weight change [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.9506</td>
<td>15.2157</td>
<td>-0.0190</td>
</tr>
</tbody>
</table>

It was seen that the average weight loss was very small compared to both the sample weight and the total sample and crucible weight. The average relative weight losses were approximately 0.38% and 0.12% respectively. This indicates that the exchange of material with the surroundings was limited. The slag components and the crucible should thus not have been reduced or oxidized to any large extent. Furthermore, no large amounts of material should have been lost through evaporation. Accurate analysis of the total slag compositions could be used to verify the approach additionally.

As mentioned, all the compositions and composition ranges presented have been normalized with molybdenum excluded. In general, molybdenum was primarily detected in the spinel phase during the EDS analyses. The molybdenum content in the spinel phase, analyzed and presented as MoO$_2$, was in the range 2-6 mass%. Assuming that this is the main part of the molybdenum dissolved, the total molybdenum content should be significantly lower. Since molybdenum was practically not found in the liquid phase it can be expected that the effect of the dissolved molybdenum on the presence of free
silica was small. To further investigate the effect of the molybdenum on the results, more experiments using alternate crucible materials, e.g. platinum, could be used.

The compositional variations in the individual samples were in general small. As an illustration, the results from the EDS analysis of four different spinel particles and four different areas of “liquid” in sample 5 are shown in Table 8. Note that the presented data is the compositions obtained from the analyses, with molybdenum included.

**Table 8. Compositions of the spinel phase and the liquid phase obtained from EDS analysis of sample 5**

<table>
<thead>
<tr>
<th>Comp. [mass%]</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>FeO</th>
<th>MnO</th>
<th>SiO₂</th>
<th>V₂O₃</th>
<th>MoO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinel</td>
<td>4.38</td>
<td>-</td>
<td>41.46</td>
<td>4.29</td>
<td>-</td>
<td>45.78</td>
<td>4.10</td>
</tr>
<tr>
<td>4.81</td>
<td>-</td>
<td>40.66</td>
<td>4.24</td>
<td>-</td>
<td>45.17</td>
<td>5.12</td>
<td></td>
</tr>
<tr>
<td>4.82</td>
<td>-</td>
<td>40.56</td>
<td>4.33</td>
<td>-</td>
<td>45.54</td>
<td>4.75</td>
<td></td>
</tr>
<tr>
<td>4.41</td>
<td>-</td>
<td>41.30</td>
<td>4.39</td>
<td>-</td>
<td>45.38</td>
<td>4.53</td>
<td></td>
</tr>
<tr>
<td>Liquid</td>
<td>5.97</td>
<td>10.86</td>
<td>49.48</td>
<td>8.91</td>
<td>24.55</td>
<td>0.23</td>
<td>-</td>
</tr>
<tr>
<td>6.46</td>
<td>11.59</td>
<td>47.07</td>
<td>8.55</td>
<td>25.99</td>
<td>0.34</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>6.36</td>
<td>11.23</td>
<td>48.08</td>
<td>8.65</td>
<td>25.33</td>
<td>0.35</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>6.47</td>
<td>11.11</td>
<td>48.36</td>
<td>8.39</td>
<td>25.02</td>
<td>0.64</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

The results presented in Table 8 are representative of what was typically observed from the analyses and suggest that the samples were relatively homogeneous with respect to composition of the phases. To further investigate the compositional variations in the samples, line analyses of spinel particles were made. The results from a line analysis of a spinel particle in sample 1 are presented in Fig. 21.
Fig. 21. SEM (BSE) micrograph at 1500x magnification of a spinel particle in sample 1 and the analyzed contents of Al, Fe, Mn, Si and V along the marked line.

Fig. 21 shows that the average compositions of the components analyzed are relatively constant over the spinel particle with no overall gradients. An abrupt change in the compositions is however seen at the interface between spinel particle and matrix. The absence of gradients in the spinel phase indicates that the holding time at 1673 K was enough with respect to equilibrium.

The uneven phase distribution in the samples resulted in large variations in the measured fraction of spinel phase in the same sample. An example of this is shown in Fig. 22, were two LOM images with the corresponding histograms for sample 8 are presented.
Fig. 22. LOM images of sample 8 with the corresponding histograms. The bars in the histograms represent the areas interpreted as spinel phase (right bar) and matrix (left bar) respectively.

From Fig. 22 it becomes evident that the distribution of the phases have a large effect on the estimated fractions. Comparing the two images and the corresponding histograms it is seen that the phase fractions practically become opposite. Due to the issues mentioned the result from the estimation of the fraction of spinel phase should primarily be used to detect overall trends. Preferably, the results from the investigation of the phase fractions and phase compositions should be interpreted jointly.
6 SUMMARY

In this thesis the effect of Al$_2$O$_3$, CaO and SiO$_2$ on the phase relations in vanadium containing slags has been investigated experimentally. Synthetic slags with varying Al$_2$O$_3$, CaO and SiO$_2$ contents were prepared and equilibrated at 1673 K followed by quenching. The effect of the individual components on the phases present, the phase compositions and the phase fractions were studied using SEM-EDS and LOM. The results indicate that

- The phases present at 1673 K were a vanadium and iron rich spinel phase and an iron and silicon rich liquid phase
- Practically all the vanadium was concentrated to the spinel phase
- No free silica or solid phases into which both calcium and vanadium concentrate to a significant extent were observed
- The effect of Al$_2$O$_3$ on the phase compositions and phase fractions was limited
- An increasing CaO content primarily affected the composition of the liquid phase. The main effect was a substitution of FeO with CaO. The effect on the phase fractions was limited
- An increasing SiO$_2$ content affected both the phase compositions and the phase fractions. The main effect was a decreasing spinel fraction resulting in an increasing vanadium content in the spinel phase
7  FUTURE WORK

The work done in this thesis has been focused only on the effect of the studied components on the phase relations in the slag. From an industrial perspective, it would be interesting to perform roasting and leaching trials based on the results of this thesis. Only by doing this, the effect of the studied components on the vanadium extraction process as a whole can be evaluated. Furthermore, the scope of this thesis was limited to a given slag composition range. To get more general and complete picture of the effect of the investigated components it would be interesting to study a wider composition range. As mentioned, this could also help making any trends clearer.
REFERENCES


