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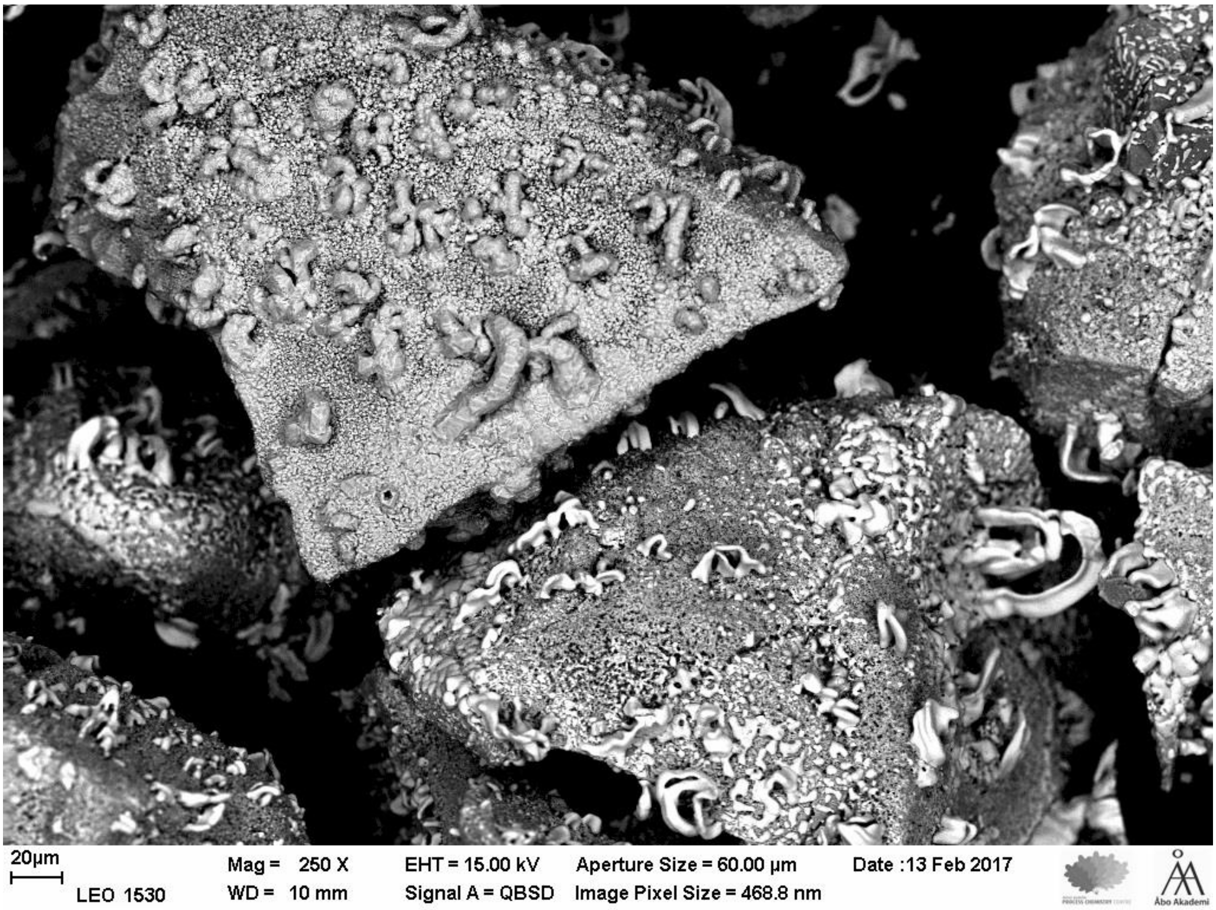

Interaction between potassium salts and ilmenite under reducing conditions relevant for Chemical Looping Combustion (CLC)

Master’s thesis in Innovative and Sustainable Chemical Engineering, CTH

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Division of Energy and Materials
CHALMERS UNIVERSITY OF TECHNOLOGY
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Cover:
The figure shows a Scanning Electron Microscopy (SEM) picture of an ilmenite particle that has been heated to 850 °C for 6 hours in reducing environment in the presence of potassium sulfate.

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Abstract

Combustion of fossil fuel, such as coal for electricity production, is one of the greatest sources of CO_2 emissions that contribute to climate change. Carbon capture and storage (CCS) is a technique to reduce the CO_2 emissions to the atmosphere by injection of the CO_2 to the earth crust. To inject CO_2, the CO_2 needs to be captured. However, today this is a very expensive process since it requires an expensive gas separation. Chemical looping combustion (CLC) is a technique that can be used to isolate CO_2 directly in the combustion process, without any gas separation so that the CO_2 emission can be prevented. If CLC is applied on biofuels (Bio-CLC) negative emissions of CO_2 can be achieved.

The CLC process uses a so-called oxygen carrier (OC) that transports the oxygen between the two separate reactors. These OC's are commonly a metal oxide based on the transition metals. Unfortunately, many of these are too expensive to be conventionally used when solid fuels are combusted in a CLC process since the precense of ash deactivates the OC. The iron and titanium based ore ilmenite are a material that can be used as an OC that is not too expensive. However, how ilmenite interacts with salts present in bio ash is not well studied in reducing conditions relevant for the fuel reactor in the CLC process.

In this work interaction of ilmenite with potassium salts was studied. Ilmenite particles were mixed with potassium salts and reduced with CO at 850°C, both in the presence of steam and without steam. The potassium salts for these experiments where K_2CO_3, KCl, K_2SO_4 and KH_2PO_4. The retrieved samples were analyzed using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and powder X-ray diffraction (XRD). Mixtures of ilmenite and potassium salts were also investigated using thermogravimetric analysis (TGA), at 850°C under dry conditions.

From these experiments, it was concluded that the potassium salts K_2CO_3, KCl and K_2SO_4 increase the reactivity of the ilmenite. Chlorides left the samples either as KCl when no steam was present or as KOH and KCl if steam was present. KH_2PO_4 formed KPO_3 that melted and formed a protective coating of the particles. This coating may cause the sample to agglomerate and decrease the reaction rate of the ilmenite OC. It was also concluded that steam has a great effect on the behavior of the ilmenite and potassium salt interaction.

Keywords: Chemical looping combustion, oxygen carriers, ilmenite, bio ash, potassium salts, alkali roasting, agglomeration and sintering

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Fredrik Hildor, Turku, May 2017

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1 Introduction

One of today's greatest challenges is climate change mitigation. CO_2 emissions from burning fossil fuels for the production of electricity are one of the greatest contributors to greenhouse gas emissions which contribute to climate change. Today the energy sector contributes to some 35 % of the total greenhouse gas emissions and is thereby the largest contributing sector to global warming (IPCC, 2014). To mitigate the climate change, several possible technical solutions exist for the energy sector. The International Panel about Climate Change, IPCC, published a special report regarding one of the opportunities for CO_2 reduction, Carbon Capture and Storage (CCS). With CCS, the emissions of CO_2 from humans can be reduced to closely zero or even become negative if the CO_2 from combustion of biofuels is captured and stored. Negative emissions can have a great economic importance in the future depending on the cost of CO_2 emissions. Negative emissions will be an important tool to restore the CO_2 level to a sustainable level (IPCC, 2005). CCS using either fossil or biofuels are illustrated in C and D in Figure 1. Here the flow of carbon either goes from the ground back to the ground or from the atmosphere to the ground. The coal flow of CCS can be compared to conventional combustion of fossil fuel and biofuel, A and B in the same figure. Here the coal either is extracted from the ground and emitted as CO_2 to the atmosphere or recirculated from the atmosphere via biomass and combustion of biofuel.

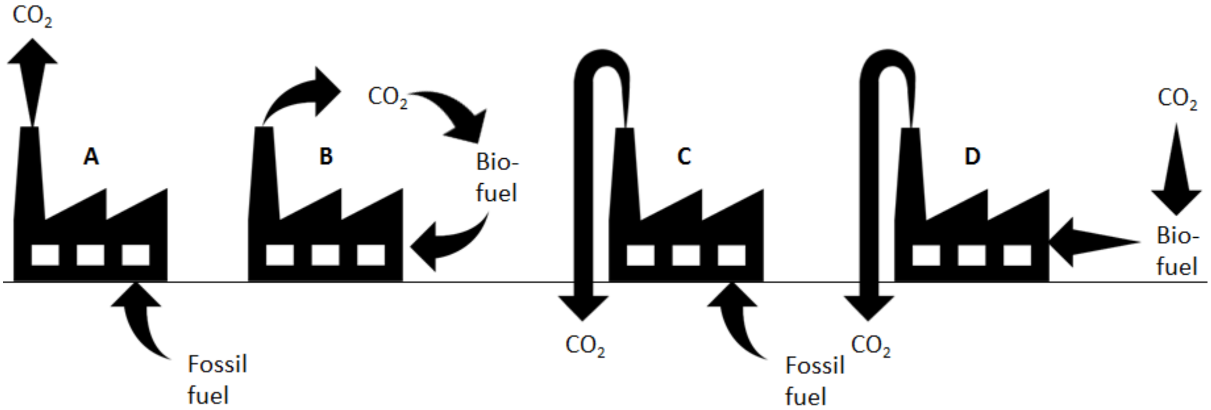

Figure 1. The coal flow for fossil and biomass fuels using conventional combustion or CCS. A) Conventional combustion of coal with CO_2 emissions to the atmosphere. B) Conventional combustion of biomass with a circulation of carbon through the atmosphere to the biomass. C) CCS using coal where the carbon emitted from the coal combustion is reinstated to the earth crust. This technique contributes to ZERO CO_2 emission to the atmosphere. D) CCS using biomass where the carbon is absorbed by the biomass and then, after combustion, introduced to the earth crust. This results in NEGATIVE emissions (IPCC, 2005).

To be able to store the CO_2 it needs to be captured. Generally, the cost of the capturing is the largest. The cost can be several times higher compared to the cost for storage and injection into the earth crust. Several techniques to separate the CO_2 from combustion processes are available. These techniques can be divided into three different systems: pre-combustion, oxy-fuel and post-combustion separation systems (IPCC, 2005).

A post-combustion system means that the CO_2 is separated from the flue gasses of a power plant. These types of techniques can normally be applied to existing plants increasing the interest of these technologies. However, flue gas contains a relatively low concentration of CO_2 and a high content of N_2 when combusting with air. This requires a gas separation that is both technically challenging and expensive which results in an energy penalty for these types of combustion technologies. Usually, not all CO_2 can be extracted and the plant will only decrease its CO_2 emissions, not erase them when using fossil fuel (IPCC, 2005).

Pre-combustion technologies will separate the carbon before the combustion with air. The separation can be done by gasifying the fuel to syngas either by steam reforming or partial oxidation (gasification if solid fuels) followed by a water gas shift reaction. This produces a gas containing hydrogen and CO_2 that is easy to separate. After the separation of CO_2, hydrogen can be used in a conventional combustion process, in fuel cells or other industrial applications (IPCC, 2005). However, this technology still comes with a cost penalty for the separation and for the pure oxygen that is needed for the partial oxidation (Hossain & de Lasa, 2008).

Oxy-fuel combustion technologies use pure oxygen as oxidation media mixed with recycled CO_2 from the flue gasses. This results in concentrated CO_2 and steam together with gaseous residues from the fuel in the flue gas. After gas treatment and condensation of steam more or less pure CO_2 is gained. However, this technology requires large quantities of pure gaseous oxygen. Pure oxygen is obtained by an expensive gas separation of oxygen from the air that results in an energy penalty that also makes this technology expensive (IPCC, 2005; Hossain & de Lasa, 2008).

As a sub-category within the oxy-fuel combustion, is one developing technology called Chemical-Looping Combustion (CLC). This technology uses a so-called oxygen carrier (OC), often a transition metal oxide, to separate the oxygen from the air with low or no energy penalty. The OC is oxidized in a separate reactor and then relocated into another reactor where it can oxidize the fuel. This generates a flue gas containing CO_2, steam and gaseous residues from the fuel. This flue gas is treated to condense the steam and remove the residues to achieve pure CO_2 that can be stored to prevent greenhouse gas emissions. The reduced OC is then reentered to the air reactor there it is oxidized again to be used again to move oxygen. The advantage of this technique is that it does not require an expensive gas separation as the other techniques described above (IPCC, 2005; Hossain & de Lasa, 2008).

For a metal oxide particle that serves as OC several conditions need to be fulfilled such as low cost, low toxicity and good reactivity. A more detailed list can be seen in section 3.2 (Cuadrat et al., 2012). Most of these conditions are fulfilled by the transition metals such as iron, nickel, cobalt, manganese and copper (Hossain & de Lasa, 2008). Iron based OCs are particularly interesting since they are abundant, cheap and non-toxic (Fan et al., 2012). Ilmenite is an iron-titanium oxide mineral that is particularly interesting to apply in CLC since it is naturally abundant and fulfills all criteria's given by Cuadrat et al. (2012).

Many different aspects of CLC and OCs have been studied using gaseous fuels. More recently solid fuels have been more investigated (Leion, Mattisson & Lyngfelt, 2008).The reason why solid fuels, such as coal, are of great interest for CCS and therefore also CLC is due to their great abundance in the world and their large potential contribution to global warming. The abundant coal reserves have an estimated potential to contribute to 3260 billion ton CO_2 (EIA, 2011) compared to 385 billion ton CO_2 (CIA, 2016) stored in abundant natural gas reserves.

Unfortunately, the ash content in solid fuel is much higher compared to gaseous fuels. This increases the strains on the OC. In addition, biofuels have a high concentration of alkali metals that make the ash even more reactive and corrosive (Demirbas, 2005). Alkali metals, such as potassium, are also known to increase the agglomeration tendency of bed material in a fluidized bed boiler. Agglomeration can lead to defluidization and collapse of the boiler (Elled, Åmand & Steenari, 2013).

2 Aim of the study

The aim of this study is to investigate the interaction between ilmenite and potassium salts to understand the properties of ilmenite in a CLC process better. Studies of ilmenite as an OC have been done before (Knutsson & Linderholm, 2015; Leion, Mattisson & Lyngfelt, 2008; Linderholm et al., 2016). However, only a few have considered the interaction with bio ash separately and what effects that will have on the properties of the OC (Azis et al., 2013; Corcoran et al. 2014).

The focus of this study is to investigate the interaction between potassium salts and ilmenite under conditions that are relevant for the reducing fuel reactor in a CLC process i.e. where the concentration of ash is the largest. The conditions mimic the complex environment in a simplified way to be able to determine the effect of different salts present in bio ash.

2.1 Restrictions of the present work

This study will only investigate potassium salts since these contribute most to the agglomeration in fluidized beds where the bed material is silicon (Elled, Åmand & Steenari, 2013). The investigation will mostly be performed in reducing conditions since the same investigation of the interaction between ilmenite and potassium salts in oxidative conditions has already been performed (Zevenhoven et al., 2017).

3 Background and Theory

3.1 Chemical-looping combustion

CLC is a technique where the oxidation of the fuel with oxygen from the air is performed in two separate reactors, normally circulating fluidized bed reactors, using a solid OC. The first reactor is the so-called "air reactor" where the OC is oxidized by the oxygen in the air. Thereafter, the oxidized OC is introduced into the second reactor, the so-called "fuel reactor". In this reactor, the fuel is introduced resulting in a reducing environment where the OC give up its oxygen to the fuel that is oxidized producing CO_2 and steam. The CO_2 and steam can easily be separated by condensation of the steam. The more or less pure CO_2 gas can then be compressed and injected into the storage area in the earth crust. The fuel reactor uses steam with recirculated flue gasses as fluidization media. After the fuel reactor, the OC is recirculated into the air reactor to be oxidized and then used again in the fuel reactor (Hossain & de Lasa, 2008). Figure 2 illustrates the general CLC process that is described above.

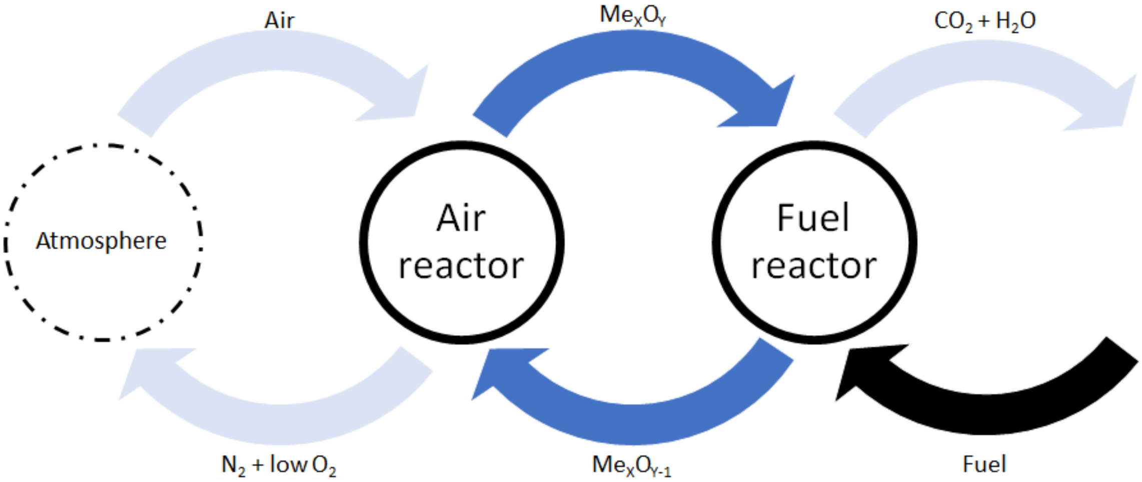

Figure 2. A general flow sheet for the CLC process with the OC loop in the center of the figure (Leion et al., 2008).

When using solid fuels gasification of the fuel will occur in the fuel reactor. Reaction (1) and (3) describes some of the most common gasification reactions. Reaction (2) describes the shift reaction (Leion, Mattisson & Lyngfelt, 2007). The two reactions that occur in the fuel reactor with syngas and OC are described below with reactions (4) and (5). The regeneration of the OC is then performed according to reaction (6) in the air reactor (Cuadrat et al., 2012).

$$C + H_2O \rightarrow CO + H_2 \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2}$$

$$C + CO_2 \rightarrow 2CO \tag{3}$$

$$Me_XO_Y + H_2 \rightarrow Me_XO_{Y-1} + H_2O \tag{4}$$

$$Me_XO_Y + CO \rightarrow Me_XO_{Y-1} + CO_2 \tag{5}$$

$$2Me_XO_{Y-1} + O_2 \rightarrow 2Me_XO_Y \tag{6}$$

Reaction (6) that occurs in the air reactor is the most exothermic reaction (Cho, Mattisson & Lyngfelt, 2006).

Several studies have been performed to investigate the process for gaseous fuels, both using natural gas and syngas from gasification of solid fuel (Leion, Mattisson & Lyngfelt, 2008; Dennis & Scott, 2010). These experiments have shown that the concept works well. Solid fuel CLC has been investigated more recently (Leion, Mattisson & Lyngfelt, 2008).

Why previous research mainly focused on gaseous fuels are partly due to the problems of separating the OC from the char and ash in the fuel reactor (Dennis & Scott, 2010). A so-called carbon stripper which separates the char and ash from the OC has therefore been introduced. The carbon stripper contributes to additional residence time. This guarantees full char conversion can be achieved as well as separation of char and/or ash from OC. Char needs to be separated from the OC to prevent the char from entering the air reactor. If char enters the air reactor, it will oxidize to CO_2 that will be emitted with the oxygen reduced air resulting in a reduced carbon capture (Lyngfelt, 2014; Cuadrat et al., 2012). The carbon stripper is also necessary for the drainage of ash so it not will accumulate in the system. Unfortunately, the carbon stripper will also remove some of the OC together with the char and ash. This loss of OC increases the need for a low-cost OC since the lifetime of the particles will be limited (Cuadrat et al., 2012; Lyngfelt, 2014). However, in larger plants such as 1000 MWh_{th} power plants, a carbon stripper may not be needed due to the longer distances for the char to diffuse in the bed. In one plant design, the distance was determined to be 5 m between the fuel feed and exit. This design might provide time enough for sufficient conversion of char into CO_2 and steam without a carbon stripper (Lyngfelt & Leckner, 2015).

A critical feature of the design of a solid fuel CLC is the fuel transport through the fluidized bed in the fuel reactor (Wu et al., 2015). The syngas and volatiles from the solid fuel will be produced in the fuel reactor bed compared to gaseous fuels that are introduced at the bottom. For solid fuels, this leads to insufficient contact time with the OC for the gasses originating from the fuel and this result in a low conversion rate. This is especially the case for methane gas, one of the common volatile gases, when using a low-cost OC that has a tendency to have a low conversion rate for methane gas. To solve this problem oxygen polishing, recirculation of combustible gases or serial fuel reactors can be introduced. Oxygen polishing means that pure oxygen is introduced to the flue gases to oxidize them separately. Recirculation of combustible gases can be performed after CO_2 is condensed in the CO_2 liquefaction step. CO_2 liquefaction is used in CCS to decrease the volume of the gas for transportation and storage. These gases can then be introduced at the bottom of the fluidized bed. The use of serial fuel reactors means that an additional reactor is introduced where the flue gasses of the first reactor can react with the OC in a separate additional step (Lyngfelt, 2014).

Instead of additional equipment, the fuel reactor can be redesigned. The common bubbling fluidized bed (BFB) fuel reactor can be replaced by a circulating fluidized bed (CFB). This reactor system is often called Dual circulating fluidized bed (DCFB). In a DCFB the interaction between the gases and OC is much higher due to increased turbulence. Another positive effect of this design is that the volume in reactors is decreased and therefore decreasing the solid inventory as well making this design interesting for future scale-up. A 120 kW CLC reactor with DCFB design has been tested using ilmenite as OC with promising results. It was shown that the gas conversion was highest if hydrogen rich gas was used as fuel, such as if coal gasification with steam is applied (Kolbitsch et al., 2010).

Three categories of solid fuel combustion processes with CLC exist (Adanez et al., 2012). Syngas-CLC and in-situ gasification CLC (iG-CLC) are discussed below while CLC with CLOU is described in section 3.2.1.

- In Syngas-CLC, syngas is produced using pure oxygen in a separate gasification plant next to the CLC. The syngas is then used as a gaseous fuel in the CLC process.
- In iG-CLC, the fuel is gasified in the fuel reactor using the OC as oxidation medium.
- In CLC with CLOU, the fuel is oxidized in the fuel reactor using free oxygen released from the OC as an oxidation media. CLOU requires an OC that can release gaseous oxygen.

Compared to syngas-CLC it has been shown that iG-CLC can generate almost 5 % more electricity (Mukherjee et al., 2015). The loss of efficiency in the syngas-CLC is due to pure oxygen that the gasifier requires. However, this oxygen separation plant is only about one-third of the size of what would be required in an oxy-fuel plant i.e. if the coal would be fully combusted using pure oxygen (Dennis & Scott, 2010). Gasification of the char is the rate determining step due to the limited reaction between the solid char and solid OC. The reaction of the syngas with the OC is very fast in comparison. Compared to conventional gasification, the gasification reaction rates will benefit from the high CO_2 and/or steam concentration in the fuel reactor. This can also be seen from the gasification reactions (1)-(3) above (Leion, Mattisson & Lyngfelt, 2007). All forward reactions benefit from increased steam and CO_2 concentration. It is only reaction (1) that is not affected by the CO_2 concentration directly.

An advantage of the CLC process is the absence of nitrogen from air in the fuel reactor. This means that a lower amount of NOx will be produced compared to conventional combustion. The temperature in the air reactor is generally too low to produce any thermal NOx. Therefore only the nitrogen content in the fuel will contribute to NOx formation. The nitrogen free combustion also simplifies the flue gas treatment of NOx and sulfur, this due to the reduced gas volumes and increased concentration of the gasses after the removal of moisture. The flue gas treatment can be done with conventional techniques (Teyssié et al. 2011). The relative higher concentration of sulfur in the fuel reactor, such as SO_2, compared to conventional combustion can also have favorable effects on the char conversion. When SO_2 is present, faster char gasification has been observed. The presence of Fe_2O_3 will catalyze the oxidation of elemental sulfur that is formed to SO_2 that will enhance the char gasification (Lyon & Cole, 2000). This suggests that an OC that contains iron can be extra good to reduce the residence time in the fuel reactor of the char since the gasification of the fuel is the rate limiting step (Leion, Mattisson & Lyngfelt, 2007).

3.1.1 Oxygen Carrier Aided Combustion (OCAC)

Oxygen Carrier Aided Combustion (OCAC) uses a conventional fluidized bed combustor (FBC) where part of the bed material is changed to an OC. This change of bed material allows the FBC to exploit the OC properties in a conventional process without any changes in the plant design. This active bed of OC regulates the oxidation level in relation to the local surroundings in the fluidized bed. This regulation means that the OC will be reduced in locations with high levels of fuel and be oxidized by adsorbing oxygen in oxygen rich locations. This will make the oxygen level in the bed more homogeneous and thereby provide better combustion conditions (Thunman et al., 2013; Rydén et al., 2016).

This technique gives several advantages. For example, the air to fuel ratio can be decreased due to the better distribution of oxygen. This also means that the plant can increase the fuel flow with decreased fan power and heat losses are minimized at the same time (Rydén et al., 2016). Other advantages that have been observed when using ilmenite as OC in OCAC are reduced NOx emissions (Thunman et al., 2013; Zhao et al., 2014) as well as reduced CO emissions (Thunman et al., 2013).

Corcoran et al. (2014) have analyzed biofuel conversion using a mixture of ilmenite together with silica bed material in a 12 MW OCAC plant. It was observed that the potassium from the biofuel was adsorbed homogeneously by the ilmenite. Together with the titanium oxide, potassium formed KTi_8O_{16}. At the same time, the iron was segregated towards the surface of the particles. This property of ilmenite is attractive since the titanium bonded potassium reduces agglomeration and corrosion on heat exchangers (Corcoran et al., 2014).

3.2 Oxygen carriers

The oxidation and reduction "loop" that the OC do in the CLC process require good chemical and mechanical properties (Knutsson & Linderholm, 2015; Adánez et al., 2004; Cuadrat et al., 2012; Lyngfelt, 2014). OC's should:

- Show sufficient reactivity kinetics with both oxygen and fuel.
- Have a sufficient oxygen transport capacity to reduce the amount of OC needed.
- Have a high melting temperature to avoid sintering.
- Not be environmentally harmful.
- Have relative high mechanical strength at high temperature to avoid attrition to increase OC lifetime.
- Be available at low cost. The low cost for OC is especially essential for solid fuel CLC due to the unavoidable losses of OC in the carbon stripper and deactivation due to the ash.

There exist mainly three ways of oxygen release and adsorption for an OC. The basic one is the one described with reactions (4)-(6) in section 3.1. Here the OC reacts with CO and hydrogen in the fuel reactor, not with a solid fuel directly. While in the air reactor the OC reacts with the oxygen. The two other, Chemical-looping with oxygen uncoupling (CLOU) and oxygen carriers with perovskite structure are described below.

3.2.1 Chemical-Looping with Oxygen Uncoupling (CLOU)

The concept of Chemical-Looping with Oxygen Uncoupling (CLOU) was proposed in 2005. The CLOU effect occurs with certain kinds of OC's that have special thermodynamic properties that make them able to release gaseous oxygen in an inert environment. Reaction (7) and (8) describe this passage of events. Examples of OC's with CLOU properties are Mn_2O_3/Mn_3O_4 and CuO/Cu_2O (Mattisson, Lyngfelt & Leion, 2009).

$$\mathrm{Me_xO_y} \rightarrow \mathrm{Me_xO_{y-2}} + \mathrm{O_2(g)} \tag{7}$$

$$\mathrm{Me_xO_{y-2}} + \mathrm{O_2(g)} \rightarrow \mathrm{Me_xO_y} \tag{8}$$

Reaction (7) is the dominant reaction in the fuel reactor where the oxygen level is low and reaction (8) is dominant in the air reactor where the oxygen level is high. The combustion will be very similar to conventional combustion because the oxygen will be present as a gas instead of bounded to an OC (Mattisson, Lyngfelt & Leion, 2009). This means that the reaction rate can be increased significantly since the gasification step of the char is no longer the rate determining (Leion, Mattisson & Lyngfelt, 2009B; Rydén et al., 2014). Leion, Mattisson & Lyngfelt (2009B) showed that fuel conversion via CLOU could be 3 times faster for solid volatile fuels and up to 15 times faster for non-volatile fuels compared to CLC without CLOU. Another advantage of CLOU compared to conventional CLC is that it normally is easier to close the heat balance. This is due to that the reactions in the fuel reaction are more exothermic with CLOU and therefore can the solid circulation be decreased to a minimum (Rydén et al., 2014).

If an OC with CLOU properties is used in a solid fuel CLC process the problem with incomplete combustion is also reduced. The syngas and volatiles are no longer dependent on the residence time inside the fluidized bed. Oxygen will be present in a gaseous state and the oxidation of the fuel takes place even outside the fluidized bed (Lyngfelt, 2014).

3.2.2 Oxygen carriers with perovskite structure

A material with a perovskite structure has the general form of $ABO_{(3-\delta)}$. A and B are a small respectively a large cation while δ is a value that is determinate by the surrounding oxygen partial pressure or temperature. Changing temperature and oxygen partial pressure, as in the two reactors in CLC, δ will adjust and release or adsorb oxygen according to reaction (9) below. These materials can therefore also be used as OC's in a CLC process (Jing et al., 2013; Hallberg et al., 2014). In the fuel reactor where the partial pressure of oxygen is low, δ will increase so gaseous oxygen is released. In the air reactor where the partial pressure of oxygen is high, δ will decrease so the OC adsorbs oxygen (Hallberg et al., 2014).

$$2\mathrm{ABO}_{3-\delta} \rightarrow 2\mathrm{ABO}_{3-\delta-\mathrm{a}} + \mathrm{aO}_2 \tag{9}$$

An advantage of these types of OC's is that no distinct phase transition takes place. No distinct phase transition means that the phase structure will not be different at the reduced or oxidized state. This may reduce the attrition problem that occurs during phase transition (Jing et al., 2013). An example of an OC that has been investigated is $CaMnO_{3-\delta}$ (Jing et al., 2013; Hallberg et al., 2014).

3.2.3 Support material

To increase the thermodynamic stability of the OC's the active metal oxide can be supported on an inert support material. This inert support material is normally an oxide such as Al_2O_3, SiO_2, ZrO_2 or $MgAl_2O_4$ (Bhavsar, Tackett & Veser, 2014; Adánez et al., 2004).

An example of particles that normally are manufactured on a support material is nickel based OC's. Pure NiO has a low porosity that prevents high reaction rates due to mass transport limitations. Therefore the particles are normally produced on an inert support material having a higher porosity increasing the reaction rate (Adanez et al., 2012).

3.2.4 Common oxygen carriers

Several potentially good OC's are found among the transition metal oxides such as iron, copper, nickel, cobalt and manganese (Hossain & de Lasa, 2008; Cho, Mattisson & Lyngfelt, 2004). In the following sections, these types of OC will be described shortly.

3.2.4.1 Nickel based oxygen carriers

Nickel based oxides have shown to have both good chemical and mechanical properties. They can operate at high temperatures and have near full fuel conversion when firing methane gas. It has also been observed that the lifetime is adequate and that there is no decrease in reactivity during operation when operating with clean fuels such as syngas and methane (Linderholm et al., 2008; Adanez et al., 2012).

Unfortunately, nickel oxides are both harmful and expensive to use in a large plant (Mattisson et al., 2014; Adanez et al., 2012). If they are applied on a large scale, different safety measures will be needed to prevent emissions of the toxic nickel (Adanez et al., 2012). Also, sulfur will deactivate OC's based on nickel limiting the possible fuels to those with a low sulfur content (Keller et al., 2014).

3.2.4.2 Copper based oxygen carriers

Copper based OC's have a relatively high reaction rate and the oxygen transfer capacity when firing gaseous fuels. Copper based oxygen carriers are still expensive but have a lower cost compared to nickel and cobalt based OC's. Copper based OC's are also less environmental harmful compared to nickel and cobalt (Adanez et al., 2012).

Drawbacks of copper as an OC are that it is still expensive and not environmentally friendly. It has also been found that they have a tendency to agglomerate (Cho, Mattisson, & Lyngfelt, 2004). However, this agglomeration tendency has not always been observed. When copper oxide was used as an OC in a 10 kW reactor with methane as fuel the operation was successful, even after 120 h of operation (Adánez et al., 2006). As with nickel based oxygen, copper based oxygen carriers are also deactivated by sulfur according to some studies (Keller et al., 2014).

3.2.4.3 Cobalt based oxygen carriers

Cobalt is very expensive as an OC, although, it is still a potential OC. This is due to the high oxygen transport capacity and high reaction rate that can be achieved. In the CLC process, only the reaction CoO/Co is of interest since Co_3O_4 is not stable above 900 °C (Adanez et al., 2012).

Disadvantages of this OC for a large scale CLC plant are the cost and toxicity. Also, the reaction in the fuel reactor is a very endothermic reaction. This makes it harder to solve the heat balance between the fuel and air reactor in the CLC plant and a large flow of OC is needed to provide sufficient heat to the fuel reactor (Adanez et al., 2012).

3.2.4.4 Manganese based oxygen carriers

Manganese is a widely available and a non-harmful alternative to the above mentioned OC's. Manganese has a vast number of oxidation states giving OC's based on manganese a large oxygen transport capacity. This kind of OC's has been found to have an excellent conversion rate for syngas but a lower rate for methane gas. The properties of these carriers in a CLC process are also promising with low agglomeration and low attrition (Adanez et al., 2012).

3.2.4.5 Sulfated limestone as oxygen carriers

Among the low-cost OC's, but outside the transition metal OC group, limestone is a promising candidate. Limestone will, in the presence of sulfur, form an OC that will have the oxidized form of $CaSO_4$ and the reduced form of CaS. This OC has a very large potential oxygen transport capacity of 47 wt.% which is very high compared to the transition metal oxide OC's (Abad et al., 2017). A preliminary design of a 3 MW_{th} CLC plant using sulfated limestone has been suggested by Abdulally et al. (2012). This study shows that the OC works and that the total size of a plant can be heavily reduced compared to a conventional CFB plant.

A problem with this OC is that there is a large risk of sulfur emissions from the air reactor. This requires a separate flue gas treatment for the air reactor or other means to mitigate the sulfur emissions (Abad et al., 2017).

3.2.4.6 Iron based oxygen carriers

Iron based OC's are very interesting to be used in large-scale solid fuel CLC. They can be obtained at low costs, have good mechanical strength and have satisfying kinetic and thermodynamic properties (Fan et al., 2012). Another reason why iron-based metal oxides are extra interesting is that they have no negative environmental effects related to their use (Dong et al., 2010). The three iron oxide phase transitions and the oxidation states can be seen in reaction (10) below.

$$\underset{\text{Hematite}}{\mathrm{Fe_2O_3}} \xrightarrow{\text{Red}} \underset{\text{Magnetite}}{\mathrm{Fe_3O_4}} \xrightarrow{\text{Red}} \underset{\text{Wüstite}}{\mathrm{FeO}} \xrightarrow{\text{Red}} \underset{\text{Iron}}{\mathrm{Fe}} \tag{10}$$

It has been suggested that full reduction to FeO increases the risk for agglomeration if using iron-based OC's (Cho, Mattisson & Lyngfelt, 2006). This agglomeration tendency has also been observed in other studies using ilmenite, an iron-titanium based ore (Cuadrat et al., 2012). However, in the CLC process is it not likely that full reduction to Fe or even FeO will occur (Cho, Mattisson & Lyngfelt, 2006). This is due to the reduced conversion rates that have been observed when oxidizing methane gas with FeO. The reduction of hematite to magnetite had a fuel conversion level of about 100 %. Full fuel conversion was not achieved with magnetite to wüstite or wüstite to iron (Mattisson & Lyngfelt, 2001; Jerndal, Mattisson & Lyngfelt, 2006). Also, if steam is present in the fuel reactor reduction beyond Fe_3O_4 is not thermodynamically possible (Jerndal, Mattisson & Lyngfelt, 2006).

Several iron ores and residues from the steel manufacturing have been tested as OC with good results. These are cheaper alternatives compared to other OC's based on copper or nickel. However, even these have different price classes. Some iron oxides can be recycled within the steel industry and this will make them more expensive compared to other that are considered as waste and usually landfilled.

Landfilling is normally a cost for the industry and therefore these oxides will be cheap (Leion, Mattisson & Lyngfelt, 2009A). Also, other wastes containing iron oxides have been tested such as sewage sludge ash with promising results (Ksepko, 2014).

3.2.5 Combined oxygen carriers

However, besides the singular metal oxides, combined metal oxides that at least contains two different metals can be used as an OC. In this way, the best properties of different transition metals can be utilized. Manganese oxides have been used in many different combined OC's, mostly together with iron and/or silicon i.e. $(Mn_yFe_{1-y})O_x$ and $(Mn_ySi_{1-y})O_x$. Especially the OC with combined manganese and iron has shown promising properties with a good oxygen release in CLOU (Källen et al., 2015; Lyngfelt, 2014).

3.2.5.1 Ilmenite as an oxygen carrier for CLC

A suggestion of an alternative bulk chemical that can be used as an OC is the natural ore ilmenite that is mainly based on iron and titanium oxides. The ilmenite mineral consist of $FeO*TiO_2$, also written as $FeTiO_3$, in its most reduced form. It is the most abundant titanium mineral of earth and it is therefore mined in large quantities. However, the name ilmenite is also used for ores that contain only a part of the mineral ilmenite (Leion et al., 2008). Ilmenite OC properties can be defined by iron oxide being the active site for the oxygen (Cuadrat et al., 2014). Ilmenite ore has shown the similar reactive properties as synthetic iron oxide OC (Leion, Mattisson & Lyngfelt, 2008). The cost of ilmenite is low compared to manufactured oxygen carriers. Compared to manufactured nickel oxide particles the price of ilmenite is only about one percent (Adánez et al., 2010).

The reduction reaction that occurs in ilmenite is normally written as reaction (11) below. Pseudobrookite corresponds to the iron oxidation level similar to hematite while ilmenite corresponds to the oxidation level for wüstite (Lyngfelt & Linderholm, 2014). However, it is also suggested that an intermediate form such as $Fe_3Ti_3O_{10}$ can be present. $Fe_3Ti_3O_{10}$ would correspond to a combination of magnetite and rutile (Leion et al., 2008).

$$\underset{\text{Pseudobrookite}}{\mathrm{Fe_2TiO_5}} + \underset{\text{Rutile}}{\mathrm{TiO_2}} \xrightarrow{\text{Red}} \underset{\text{Ilmenite}}{\mathrm{FeTiO_3}} \tag{11}$$

The same ilmenite ore that has been used in this study have been analyzed to contain 94.3% ilmenite on a mass basis. However, in the fresh ore the ilmenite mineral content was 65.5% and the remaining 28.8% in the oxidized form as pseudobrookite and rutile (Knutsson & Linderholm, 2015). Ilmenite of the same origin, as OC for solid fuel CLC, has been tested in a lab scale (Leion, Mattisson & Lyngfelt, 2008) and in sub pilot scale, both 10 kW (Berguerand & Lyngfelt, 2008; Berguerand & Lyngfelt, 2009) and 100 kW (Linderholm et al., 2016; Linderholm et al., 2014) at Chalmers University of Technology, Sweden, with good results. Different solid fuels have been used such as coal from Poland and South Africa and wood char. The largest CLC pilot plant using ilmenite as OC is a 1 MW_{th} plant at the Technische Universität Darmstadt, Germany, using coal as fuel. Ilmenite as an OC showed promising properties in the large pilot plant. However, the gas conversion in the fuel reactor and the CO_2 capture were low due to several design errors (Ohlemüller et al., 2016).

It has been observed that the iron in the ilmenite ore has a tendency to migrate to the surface of the OC particles under CLC conditions. This migration has been accompanied with increased porosity in the particle that reduced the crushing strength of the particles (Knutsson & Linderholm, 2015; Cuadrat et al., 2012; Adánez et al., 2010). It is considered that this migration of iron oxide towards the surface increases the reactivity of the OC due to the free hematite that is produced. However, the oxygen transport capacity is decreased. Pseudobrookite, the oxidized form of ilmenite, have OC potential of about 5 wt. %. In comparison, segregated pseudobrookite, a mixture of hematite and rutile, have only about 1.7 wt. % oxygen carrier potential (Adánez et al., 2010; Azis et al., 2013). In several experiments, the migration formed an iron rich shell around the particles. However, this was not observed in the 100 kW CLC. Here the migrated iron was concentrated to islands within and on the surface of the particles. This was explained by the fact that the particles withstand greater chemical and mechanical stresses that result in cracks and pores in the 100 kW CLC pilot plant compared to lab scale experiments. These cracks and pores increases the oxygen transport through the particle that could contribute to the segregation (Knutsson & Linderholm, 2015).

It has been observed that sintering of ilmenite is reduced if the ore is pretreated at high temperatures (Zhang & Ostrovski, 2002; Pröll et al., 2009). Heat pretreatment causes reduction of the specific surface area (Zhang & Ostrovski, 2002). This is caused by thermal sintering of iron oxide that occurs at temperatures above 800 °C (Dueso, Thompson & Metcalfe, 2015). Adánez et al. (2010) showed that the oxidation of 6 hours is sufficient to obtain fully oxidized ilmenite.

Alkaline roasting in reducing environment has been performed in earlier experiments at temperatures about 1000°C to investigate possible improvements for the titanium oxide production process. The reducing environment has been obtained by mixing of coal with ilmenite samples followed by partial oxidation to obtain CO. Sodium atoms have then been observed to diffuse easily into the ilmenite where it reacts with titanium oxide (El-Tawil et al., 1996). These tendencies have also been observed for potassium (Corcoran et al., 2014). The formation of these so-called alkali-titanates leads to structural breakdowns of the ilmenite resulting in an accelerated reduction of the iron oxides. An increased nucleation rate and growth rate are also expected in the presence of sodium due to the diffusion of sodium into the iron oxide lattice (El-Tawil et al., 1996). It has been concluded that the chemistry of potassium and sodium is similar when studying interaction with ilmenite, at least in an oxidative environment (Foley & MacKinnon, 1970).

3.3 Ash

Ash is the inorganic residuals that are left from the fuel after combustion. It is normally divided into fly ash and bottom ash. Fly ash contains mostly of small particles that will exit the combustion chamber with the flue gas. Bottom ash contains larger and heavier particles that will not leave with the flue gas. From some types of fuels, e.g. sawdust, the bottom ash can be collected as vitrified agglomerates (Nunes, Matias & Catalão, 2016).

In general, biofuel is considered to be a renewable energy source. Biomass for biofuel can originate from all different kinds of living organic material that can be used as energy sources, all from the smallest algae to the largest trees. Woody biomass can be defined as lignified biomass such as trees and bushes. The main components of woody biomass are cellulose, hemicellulose, lignin as well as extractives. Woody biomass is used as an energy source for a vast number of applications. Different applications also require different amounts of woody biomass. Examples of applications are as fuel for food cooking in small ovens, as fuel in larger energy and heating plants or as an energy and raw material source in large pulp industries (Werkelin et al., 2010).

Wood contains only small amounts of ash, about 0.5-4wt.%. However, due to the high concentrations of alkali and alkaline earth metals, it can be both harmful to equipment, nature and animals (Steenari, Karlsson & Lindqvist, 1999). Compared to coal ash, bio ashes do contain much more chemically available alkali such as sodium and potassium. Many alkali salts decrease the first melting temperature of the ash that increases the risk of fouling and agglomeration. The presence of alkali chlorides also increases the corrosion on the walls and heat exchangers. As a consequence that more expensive materials are needed for the construction of the plant. Also, low superheater temperatures are needed to decrease the corrosion. Decreased superheater temperature reduce the electricity output from the plant (Demirbas, 2005, Zevenhoven, Yrjas & Hupa, 2010).

To understand the properties of the ash the ash-forming elements in the fuel need to be known. The main ash-forming elements are Si, Al, Fe, Ca, Mg, Mn, Na, K, P, S, and Cl. These elements are associated with the fuel as different salts, organic structures or as minerals in the fuel (Reid, 1984; Werkelin et al., 2010). Potassium in bio ash is normally associated with water soluble salts such as KOH, KCl, K_2CO_3, K_2SO_4 and KH_2PO_4. Sodium has a similar chemistry to potassium. However, the concentration of sodium in bio ash is typically lower than potassium by order of magnitude. The element that is present at the highest concentration in bio ash is calcium that is mostly present as calcium oxalate (Zevenhoven, Yrjas & Hupa, 2010; Werkelin et al., 2010).

The interaction between ilmenite and bio ash has previously been studied in a 12 MW_{th} CFB reactor under oxidizing conditions as OCAC. It was found that potassium was adsorbed into the particles and calcium created layers together with iron. The potassium content of the particles was 4 wt. % after three days of continuous combustion and almost all potassium had reacted into KTi_8O_{16} and was not leachable. Calcium had formed $Ca(Ti_{0.7}Fe_{0.3})O_{2.85}$ in two layers around the segregated iron layer. However, in the fuel reactor in a CLC the environment is reducing and will not behave in the same way (Corcoran et al., 2014). In comparison to bio ash, several studies using different types of coal ashes have been investigated. These in laboratory scale CLC plants, using ilmenite as an OC, indicates that the reactivity towards both methane and CO was reduced at low ash levels and increased at high ash levels. This was probably due to the high calcium or iron content in the different ashes. However, there were no indications that the different coal ashes should have any affected on the fluidization properties or caused any agglomeration (Azis et al., 2013).

3.4 Agglomeration

Agglomeration or sintering is a condition that can occur between particles that make them stick to each building agglomerates. In a fluidized bed heavy agglomeration of bed material can cause defluidization and collapse of fluidized bed boilers (Salour et al., 1993; Elled, Åmand & Steenari, 2013). For conventional fluidized bed boilers using quartz, it has been observed that the coating composition of the quartz is related to the fuel used. It is also concluded that it is the coating formed on the particles that are responsible for the agglomeration by reducing the first melting temperature of the sand particles (Öhman et al., 2000). Elled, Åmand & Steenari (2013) summarized the agglomeration process to two different mechanisms. The first mechanism is that the ash from the fuel has a low first melting point. The ash melts and sticks on the bed particles and acts as glue between the particles that causes the agglomeration. The ash is then not reactive towards the bed material. The second mechanism is when the ash has a reactive nature and reacts with the bed particle to form other compounds that melt. This type of interaction normally generates homogenous coatings on the particles (Elled, Åmand & Steenari, 2013).

Several experiments have shown that potassium contributes to agglomeration in fluidized beds due to interaction with silica sand that is widely used as a bed material. In these experiments, they have used straw that is a biomass that contains much potassium (Lin, Dam-Johansen & Frandsen, 2003; Ergudenler & Ghaly, 1993). Examples of ash compounds that are known to interact with quartz are KCl, KOH and K_2CO_3 (Elled, Åmand & Steenari, 2013).

It has also been observed that the coatings of the particles haves two layers. The inner layer had more potassium in the form of K_2SiO_9 while the outer layer had more calcium in the form of $CaSiO_3$ (Elled, Åmand & Steenari, 2013; Steenari, Åmand & Bohwalli, 2011).

3.4.1 Additives to prevent agglomeration

There exist several ways to avoid agglomeration in a fluidized bed boiler. One example is to change bed material to one that does not contain quartz. Examples of materials that can be used are olivine sand, diabase and blast-furnace slag. Another way is to add material that will reduce the effects of the agglomeration (Davidsson, Steenari & Eskilsson, 2007).

Two common additives to prevent agglomeration are limestone and kaolin. Limestone is claimed to adsorb some alkali that will prevent agglomeration (Aho, 2001; Bartels et al., 2008). To add kaolin to the bed material has also been shown to prevent agglomeration. The kaolin removes the potassium from the bed to the fly ash and thereby increases the sintering temperature (Öhman & Nordin, 2000; Davidsson, Steenari & Eskilsson, 2007). It has also been observed that using fuel with much phosphorus, such as rapeseed meal, the tendency of agglomeration will decrease. This is due to that the phosphor binds the potassium in K-Ca-Mg-phosphates/silicates and in that way prevents it from interaction with the silica bed material (Boström et al., 2009).

Another alternative is to add sulfur to the fluidized bed. The purpose of the sulfur is to transform KCl to K_2SO_4 that has a higher melting temperature. The chloride will then be emitted with the flue gasses as HCl. This will therefore at the same time reduce the amount of chloride in the fouling deposits reducing problems with corrosion (Aho et al., 2008; Wang et al., 2012).

4 Method and Experimental

4.1 Material

The ilmenite used for these experiments was a treated natural ore delivered by Titania A/S via Chalmers University of Technology originating from Norway. The particle size ranged from 100-300 µm. The ore contained 94.3 % of the mineral ilmenite on a mass basis (Knutsson & Linderholm, 2015).

The potassium salts that were used as ash components for the different experiments are described in Table 1.

Table 1. The origin and purity of the different potassium salts used during the project.

Ash component	Molar mass	Composition	Origin
K_2CO_3 - Potassium carbonate	138,21	≥99,8%	J.T. Baker
KCl - Potassium chloride	74,56	≥99,5%	Merck
K_2SO_4 – Potassium sulfate	174,26	≥99%	Riedel-de Maën
KH_2PO_4 – Monopotassium phosphate	136,09	≥99,5%	Merck

4.2 Pretreatment

The ore was pretreated at 950°C for 6 hours under oxidative atmosphere of air. It has been shown in earlier experiments that an oxidation time of 6 hours at 950°C is sufficient (Adánez et al., 2010). The pre-treatment was performed in an oven under atmospheric conditions so the conditions were oxidizing. The oxidizing state of ilmenite would be similar to the OC emerging the fuel reactor in CLC.

During the time when the samples were not in use, they were stored in a desiccator to prevent changes in the samples due to the air humidity.

4.3 Reduction

For the reduction tests, a tubular oven was used as illustrated in Figure 3. The oven was a Carbolite oven of model VST 12/600 with a maximum temperature of 1200 °C equipped with a silicon glass tube. The temperature inside the oven was monitored with a thermal element that was located next to the sample in the middle of the oven. Another thermoelement was located in the evaporation bed in the preheater to monitor the temperature in the preheater. The main purpose of the preheater was to evaporate incoming liquid water. For experiments that were performed without steam, the water pump and the preheater were switched off without any further changes in the setup design.

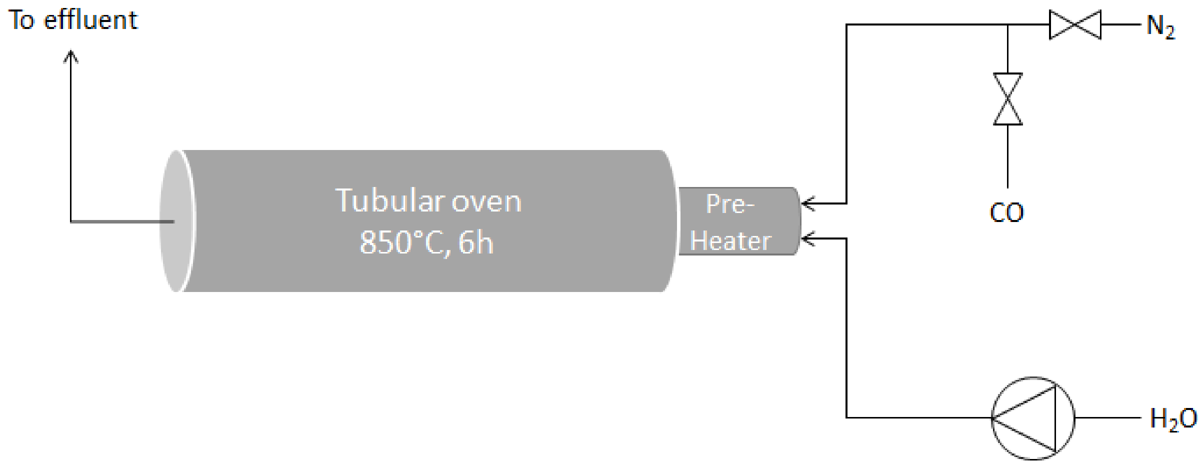

Figure 3. The experimental setup for the reduction experiments.

The reduction tests were performed with 1 g samples using the experimental setup above. For these tests, a control sample of pretreated ilmenite and samples containing mixtures of pretreated ilmenite together with a grinded potassium salt were investigated in two different atmospheres. The potassium based ash components K_2CO_3, KCl, K_2SO_4 and KH_2PO_4 were used and mixed with pretreated ilmenite so the potassium content was equal to 4 wt. % in every sample. This level of potassium was observed when using ilmenite as a bed material in a 12 MW_{th} CFB and is therefore also credible to have in the fuel reactor in a CLC process (Corcoran et al., 2014). These samples were heat treated at 850°C for 6 hours and left for cooling during night. The atmosphere for the first experimental round was reducing with 5% CO and 95 % N_2 with a gas flow of 1 Nl/min. For the second experimental round, the atmosphere was also reducing but with the addition of steam to simulate the conditions in CLC fuel reactor. The gas flow was 1 Nl/min containing 5 % CO, 50 % H_2O and 45 % N_2. The presence of steam made the gas less reducing compared to the gas mixture without steam.

4.3.1 Mixing test

To investigate the importance of the mechanical mixing prior to the reduction tests two samples were compared. The mixing test was performed with K_2SO_4 due to the easily visible changes that were observed with SEM after the heat treatment. The first sample was from the reduction test where the pretreated ilmenite was mixed with ground K_2SO_4. Here the mixing was performed carefully for about 4 minutes. The second sample was a sample with the same salt where the sample was mixed only for about 2 min. These samples were compared afterward in order to identify if any differences could be observed due to the difference in mixing. The mixing was performed by hand with a spatula in a beaker.

4.3.2 Stationary test

For samples that showed tendencies to lose a component of the salt, i.e. samples treated with KCl and K_2SO_4, an additional test was performed. The samples were mixed so that the potassium content of 4wt.% were obtained as with the reduction tests. Then they were placed in small holders of Al_2O_3. These sample holders were the same that was used in the thermogravimetric analysis. These were then treated in the tubular oven in the two different reducing atmospheres as described above in section 4.3.

Hereafter, the samples were stabilized together with the sample holders in polyester resin so that the particles were not dislocated. After hardening of the polyester, the samples were cut in half in order to obtain the cross section in the sample in the sample holder. With this method, it was possible to maintain the orientation of the particles so that the influence of gravity and evaporation could be investigated further.

4.4 Alternating reduction and oxidation with TGA

For the thermogravimetric analysis (TGA) a TA instrument of model Q600 SDT was used. TGA was used to monitor the weight change during the reduction phase in real time. With this equipment, it was also possible to alternate between reducing and oxidizing conditions.

Two different gas shifting programs were used, see Table 2. The first program was to mimic the interaction between ash and ilmenite in the fuel reactor. The second program was to mimic the interaction when the particles and ash have interacted in the fuel reactor and then transferred to the air reactor and then transferred back into the fuel reactor again.

Table 2. The two experimental set-ups that were used for the alternating reduction and oxidation experiments. Program 1 imitates the atmosphere in the fuel reactor. Program 2 imitates the condition for the looping cycle there a particle with ash is first reduced in fuel reactor and then oxidized in the air reactor to be again reduced in the fuel reactor.

Program 1: Heating⇨ Red.	**Program 2: Heating⇨Red. ⇨Ox. ⇨Red.**
Heating 15°C/min up to 850°C in 100 Nml/min N_2	Heating 15°C/min up to 850°C in 100 Nml/min N_2
Stabilizing 5 min in 100 Nml/min N_2, isothermal	Stabilizing 5 min in 100 Nml/min N_2, isothermal
Reduction 60 min in 95 Nml/min N_2+5Nml/min CO, isothermal	Reduction 60 min in 95 Nml/min N_2+5Nml/min CO, isothermal
Cooling to room temperature in 100 Nml/min N_2	Stabilizing 5 min in 100 Nml/min N_2, isothermal
	Oxidizing 17 min with 100 Nml/min synthetic air, isothermal
	Cleaning balance housing for 25 min with 150 Nml/min N_2, isothermal
	Stabilizing 5 min in 100 Nml/min N_2, isothermal
	Reduction 60 min in 95 Nml/min N_2+5Nml/min CO, isothermal
	Cooling to room temperature in 100 Nml/min N_2

The reducing gas was introduced to the sample by a separate line that did not pass the balance house. However, both the nitrogen and synthetic air passed the balance house and worked as protection gas for the sensitive instrument. The balance house has a volume of 0.75 liters. This caused dilution of the gasses when changing between nitrogen and synthetic air. Therefore the cleaning time when changing from oxidizing to reducing conditions was prolonged. If the synthetic air would be mixed with the incoming reducing gas of CO, CO would oxidize decreasing the reducing properties of the gas. Therefore, rinsing of the balance house with N_2 was important to ensure that all oxygen was removed.

The reduction and oxidation time were determined from the control sample containing no ash component. The aim was to reduce the sample until the ilmenite weight was reduced by 3 wt.% and then to oxidize back to the original weight. This 3 wt.% reduction represents double the reduction amount that has been suggested for a theoretical 1000 MWh_{th} CLC power plant designed for solid fuels. This relative low reduction rate compared to the oxygen carrier potential, about 5 wt.% for ilmenite, is due to the heat balance limitations in the two reactors (Lyngfelt & Leckner, 2015). This weight reduction was obtained after 60 min when performed in 95 Nml/min N_2 and 5Nml/min CO at 850°C. The time for oxidizing the control sample to obtain original sample weight, using 100 Nml/min synthetic air containing 20% O_2 and 80% N_2, was 17 min.

Pretreated ilmenite particles mixed with the potassium salts K_2CO_3, K_2SO_4 and KH_2PO_4 were tested in this equipment. Analyses of samples were performed with SEM and EDS to see how the interaction had developed. The interaction of ilmenite and KCl could not be investigated with this equipment due to the risk of crystallization of the volatile and corrosive salt inside the equipment.

4.5 Analytical methods

The analysis was done primarily by using SEM on the particle surface and SEM-EDS on particle cross-sections. The cross sections were prepared by stabilizing the samples in polyester casting resin and then polish the samples so the cross-section was exposed. EDS was used to investigate the areas where the interaction may have occurred and see eventual changes in concentration gradients of the elements.

The second main tool for analysis was XRD, used to investigate the different phases of the ilmenite and ash components that were present after the heat treatment. XRD was used to determine the state of reduction of ilmenite and if new compounds were formed from the interaction with the potassium salts.

TGA was used to investigate the reduction and oxidation processes and relative kinetics of the ilmenite mixed with potassium salts. The weight reduction and growth, combined with other analysis, could then be linked to changes in the ash components and oxygen level in the ilmenite.

In some cases have equilibrium analysis also been performed with the simulation program FactSage 6.4. These simulations were performed to see what stable compounds could be expected in the sample and the gas phase. The information about the most probable gasses to leave the sample was important since no analysis of the exiting gas from the tubular oven was performed.

4.5.1 Scanning Electron Microscope

Scanning Electron Microscope (SEM) is a powerful tool to investigate the appearances of solid samples. It uses an electron beam of 1-30 keV that is radiated towards the sample that is held under vacuum. Electron detectors are used to detect different signals generated from the sample where the primary electron beam interacts. The two most common signals that are used to produce a SEM image are coming from backscattered electrons (BSE) and secondary electrons (SE). SE is electrons that are scattered from the surface and have low energy. BSE is electrons that are scattered from deeper parts of the sample and have high energy (Khursheed, 2011).

An important parameter to understand while using SEM is the way the primary electron beam is shattered inside the sample since this will affect the final resolution. The number of scattered electrons that leaves the surface and the area where they are emitted from the sample is dependent on electron beam energy, sample thickness and the sample material. Depending on the thickness of the sample different electron beam energies should be used. If the sample is thin, a high energy is used so much of the primary electron beam is transmitted through the sample to gain the highest resolution. If the sample is thick, the energy of the electron beam must be as low as possible so that the area of emitting electrons is minimized to obtain higher resolution. However, this can be problematic if EDS-analysis shall be applied at the same time to the sample (Khursheed, 2011).

4.5.2 Energy Dispersive Spectroscopy

Energy Dispersive Spectroscopy (EDS) is an elemental analyses technique that is commonly assigned together with SEM. The techniques build on analyzing the x-rays that are produced from the sample by the primary electron beam used in SEM. By analyzing the frequency of the x-rays from the sample the elements that have been radiated can be identified. This makes EDS to a very powerful tool for analysis of samples (Khursheed, 2011).

However, since it is the x-rays that are analyzed in EDS the energy in the primary electron beam will normally be increased. This reduces the resolution of the analysis. Also since the x-rays are generated within the sample and not generated at the surface of the particle the resolution will be reduced further. Another limitation with analysis with EDS is that it cannot detect light atoms with an atom number lower than 4, i.e. hydrogen, helium and lithium (Khursheed, 2011).

4.5.3 X-ray Diffraction

X-ray diffraction (XRD) can be used on solid crystalline samples for qualitative identification of different crystal structures. The basis is that the specimen is exposed to parallel x-rays. To achieve parallel x-rays, they will have to origin from a relatively far distance compared to the distance between the reflecting planes in the crystal. The diffraction pattern of the specimen can then be observed with a detector at certain angles. The peaks in the diffraction pattern come from the constructive interference reflections of two or more parallel reflecting planes within the specimen. The diffraction pattern is unique to every crystal structure and the elements in the crystal structure and can, therefore, be used as a fingerprint for a specific crystal. The unique diffraction pattern is defined by the distance between the reflective planes in the studied crystal. The angle of the diffraction was defined by W.L. Bragg in 1913 and is normally called *Bragg's Law*, defined as equation E1 (Suryanarayana et al., 1998):

$$n\lambda = 2d\ sin\theta \qquad \text{E1}$$

The definitions of the terms in E1 above can be seen in Figure 4 below.

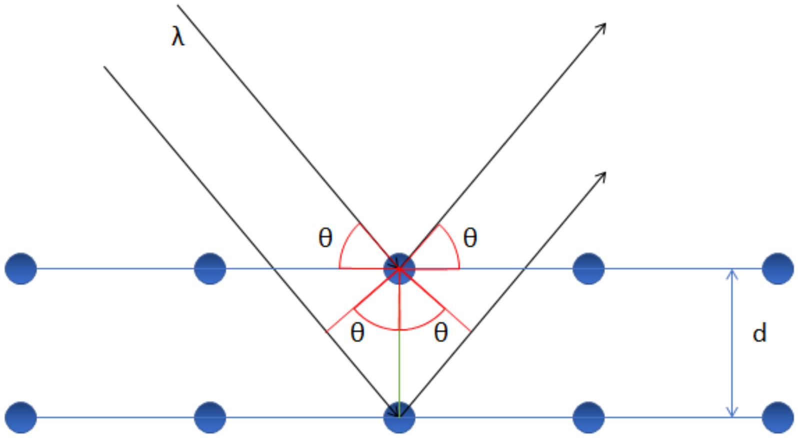

Figure 4. The diffraction of the parallel x-rays when reflecting on two reflective planes in a crystal structure.

This technique becomes problematic when mixtures of different phases are present. Then it can be difficult to identify each individual fingerprint from the different phases. The database may also lack the information about some crystals that will make it impossible to identify (Suryanarayana et al., 1998).

5 Results & Discussion

5.1 Pretreatment

The fresh particles were homogeneous with only some areas, dark grey in Figure 5 A), where the concentration of magnesium and silicon were dominant. XRD analysis of the fresh ilmenite showed that the ilmenite sample contained mainly ilmenite and probably magnesium silicate, $MgSiO_3$. $MgSiO_3$ as an impurity has also been observed by others that have used ilmenite of the same source (Adánez et al., 2010). These types of areas could also be found in other samples.

After the pretreatment of the particles, some structural changes in and at the surface of the particles could be observed. Segregation of iron towards the surface of the particles was noticed. A few internal cracks in the otherwise homogeny structure had appeared. These cracks can easily be seen inside the particles (Figure 5 B)). The appearance of the cross-section and surface of the particles obtained in this study, both fresh and pretreated, were similar to the study of Adánez et al. (2010).

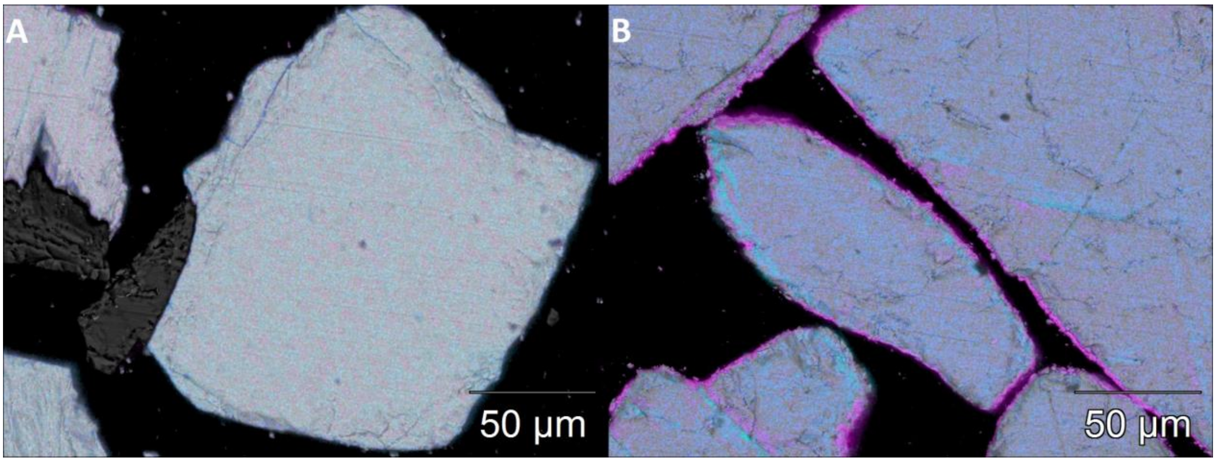

Figure 5. The difference between A) the fresh ilmenite and B) the pretreated ilmenite that have been pretreated at 950°C for 6 h in an oxidative atmosphere. The figure shows the SEM-EDS images of the cross section of the particles where areas colored in purple have higher concentrations of iron; turquoise areas have a higher concentration of titanium. Some segregation of iron can be observed on the surface of pretreated ilmenite and some internal cracks in the structure.

From the XRD analysis of the pretreated ilmenite, it can be concluded that the ilmenite had not converted entirely to pseudobrookite but also contained hematite and iron titanium oxide, $Fe_3Ti_3O_{10}$. Iron-titanium oxide has a lower oxidation level of iron compared to pseudobrookite which indicates that the oxidation time was too short to reach full oxygen carrier capacity. Prolonged time might be needed to reach full oxidation. The mass gain from the oxidation was calculated to be 3.2wt.% compared to 3.5wt.% that was obtained in an earlier study (Adánez et al., 2010). However, to be able to confirm if the 6 hours of pretreatment was enough for this specific ilmenite batch several more tests with different times would be needed. This was not the intention of this study and these tests were therefore not performed.

After the pretreatment, the particles had sintered and adhered to the ceramic crucible. This agglomerate was very strong and was hard to disintegrate and remove from the crucible. This strong agglomerate could lead to defluidization in a fluidized bed when formed and has been seen in a previous study as well (Pröll et al., 2009). From the SEM-images of the surface and cross-section of the pretreated ilmenite, it appeared as iron oxide diffused outwards and interacted with the other particles, this leading to sintering. The diffusion of iron towards the surface after one pretreatment step at 950°C was also found by Adánez et al. (2010).

5.2 Reduction in tubular oven

The control samples showed that in a reducing environment, regardless if steam was present or not, the pretreated ilmenite will be reduced to ilmenite and some segregation of titanium and iron will occur. For the sample treated without steam, some of the segregated iron was reduced all the way to elementary iron. For the sample with no steam, the segregation was located both in the bulk and at the surface where it accumulated in islands of iron as shown in the cross-section. This iron segregation can be seen as purple areas in Figure 6 A).

With the presence of steam, the reduction level and the segregation of iron and titanium were significantly reduced. For the control sample with steam, the segregation was limited and mostly located to the edges of the particles and to the cracks to some extent. However, from the SEM-EDS analysis of the cross-section, it was impossible to tell if the segregation had increased compared to the segregation already obtained during the pretreatment of the particles.

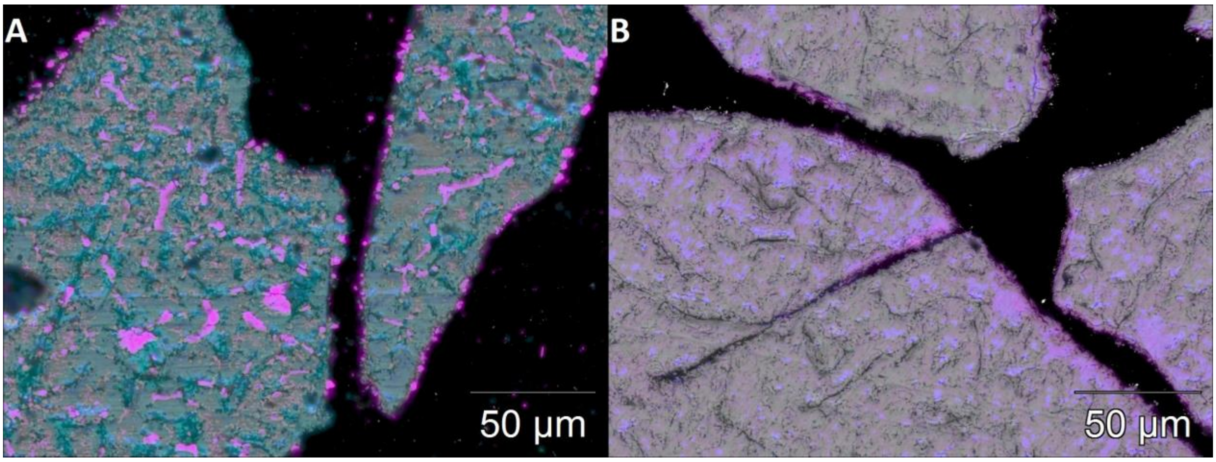

Figure 6. SEM-EDS analysis of the cross-section of the two control samples heated to 850°C for 6 h in reducing environment A) without steam and B) with steam. Areas colored in purple have higher concentrations of iron and turquoise areas have a higher concentration of titanium. The figure shows that iron and titanium were clearly more segregated if no steam was present compared to if steam was present.

When comparing the weight reduction of the different samples treated with or without steam at reducing conditions for 6 h at 850°C some trends can be observed, see Table 3. All samples except samples treated with KH_2PO_4 have a significantly larger degree of weight reduction compared to the control sample. Also, when steam was present, the weight reduction of almost all samples was decreased compared to the experiments using a dry atmosphere. Only the sample treated with KH_2PO_4 showed that the weight reduction increased when steam was present in the atmosphere.

Table 3. The weight reduction for the samples treated in the tubular oven at 850°C for 6 h in an atmosphere of 5 % CO and 95 % N_2 or 5 % CO, 45 % N_2 and 50 % steam. The potassium content for all samples, except the control sample, was 4 wt.%.

Ash component	No steam [wt.%]	Steam [wt.%]
Control	-7,51	-4,02
K_2CO_3	-17,14	-7,70
KCl	-17,14	-10,53
K_2SO_4	-14,71	-3,84
KH_2PO_4	-5,36	-8,79

Since the mass reduction in Table 3 is only based on the total mass reduction of the sample the oxygen release from the OC is not the only contributor. The mass reduction is also due to losses of the potassium salts that leaves the sample by evaporation or reaction where volatile gases is produced. Due to the small sample volumes, it was impossible to quantify the elements that were present after the reduction. Thus it was impossible to identify which part of the weight reduction originates from the reduction of ilmenite only.

The reduction test shows that only the ash component KH_2PO_4 contributed to agglomeration. This tendency was named “heavy agglomerated” in Table 4. All the other investigated ash components only contributed to weak or no agglomeration tendencies that would not have any effects on the operation of a fluidized bed due to the mechanical forces disintegrating the week agglomerates. However, since no actual fluidized bed was used, the claim that only KH_2PO_4 of the tested salts can cause defluidization is only an estimation.

The general pattern for the agglomeration was that the tendencies slightly decreased when steam was present. For samples treated with KH_2PO_4, there was no difference in the agglomeration with or without steam. Only the sample treated with KCl indicated increased agglomeration in the presence of steam. This can be due to decreased evaporation of potassium and increased interaction between potassium and ilmenite that was indicated by the EDS analysis of the samples.

Table 4. The observed tendencies for agglomeration after the reduction tests. Only KH_2PO_4 had a tendency to agglomerate to such an extent that it can cause defluidization in these conditions.

Ash component	No steam	Steam
Control	Weak to no agglomeration	No agglomeration
K_2CO_3	Weak to no agglomeration	No agglomeration
KCl	No agglomeration	Weak to no agglomeration
K_2SO_4	Weak agglomeration	No agglomeration
KH_2PO_4	Heavy agglomerated	Heavy agglomerated

From the SEM-EDS analysis, some trace elements could be detected. These trace elements were magnesium, silicon, aluminum, calcium and sodium. Some of these trace elements appeared as impurities on the particles that were constructed of another phase than the ilmenite phase. In general, the impurities were silicon based. In these areas of silicon, a mixture of aluminum, magnesium, calcium and sodium were present as well. The silicon phase with the other impurities did not appear to have any direct effect upon the ilmenite even when treated with potassium salts.

Magnesium and sodium, that was present in the ilmenite, showed a more clear interaction with the ilmenite compared to aluminum, silicon and calcium. When a phase separation appeared in the sample between iron and titanium, the magnesium and sodium also segregated. Magnesium was segregating into the titanium rich phase. Unfortunately, these concentrations were too low to be able to detect with XRD so no reaction could be confirmed. Sodium, on the other hand, segregated into the elementary iron crystals. This was particularly clear in the sample where K_2SO_4 was present in the experiment without steam. This was not predicted since potassium interacted with the titanium and formed different types of potassium-titanates. This suggests that even although both sodium and potassium have shown to have similar activity with ilmenite (Foley & MacKinnon, 1970) they may interact through different mechanisms. However, further studies need to be carried out to clarify if sodium from sodium rich ashes interacts with the elementary iron in a similar manner as the trace elements in this study.

5.2.1 Mixing test

A mixing test was performed to show that the time of mixing did not affect the outcome of the heat treatment performed during the reduction test to any large extent. Therefore, a well-mixed sample was compared to a sample where the mixing was performed for a shorter time. For this test, the sample treated with K_2SO_4 used due to the characteristic surface changes that occurred during the reduction without steam described more closely in section 5.7.

It was seen that the mixing could have some effect. The surfaces of the particles appeared to be the same with the same characteristics of iron distribution on the surface. However, the mass reduction after the heat treatment was different. The mass reduction was -12.35wt.% compared to the longer mixing that had a reduction of -14.71wt.%. This suggests that the mixing has some importance and that the increased interaction between K_2SO_4 and ilmenite increases the reduction rate at 850°C.

5.2.2 Stationary test

From the stationary test, it was observed that no diffusional differences due to gravity could be determined at these conditions. The stationary particles appeared to have the same characteristics in elemental distributions as the particles that had not been stationary orientated. Table 5 below shows the weight reduction in the stationary tests. These are similar, but not the same, as the tests there the particles were not maintained in the same positions. This indicates that there will be some variations regarding the weight analysis and that more tests need to be performed to get a statistical value of weight reduction for this ilmenite.

Table 5. The weight reduction obtained for the stationary tests in the tubular oven at 850°C for 6 h.

Ash component	No steam [wt.%]	Steam [wt.%]
KCl	-19,86	-7,04
K2SO4	-15,22	-7,00

However, the sample containing K_2SO_4 treated with steam did not show the same fractionation behavior as the sample treated in a ceramic boat under the same conditions. Also, the weight reduction was much higher for the same sample compared to earlier reduction test (Table 3). These differences can be due to absorbed moisture, see discussion in section 5.7.

5.3 XRD analysis

Generally, the XRD diffraction patterns were hard to interpret since the background noise was relatively large compared to the diffraction peaks. Therefore, the analysis of trace elements, such as $MgSiO_3$, was very uncertain since signals from these compounds were impossible to separate from the background noise.

Table 6. Results from the XRD analyses of the samples reduced at 850°C for 6h. The results from the analysis are divided into groups that contain only iron and titanium as ilmenite (oxygen carrier) and phases that have been produced by the interaction with the potassium salts (potassium salt interactions).

Sample	Without steam		With steam	
	Oxygen carrier	Potassium salt interactions	Oxygen carrier	Potassium salt interactions
Control	Fe, $Fe_{1.1}Ti_{0.9}O_3$, Fe_2O_3, TiO_2	No salt	$FeTiO_3$, Fe_2O_3	No salt
K_2CO_3	Fe, $FeTiO_3$, TiO_2	$K_{0.012}Ti_8O_{16}$	$FeTiO_3$, Fe_2TiO_4	$K_6Ti_4O_{11}$
KCl	Fe, $FeTiO_3$, Fe_2TiO_4, TiO_2	No K or Cl found	$FeTiO_3$, Fe_2O_3, $Fe_{2.5}Ti_{0.5}O_4$	$K_{0.012}Ti_8O_{16}$
K_2SO_4	Fe, $Ti_{1.878}O_3$	$Fe_{0.975}S$, $K_{0.012}Ti_8O_{16}$	$FeTiO_3$, Fe_2TiO_4, $Fe_{2.936}O_4$	K_4TiO_4, $K_{0.48}H_{0.22}Ti_{1.825}O_4(H_2O)_{0.52}$
KH_2PO_4	Fe_2TiO_5, TiO_2	KPO_3, P_2O_5	$Fe_{1.1}Ti_{0.9}O_3$, Fe_2O_3, TiO_2, Fe_2TiO_5	KPO_3, P_2O_5

As can be seen from Table 6 ilmenite in all samples, except in samples mixed with KH_2PO_4, treated in a dry atmosphere reduced all the way to elementary iron. The formation on elementary iron was not obtained in the presence of steam; here the oxidized ilmenite only reduced into ilmenite.

Of the samples containing potassium salts, it was only the samples mixed with KH_2PO_4 and KCl that did not show any presence of potassium-titanates. No potassium or chloride phase of samples mixed with KCl treated without steam could be confirmed with XRD. This probably since most of the KCl evaporated.

5.4 TGA test

As concluded by both El-Tawil et al. (1996) and Foley & MacKinnon (1970) a high alkali concentration in the sample does increase the reaction and segregation rate in the ilmenite. However, this was only observed for the samples containing K_2CO_3 and K_2SO_4. The sample containing KH_2PO_4 had a significantly reduced reaction rate, see Figure 7 below. These results were consistent with the findings from the reduction experiment displayed in Table 3. The only difference was that the reduction rate of the sample treated with K_2CO_3 was larger than K_2SO_4 after 6h. This is probably due to that more of the potassium salt K_2SO_4 is present after full reduction is achieved since sulfur bonded to iron while the carbonate left the sample. However, to prove if there are any significant differences several more tests need to be performed in the future to have a statistical relevance.

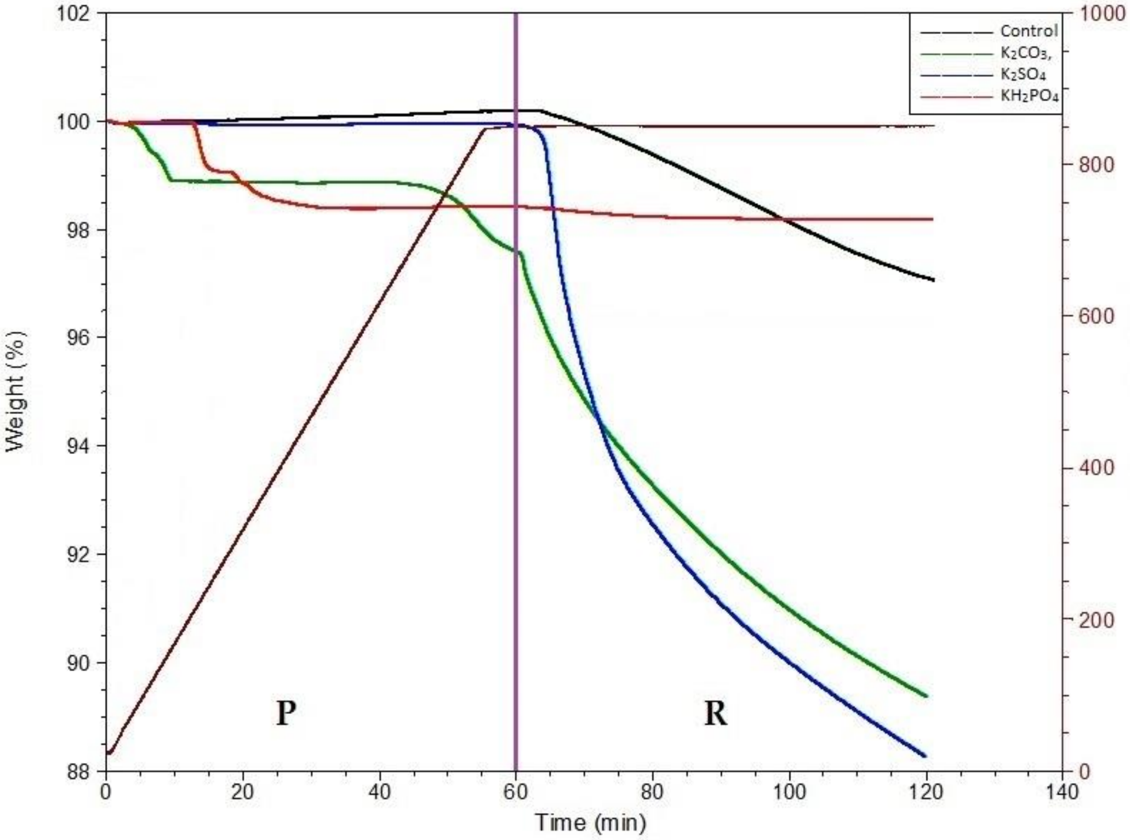

Figure 7. The reduction process of ilmenite samples in the TGA. Protecting atmosphere (P) during the heating and then reducing (R) with 5% CO at 850°C. The purple line shows the change of atmosphere from protective to reductive. The brown line shows the temperature.

During the heating period of the samples, the atmosphere was composed of only nitrogen. However, due to the high temperature, some changes of the masses were observed as shown in Figure 7 above, especially for samples containing K_2CO_3 and KH_2PO_4. This is due to KH_2PO_4 decomposes to KPO_3 and steam at about 200 °C according to reaction (12). The weight reduction in the figure corresponds to the loss of water that can be expected from that decomposition reaction (Wu et al., 2011). XRD could confirm the presence of KPO_3 in both samples treated with KH_2PO_4.

$$KH_2PO_4 \rightarrow KPO_3 + H_2O_{(g)} \tag{12}$$

Figure 7 shows that the curve for K_2CO_3 has two significant steps, one at temperatures about 100°C and one at about 800°C. The weight reduction that occurs at about 100°C was most likely caused by evaporation of adsorbed moisture. The decomposition of K_2CO_3 to K_2O and CO_2 that occurs at high temperature is very dependent on the partial pressure of CO_2. The decomposition reaction can occur at 800 °C if the partial pressure of CO_2 is more or less zero. However, with increased partial pressure of CO_2, the temperature of decomposition reaction will increase and get closer to the melting point (Lehman, Gentry & Glumac, 1998). This suggests that the second weight reduction at 800°C can be attributed to the decomposition of K_2CO_3. The observed weight reduction in Figure 7 also corresponds well with the expected weight reduction if this reaction would have occurred. However, in the fuel reactor, the CO_2 level will be higher. This may prevent the decomposition reaction of K_2CO_3 in the fuel reactor and this may have an effect on the properties of the bed since K_2CO_3 has a melting temperature at about 900°C (Lehman, Gentry & Glumac, 1998). This temperature is fairly close to the operating temperature meaning the K_2CO_3 might have a sintering effect on the fluidized bed. K_2O has a lower melting temperature, about 740°C (Haynes, 2014) that would have led to sintering of the particles. However, no agglomeration was observed and with XRD was no alkali salt detectable. This suggests that no K_2O was present after the reduction and that potassium reacts with the ilmenite immediately. Reaction (13) suggests the pass of events that produces the potassium-titanates in the sample of activated ilmenite mixed with K_2CO_3.

$$\mathrm{K}_2CO_3 \xrightarrow{-CO_2} K_2O \xrightarrow{+ilmenite} K - titanate \tag{13}$$

For the experiments with two reduction sequences with an intermediate oxidation step, the reaction rate for the second reaction was slightly increased for K_2SO_4 and K_2CO_3. The reaction rates for the oxidation were significantly higher for all experiments compared to the reduction rate. However, this can originate from the fact that the oxygen flow rate was four times higher compared to the CO flow. According to previous studies, the reaction rate of oxidation is fast compared to reduction with only CO (Cuadrat et al., 2012). The weight curves for the different samples that were reduced, oxidized and reduced again can be seen in Figure 8 below.

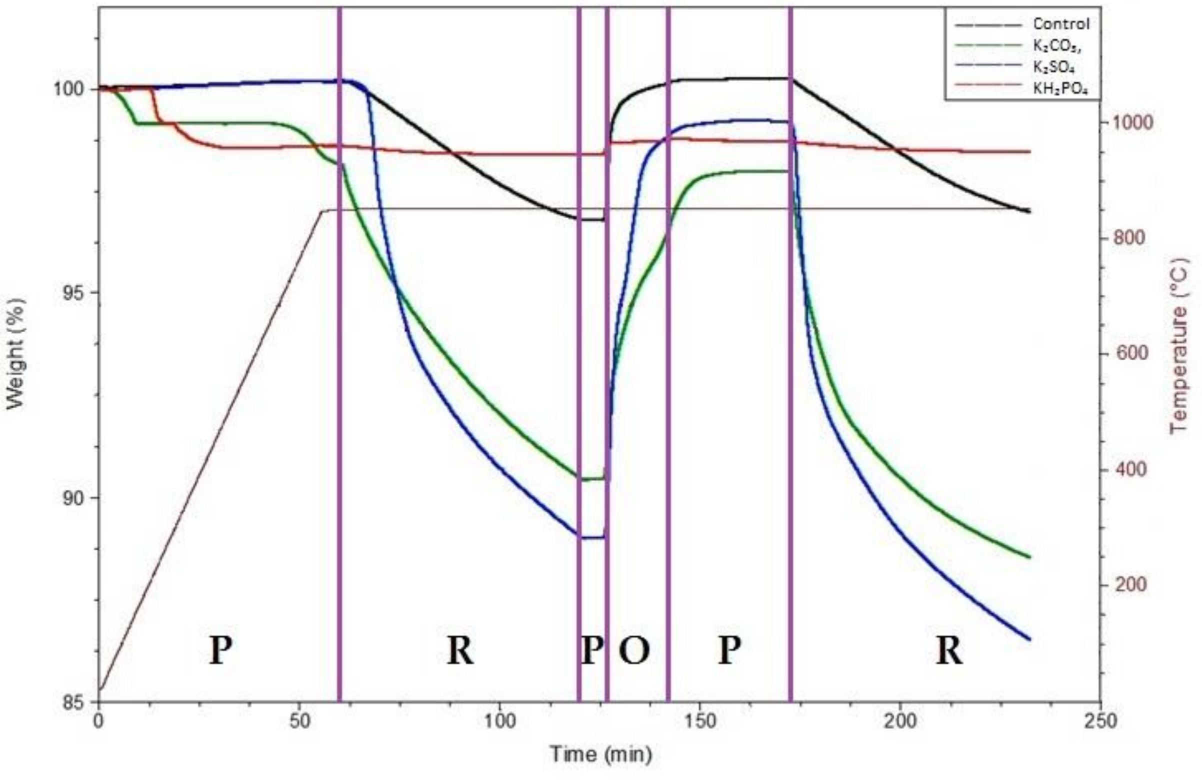

Figure 8. The reduction and oxidation process in the TGA. The purple lines show the change of atmosphere between protective (P), reductive (R) and oxidative (O). The brown line shows the temperature.

The oxidation reaction in Figure 8, i.e. weight growth, did not stop at the instant the synthetic air was exchanged to pure nitrogen. This was most likely due to that oxygen still was present in the pores of the particles and the slow dilution of oxygen in the balance house during purging. It can be observed that the time for oxidation was not enough to oxidize the samples to the weight they had before the reduction except for the control sample. This suggests that the reaction rate for oxidation is not affected exactly proportionally to the reaction rate of reduction in the presence of ash components. However, to investigate this further, more tests and red-ox-loops are needed. Another study of Adánez et al. (2010) has shown that after some cycles the reduction and oxidation will reach more stable red-ox-loops so the same reaction rate is obtained for every cycle. However, these tests did not introduce any ash components that change the reaction behavior of the ilmenite.

The TGA analysis indicates that the weight reduction for samples containing K_2CO_3 and K_2SO_4 well exceeds the oxygen carrier capacity of ilmenite. Instead of the theoretical 5 wt.% for ilmenite, the weight reduction was during the reduction 7.7 wt.% and 11 wt.% for the first reduction stage for K_2CO_3 respectively K_2SO_4. For the second reduction stage this weight reduction was even larger, 9.5 wt.% respectively 13 wt.%. This can be compared to the theoretical weight loss of -15wt.% for a sample containing only pseudobrookite and rutile that is reduced to rutile and elementary iron. This indicates that the reduction proceeds too far and iron is segregated to form fully reduced iron, i.e. elementary iron. This has also been observed in the EDS and XRD analysis of the samples.

5.5 Potassium carbonate

At the surface of the particles, no significant difference could be seen when comparing the control samples with the samples containing K_2CO_3. In samples with no presence of steam crystals containing iron were observed on the surface. These types of crystals were not observed in the samples when steam was present and the surface was more homogeneous.

On the inside of the particles treated in a dry atmosphere, some differences could be seen regarding the segregation of iron. In the presence of K_2CO_3, the number of islands of iron was increased in the cross section, but the sizes of every single island were smaller compared to the control sample. The presence of potassium in the structure seems to have increased the nucleation spots where to the iron can segregate. This can be compared to similar findings of El-Tawil et al. (1996). They showed that the presence of K_2CO_3 promotes the separation of iron and titanium (Tawil et al., 1996).

Increased nucleation can also be observed for the sample that was treated with steam. In this sample, the segregation is located in a very large number of small islands in the cross section. This suggests that the nucleation is further increased when K_2CO_3 is present together with steam where it can form KOH that reacts with ilmenite. This difference can be seen in Figure 9 where the particle cross section is displayed. The distribution of potassium is not homogeneously over the particle cross surface. The potassium concentration is increased in areas that have more titanium compared to iron, this indicates the presence of potassium titanates also observed by El-Tawil et al. (1996). The potassium titanates with the formulas $K_{0.012}Ti_8O_{16}$ and $K_6Ti_4O_{11}$ were also found in the samples treated without steam respective with steam.

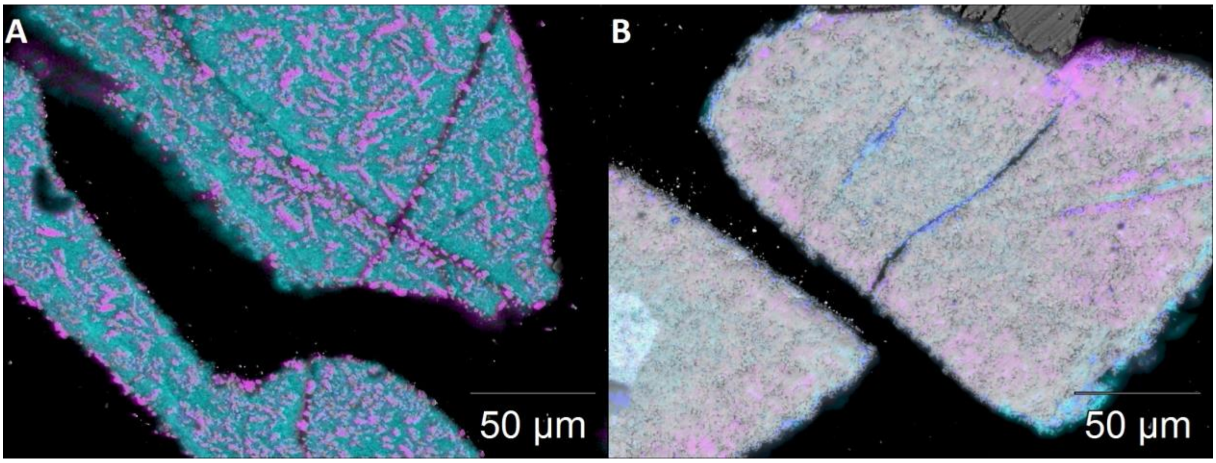

Figure 9. EDS analysis of the cross section of the particles that have been heated in the presence of K_2CO_3 at 850°C for 6 h. Figure A) reducing environment containing 5 % CO and B) reducing with 5 % CO and 50% steam. Areas colored in purple have higher concentrations of iron and turquoise areas have a higher concentration of titanium. It is clear that B) shows more small iron "islands" compared to A) that shows the presence of a less amount of large well-segregated iron "islands".

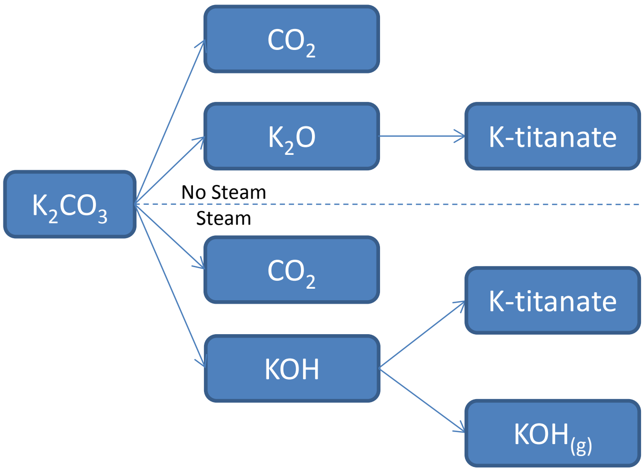

Figure 10. Suggested reactions for K_2CO_3 in dry and wet atmosphere and how it interacts with ilmenite.

The samples treated with K_2CO_3 taken from the TGA experiments show the same segregation as observed in Figure 9 A, despite the shorter reducing time. However, the segregation was mostly located towards the surface of the particles and only some 50 µm inwards. Compared to the distribution of potassium that could be detected throughout the whole particle cross section using EDS. This distribution suggests that the rate of the reducing reaction that results in segregation is determined by the mass transport of reducing gas through the particle and not by diffusion of potassium.

The surface of the sample retrieved from the TGA experiment that was reduced only once had the same appearances as the sample of the reduction test without steam, iron crystals were present on the surface of the particles. However, on the particles that were looped in TGA, the iron crystals had grown irregularly and formed a "coral reef" like structure. This structure on the surface was similar to the surface of the particles treated with K_2SO_4 without steam, see section 5.7. It is questionable if this advanced iron structure could be formed in an FBC due to attrition and abrasion. This would produce a lot of iron fines that would be removed with the ash in a CLC application. Iron-enriched fines have also been observed in earlier studies of Knutsson & Linderholm (2015) of a 100 kW_{th} CLC plant.

The TGA analysis of the mixed sample showed a significant increase in reduction and oxidation rate of ilmenite in the presence of K_2CO_3. This could also be concluded from the increased weight reduction shown in Table 3. The reaction rate was increased further for the sample after the oxidation. It was then observed in SEM-EDS that the segregation of iron within the particle was further developed throughout the cross section. The number of cracks increased and large crystals of iron were present. The increased reaction rate can be an effect of increased porosity together with the easily accessible iron that has a higher reaction rate compared to ilmenite (Adánez et al., 2010).

5.6 Potassium chloride

The surface of the particles was significantly different if the particles mixed with KCl were treated with or without steam during the reducing conditions. The particles treated without steam had iron crystals on the surface in a similar manner as the control sample and the K_2CO_3 sample. However, the surface of the samples treated with steam did not show the same feature as the other samples. The surface seemed homogeneous with respect to elements according to SEM, but with a large number of canyons on the surface. The cross section investigated with EDS also showed that the surfaces of the particles were not always built-up in the same way. Some particles had a higher concentration of iron at the surfaces while some had a higher concentration of titanium at the surface.

The cross section of the particles treated without steam shows a distinct segregation of iron towards a few larger islands. The islands were distributed evenly in bulk but with some increased frequency at the surface and in the cracks, see Figure 11. The mixture treated with steam in a reducing atmosphere showed no distinct formation of islands. However, some segregation of iron towards small islands was present in regions at the surfaces of the particles. Regarding titanium, there was no observed segregation besides areas occupied by iron islands.

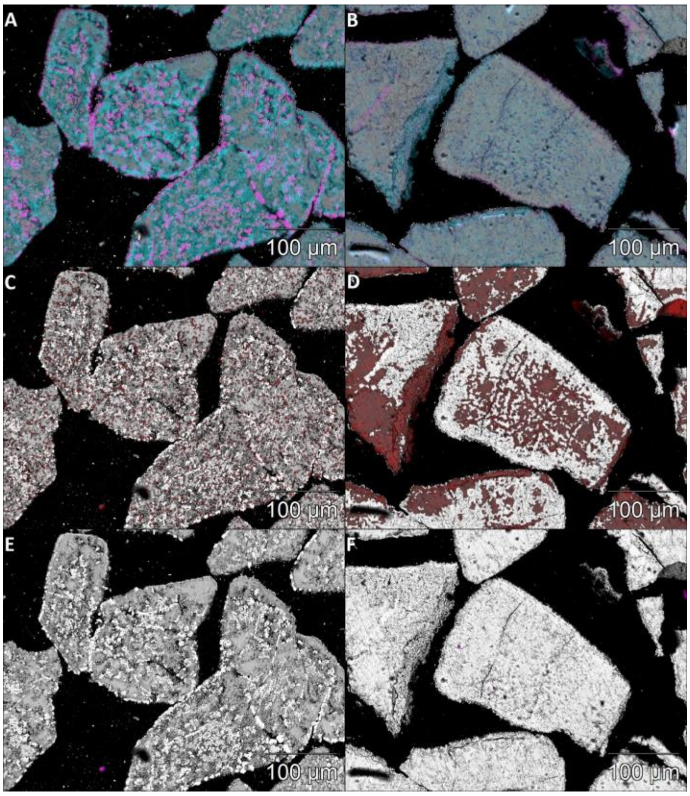

Figure 11. The EDS of the cross section for ilmenite particles mixed with KCl reduced at 850°C with 5% CO for 6 h. Left side: particles reduced without steam. Right side: particles reduced with steam. Iron marked in purple, titanium marked in turquoise and potassium marked in red. The intensity of the potassium in figure C) is very low and most intense at a point outside the particles together with chloride in E), probably KCl that has not evaporated.

Both the sample mixtures with KCl treated in different atmospheres showed that salts were evaporated from the samples. Evaporated salt did also appear as white water soluble salt deposits in the tube outside the oven where the temperature was lower. Barely any potassium or chloride could be observed in the sample treated without steam from the SEM-EDS analysis. Only one small crystal of unevaporated KCl could be observed. This crystal can be seen in Figure 11 C) and E).

The sample treated with steam showed that some chloride was present in small but high concentrated areas inside the particles. This could indicate that the chloride does not diffuse in the particle. However, the potassium had diffused into the particle and accumulated to areas where the titanium level was increased. This feature of the ilmenite interacting with the potassium is a preferable property from a perspective of OCAC since KCl are a known compound to cause agglomeration in FBC containing silicon dioxide (Elled, Åmand & Steenari, 2013).

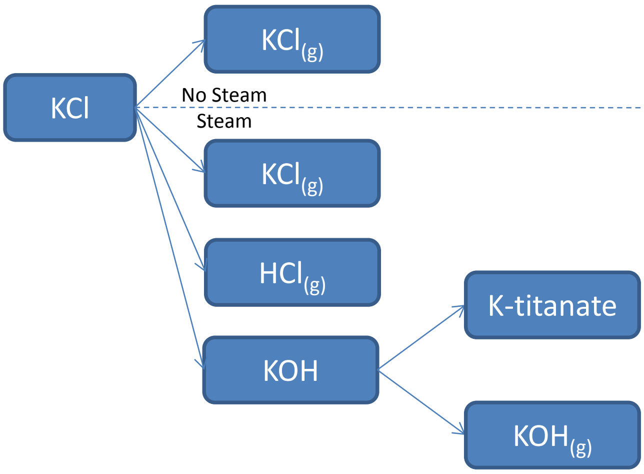

Figure 12. Suggested reactions for KCl in dry and wet atmosphere and how it interacts with ilmenite.

From the stationary test it was also clear that some potassium interacted with the impurities, but less there the aluminum concentration was higher.

Also regarding the corrosion, the attribute to spit up potassium and chloride is a good property. The amount of potassium in the sample was much higher than the amount of chloride when treated with steam. This suggests that the KCl undergoes a reaction with steam to produce HCl and KOH, this was also confirmed with FactSage. HCl would then be evaporated from the ilmenite and the KOH interact with the sample to some degree. If the presence of ilmenite increases the conversion of KCl to KOH and HCl, it would be a good feature since reduced problems with corrosion on the superheaters would be obtained. KCl is very corrosive and decreases the first melting temperature of the fly ash compared to KOH that will form carbonates in the presence of CO_2 that have a higher melting temperature. Decreased corrosion on the super heaters allows increased steam temperature that favors the electricity production from the power plant (Zevenhoven, Yrjas & Hupa, 2010). Figure 12 shows the suggested reactions that could have occurred according to the results of this study.

5.7 Potassium sulfate

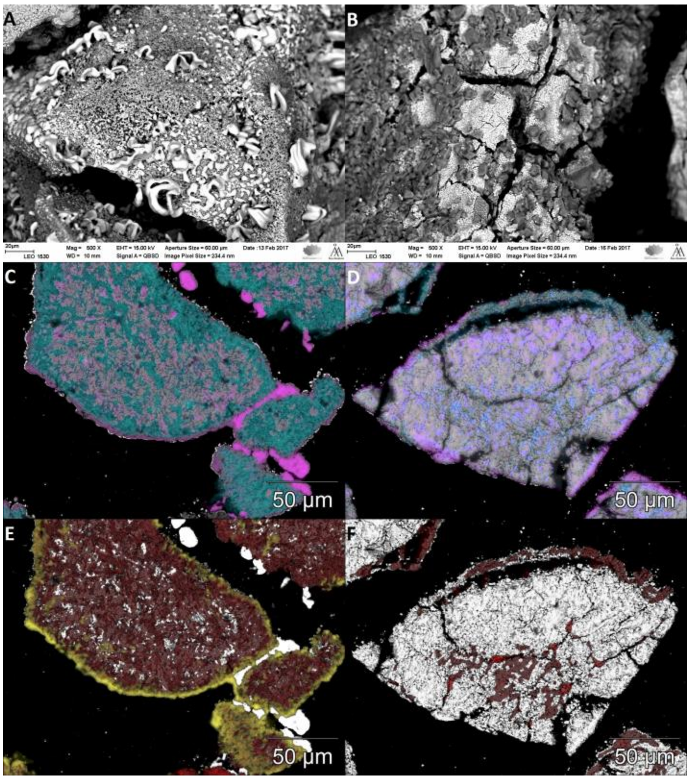

Figure 13. The ilmenite particles mixed with K_2SO_4 treated at 850°C in reducing environment for 6 h. On the left treated with 5% CO and on the right with 5% CO and 50% steam. A) and B) is SEM images of particle surface. C) and D) SEM-EDS of particle cross section, iron marked in purple and titanium marked in turquoise. E) and F) SEM-EDS of particle cross section, sulfur marked as yellow and potassium marked in red.

From the performed experiments, it was very clear that addition of K_2SO_4 has a great effect on the ilmenite. For the sample treated without steam, iron diffused towards the surface and migrated out of the particles to form arcs and crystals of elementary iron. This can be seen in Figure 13 A). This migrated iron also seems to contribute to the increased agglomeration since the particles shown in Figure 13 are fused together by elementary iron. Iron also created small islands within the particles cross section. These small islands differ from those seen in the control sample by that these islands are shaped like a grain of rice compared to the small round islands in the control sample. Titanium was more or less homogenously distributed over the sample with decreased concentration in the iron-rich grains and the migrated iron.

The same type of iron migration could not be observed for the particles that were heated under reducing conditions in the presence of steam. These particles had iron migrated to the surface as a thin coating and on this surface crystals that contained less iron were situated, shown as grey crystals in SEM picture in Figure 13 B). From the analysis with EDS of the crystals, it could be concluded that the crystals mostly contained potassium and oxygen, possibly KOH. However, it was not possible to confirm the presence of KOH with XRD.

It was also observed that the particles mixed with K_2SO_4 treated with steam had obtained many cracks and produced many smaller particles, most likely by fractionation. This fractionation can be seen in Figure 13. However, when the same mixture was investigated again in a similar stationary test with steam, only a few cracks were observed. The difference between these two experiments may be that the first reduced sample was produced during a weekend. The sample had then a longer time to interact with the remaining moisture in the tubular oven after cooling forming hydrates as $K_{0.48}H_{0.22}Ti_{1.825}O_4(H_2O)_{0.52}$ that was detected with XRD. When moisture is adsorbed and bound into the crystal structure as hydrates, the crystals will expand. This could be the cause of the severe fractionation. The adsorption of moisture can also explain the reduced weight of the sample treated with K_2SO_4 and steam were low compared to the other samples treated with steam, see Table 3. The weight reduction was also low in comparison with the stationary test seen in Table 5.

In the two different atmospheres, the K_2SO_4 and ilmenite mixture behaved differently. Regarding sulfur from K_2SO_4, it was observed that it formed a crust around the particles when no steam was present. Besides sulfur, this crust contained iron as well. From the XRD it could be concluded that the sulfur had reacted with iron and formed $Fe_{0.975}S$. However, when steam was present, no sulfur could be detected either with SEM-EDS or XRD. This indicates that the sulfur reacted with the steam to produce a volatile compound that escaped the sample. From FactSage calculations could it be calculated that H_2S and SO_2 should be present in the gasses.

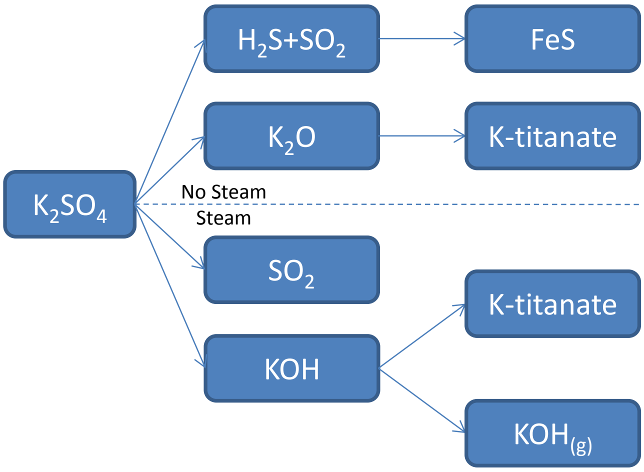

Figure 14. Suggested reactions for K_2SO_4 in dry and wet atmosphere and how it interacts with ilmenite.

Potassium was distributed evenly through the sample when no steam was present with some increased concentration in areas with increased titanium concentration. When steam was present the potassium was located to areas where the titanium concentration was increased as well as in some cracks within the particles. In both samples, treated without or with steam, it was confirmed with XRD that potassium-titanates such as $K_{0.012}Ti_8O_{16}$ respective K_4TiO_4 were formed. This means that the potassium, or some of the potassium, is chemically bonded to the titanium. However, from the SEM-EDS, it could not be determined exactly how much potassium that was left in the sample treated with steam. However, from the EDS it can be indicated that less potassium was present when steam has been used. This suggests that potassium has evaporated from the sample, probably as KOH. KOH should be present according to equilibrium calculations in FactSage® if steam is present.

When no steam was present, ilmenite could not be detected with XRD after the reduction when mixed with K_2SO_4. Only segregated titanium as titanium oxide and iron as elementary iron was observed with XRD. From the SEM-EDS it was also concluded that the segregation of iron and titanium were very clear, see Figure 13. From the TGA analysis, it was also seen that the reduction rate was very fast for this sample. Elementary sulfur has also been used to improve the reduction of iron oxide in ilmenite to elementary iron to improve separation of iron and titanium. This is done to upgrade the ilmenite to synthetic rutile (Zhang, Zhu & Cheng, 2011). Sulfur is also used as an additive at industrial scale to improve the removal of both iron and magnesium from the titanium oxide in the so-called Becher process. It is stated that sulfur reacts with the manganese that is present in the ore and also stops the formation of irreversible iron-titanium compounds (Iluka, 2012). This means that the presence of sulfates also could have these segregating effects. Sulfate and sulfur can, therefore, decrease the lifetime and decrease the oxygen carrier capacity of ilmenite if used as an OC. This makes it less profitable with sulfur-rich fuels and unwise to use sulfur as an agent to reduce corrosion in the boiler as proposed for biomass combustion (Zevenhoven, Yrjas & Hupa, 2010). However, these effects of increased iron-titanium segregation were absent when steam was present.

When steam was present, the segregation of iron and titanium was less pronounced, see Figure 13. The ratio between iron and titanium were more or less as in ilmenite, i.e. ratio 1:1. The presence of ilmenite was also confirmed with XRD. This reduced segregation can be caused by a reduced reduction compared to other samples reduced in wet atmosphere with potassium salts. This was observed from the low weight reduction, high oxidation level in EDS and XRD.

5.8 Potassium phosphate

The presence of KH_2PO_4 caused severe agglomeration in accordance with the first mechanism suggested by Elled, Åmand & Steenari (2013). The salt melted and formed a coating upon the particles that behaved as a glue between the particles. This gluing between two particles can be seen in Figure 16 A) and B). This behavior was the same regardless if steam was present or not.

No adsorption of potassium or phosphor into the ilmenite could be observed in none of the used atmospheres, only some migration of the melt into cracks within the particles could be seen. Potassium and phosphorus were always located together which indicates that KH_2PO_4 does not react with any other element in the ilmenite particles. From the TGA it was observed that the weight of the sample was significantly reduced at low temperatures (~200°C), see Figure 8. This is caused bu the decomposition of KH_2PO_4 into KPO_3 and steam. KPO_3 has a low melting temperature of 807°C. This suggests that the coating around the particles, as seen in Figure 16, most likely were formed by

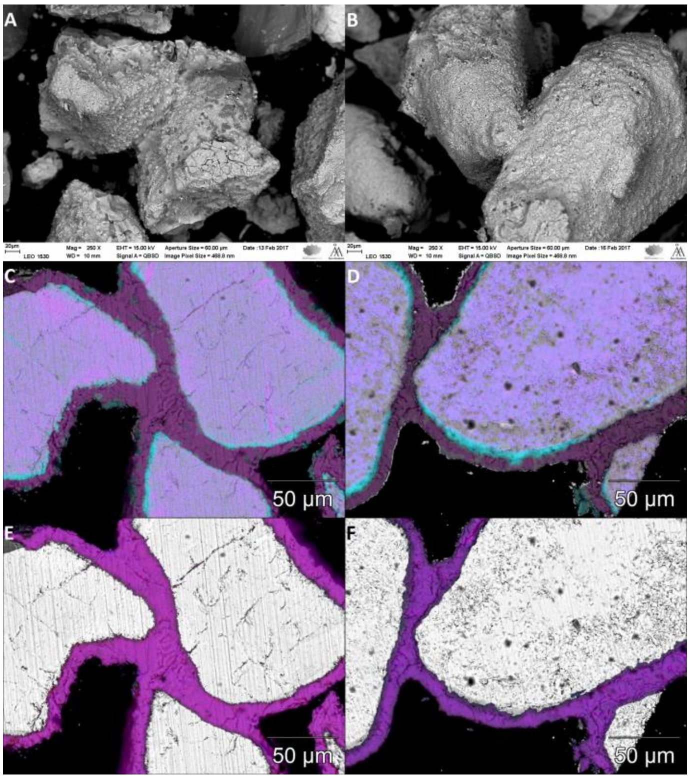

Figure 16. The ilmenite particles mixed with KH_2PO_4 treated at 850°C in reducing environment for 6 h. On the left treated with 5% CO and on the right with 5% CO and 50% steam. A) and B) is SEM images of particle surfaces there particles have sintered tohether. C) and D) SEM-EDS of particle cross section, iron marked in purple and titanium marked in turquoise. E) and F) SEM-EDS of particle cross section, phosphorus marked as blue and potassium marked in red, it was observed that no separation of phosphor and potassium had occurred in either atmosphere. A clear coating of the potassium salt can be observed.

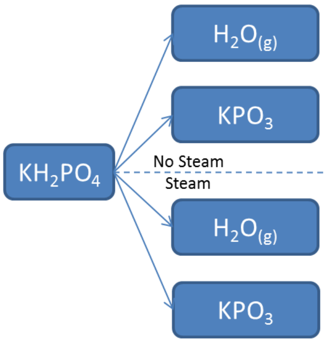

Figure 15. The suggested reaction scheme for KH_2PO_4 reactions in presence of ilmenite under reducing atmosphere with and without steam at 850°C. The formed KPO_3 melts and forms a coating around the ilmenite particles that both stops the OC from reaction with the fuel or atmosphere and also leads to agglomeration.

molten KPO_3 (Wu et al., 2011). The presence of KPO_3 could also be confirmed by XRD for both the samples treated with steam and without steam. The presence of P_2O_5 was observed. Suggested reactions are obtained from this study is seen in Figure 15.

After reduction in a dry atmosphere, the internal structure of the ilmenite particles was similar to the structure of pretreated ilmenite. These findings combined with the low reduction in weight as observed in TGA suggests that the particles have been “protected” from reduction by the phosphate coating. This was also confirmed with XRD that showed that the sample still contained pseudobrookite and rutile after reduction. From the TGA experiments, it was observed that the weight reduction of the control sample was about 15 times greater during the first reduction compared to the sample containing KH_2PO_4. This significant decrease in reactivity was probably obtained by mass transport limitations of oxygen through the molten coating. From measurements of the BET surface area of the particles treated without steam, it was observed that the surface area was decreased by half if KH_2PO_4 was present, from ~0.50m^2/g to ~0.24m^2/g. This property of phosphate can be a very serious issue for an OC. Decreased reactivity to this extent prevents the oxygen carrier behavior of the ilmenite and could stop a CLC process. However, this problem might be reduced in a CLC process due to the increased weight reduction, as seen in Table 3, when steam was present. This increased weight reduction indicates that if steam is present the reaction rate will not be decreased to the same extent. From the XRD it was also confirmed that the sample contained mostly ilmenite that suggests that the reduction occurred to a greater extent when steam was present.

Iron was evenly distributed both within the particles and the coating except for the areas where the titanium level was increased, see Figure 16. That iron diffuse into the coating of phosphate but not the titanium is already known by the industry that uses phosphate as a fluxing agent in the titanium pigment production. Phosphate is used to absorb impurities from titanium rich slags to increase the purity. The titanium rich slag is a left over after reduction of ilmenite in an electric arc furnace to extract pig iron from the ore (Van Dyk & Pistorius, 1999). Other trace elements from the ore, such as aluminum and manganese, were also observed to be diffused into the coating after the heat treatment.

At the interaction surface of particles and coating, a layer that contained mostly titanium, potassium and phosphate was observed. This film was about 0.5-5 µm for all samples mixed with KH_2PO_4, about the same thickness as found in the layer with increased iron concentration that was observed on the ilmenite after the pretreatment. This suggests that the particle surface with easily available iron interacts with the KH_2PO_4 and the iron is extracted into the flux. At the same time, some of the potassium salt will diffuse into the surface where the iron has left. Some titanium was also detected at the surface of the coating which can be some fragments of particles caused by mixing prior to the heat treatment.

From the alternating TGA test, it was observed that even some titanium had a tendency to migrate to the coating. In the coating, the titanium was located together with a higher concentration of potassium, which can be an evidence of some potassium-titanate. No iron and no magnesium were located at the same place as titanium. This suggests that when the titanium is oxidized, it will be more interacting with the coating and react with available potassium.

5.9 General discussion; Experimental constraints

5.9.1 Mixing

Mixing of solid particles of different sizes is always a problem, this study is no exception. It was observed that some samples were very hard to mix until homogeneity since the ground potassium salts were segregated from the larger ilmenite particles. Especially KCl and K_2CO_3 did segregate, even when the sample mixtures were stored in the desiccator. This makes it harder to carry out the analysis of single particles since every particle may have a different microenvironment regarding the potassium salt concentration.

5.9.2 Statistical relevance

The SEM-EDS analysis was only performed on single particles when it was not possible to investigate several at the same time. This results in a risk of drawing conclusions for the whole sample on basis of too few experiments. To minimize these risk particles were selected in such a way that they looked like the others in a zoomed-out SEM picture chosen for SEM-EDS analysis. However, even if this has been done, it was observed that particles next to the targeted particle may have a different elemental distribution. This effect of microenvironment could be reduced if a fluidized bed would have been used. In a fluidized bed, the particles and ash components would be mixed continuously and the whole sample would have a more homogeneous salt distribution.

In these types of experiments, some fluctuations will always occur that will affect the results. To prevent drawing conclusions from one single particle or one single sample it is better to replicate the experiments. Replicates will give a better statistically sound result. With repeated tests, it would have been possible to see if there is a significant difference regarding weight reduction if two different potassium salts are interacting with the OC. For example, the experiment with ilmenite and K_2SO_4 in a reducing environment without steam was repeated three times in slightly different manners. Firstly well mixed, secondly less mixed and thirdly well mixed in a stationary small ceramic sample holder. These three experiments gave different weight reduction, -14.71wt.%, -12.35wt.% respective -15.22wt.%. The first and the third should be more or less the same. However, with so few repetitions, it is impossible to show that the second test significantly differs from the other two with a statistical test.

5.9.3 Ending the experiments

To avoid oxidation of the hot samples by air after the reduction the samples were cooled down inside the tubular oven during the night under a flow of nitrogen. Also, the samples analyzed with TGA were cooled down to room temperature before they were extracted and analyzed. However, due to the experimental setup with the tubular ovens, it was impossible to control the steam generation exactly. When stopping the water pump, a certain amount of water was still present in the pre-heater in an evaporating puddle. This amount of water was not possible to quantify and therefore it was not possible to stop the steam flow after exactly 6 hours. Some water was maybe even left during the cooling stage when no CO was present. This could result in unwanted oxidation of the samples during the cooling and then wetting of the samples below 100°C when the steam condenses. To prevent this to some extent the water was pump shut off some minutes before the feed of CO were closed. In this way, the still evaporating water could react together with the CO before the gas would only contain nitrogen. However, due to the unknown water amount left in the preheater, it was impossible to determine how long the time before the feed of CO should be closed. Even this precaution seemed to be not enough since hydrates maybe were obtained in the sample treated with K_2SO_4 and steam that may be the cause the severe fractionation of the particles.

As observed from the TGA tests, the reaction rate was increased at 850°C when potassium salts were present when compared to the tests with pretreated ilmenite only. This makes this system very sensitive to changes in the gas atmosphere at this temperature. An alternative for a better steam feeding system is if aerosols could be produced of the liquid water and then preheated. This would remove the puddle of evaporating water that is hard to control. This system would react instantaneously when the water pump is turned off and then no more steam would be provided to the sample. With this kind of system, the atmosphere could be changed from reductive with steam to inert very fast and what would provide more accurate data regarding the oxidation level in the fuel reactor.

In this study, some rough estimations of the actual ilmenite reduction were performed. However, since no elemental analysis could be made, no convincing calculations could be performed. If the amounts of much of each element present after the reduction was known, calculations of more confident could be performed. From SEM-EDS, XRD and phase analysis of the SEM-EDS images, some estimations could be made. However, since it is hard to detect and identify low concentrations with XRD and the phase analysis only gives a rough estimation of the phases present too much information was unknown.

The potassium salts investigated in this project is only a few salts that can be present in bio ash. Therefore these experiments can only give a hint of what need to be considered regarding the design of a CLC power plant for biofuel and ilmenite as OC. It also gives a hint of what elements that might be problematic in a CLC and should, therefore, use fuels with less of these elements. Next step is to investigate other salts such as CaC_2O_4 and KOH and mixtures of salts to see how they interact with the ilmenite. After that, real ashes can be of interest to better understand the interaction with the OC.

6 Conclusion

From this study of potassium salts present in bio ash interaction with ilmenite under reducing conditions relevant of CLC, these following conclusions could be made:

- Steam has a great effect on the behavior of ilmenite and potassium salts in reducing environment.
- Potassium salts such as K_2CO_3, KCl and K_2SO_4 increases the oxidation and reduction rate of ilmenite. These salts do not contribute to agglomeration in either wet or dry condition.
- Iron will if reduced enough in dry conditions, diffuse to form crystals of elementary iron on both particle surface and inside the particles.
- Adsorbed potassium in the ilmenite forms potassium-titanates that increase the segregation of titanium and iron if no steam is present.
- KCl evaporates if no steam is present at 850°C. If steam is present, some KCl will produce HCl that evaporates while the ilmenite will adsorb some potassium and form potassium-titanates.
- KH_2PO_4 forms KPO_3 that creates a protective coating that causes agglomeration and decreases the reaction rate to near zero.
- KPO_3 from KH_2PO_4 also behaves as a fluxing agent that adsorbs iron and trace elements such as aluminum and manganese to the coating.
- Silicon, aluminum, calcium and magnesium impurities were more or less not affected by the treatments.

Since this study only was a first step in the understanding of the interaction of ilmenite and bio ash the possibilities to continue this work will be infinite.

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