

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Oxygen carrier aided combustion:  
Implementation of oxygen carriers  
to existing industrial settings

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## Abstract

Utilization of biomass and waste to produce heat and power is necessary for a sustainable future energy mix. Thermal conversion of biomass is considered to yield CO<sub>2</sub> neutral emissions and the utilization of waste reduces its volumes in a world struggling to dispose of ever-increasing amounts. However, these fuels can be difficult to combust as they are complex in their composition. One technology allowing for conversion of both biomass and waste is fluidized bed conversion. Commonly, fluidized bed boilers are operated with an excess of air which lowers the efficiency of the plant. Replacing the quartz sand used as bed material during biomass and waste conversion with an oxygen carrier is referred to as oxygen carrier aided combustion (OCAC). By this replacement, oxygen availability is increased throughout the combustion chamber with increased boiler efficiency as a consequence.

This thesis presents the implementation of oxygen carriers to existing industrial units. The development has been rapid due to the possibility of conducting research through integration of scales. Experiments on semi- and full industrial scale validated the improved distribution of oxygen. Bed materials extracted from the industrial units were analyzed and tested for their oxygen transferring capacity on laboratory scale. The evaluation of bed materials provided for an understanding of how oxygen carriers can be utilized for the concept. The oxygen carriers included in this work are two types of ilmenite: sand and rock, and a manganese ore.

This work provides a comprehensive understanding of how the bed material develops regarding oxygen transfer, as well as chemical and mechanical resistance. Sand and rock ilmenite show different characteristics when exposed to the process. When following their progression of iron and structural development after being subjected to OCAC, sand ilmenite develops cavities inside the particles to which iron migrates and which further causes mechanical instability and shattering of particles over time. Iron migrates to surfaces on rock ilmenite particles, which are decomposed by splitting. The materials interact similarly with main ash constituents of the fuel. A heterogenic outer layer is formed, consisting mainly of Ca but also traces of other elements from the fuel ash. Ca and K diffuse inward and are incorporated in the ilmenite structure. The ash interactions are not found to directly inhibit the oxygen carrying capacity, however, a decline in capacity is noticed as ash layers build up and become thicker.

This work shows that the oxygen carrier ilmenite can be implemented in existing industrial settings, without reconstruction of the current system. Optimization measures are proposed where magnetic separation allows for reuse of bed material that still contain oxygen transferring capacity and the regeneration of bed material can be decreased in comparison to quartz sand. Thus, the results of this thesis suggest that OCAC is a feasible concept for conversion of complex fuels.

**Keywords:** Oxygen carrier aided combustion, Ilmenite, Biomass, Fluidized-bed

# List of publications

This thesis is based on the following publications:

- I. Angelica Corcoran, Jelena Marinkovic, Fredrik Lind, Henrik Thunman, Pavleta Knutsson and Martin Seemann. Ash properties of ilmenite used as bed material for combustion of biomass in a Circulating Fluidized Bed boiler. *Energy Fuels* 2014, 28, 7672-7679.
- II. Fredrik Lind, Angelica Corcoran and Henrik Thunman. Validation of the oxygen buffering ability of bed materials used for OCAC in a large scale CFB boiler. *Powder Technology* 2017, 316, 462-468.
- III. Angelica Corcoran, Pavleta Knutsson, Fredrik Lind and Henrik Thunman. Comparing the structural development of sand and rock ilmenite during long-term exposure in a biomass fired 12 MW<sub>th</sub> CFB-boiler. *Fuel Processing Technology* 2018, 171, 39-44.
- IV. Angelica Corcoran, Pavleta Knutsson, Fredrik Lind and Henrik Thunman. Mechanism for migration and layer growth of biomass ash on ilmenite used for oxygen carrier aided combustion. *Energy Fuels* 2018, 32, 8845-8856.
- V. Malin Hanning, Angelica Corcoran, Fredrik Lind and Magnus Rydén. Biomass ash interactions with a manganese ore used as oxygen-carrying bed material in a 12 MW<sub>th</sub> CFB boiler. *Biomass and Bioenergy* 2018, 119, 179-190.
- VI. Angelica Gyllén, Pavleta Knutsson, Fredrik Lind and Henrik Thunman. Oxygen carrier activity dependence of ash layers on natural ilmenite. *To be submitted for publication*.
- VII. Fredrik Lind, Angelica Corcoran, Bengt-Åke Andersson and Henrik Thunman. 12,000 hours of operation with oxygen-carriers in industrially relevant scale. *VGB PowerTach* 2017, 7.
- VIII. Patrick Moldenhauer, Angelica Corcoran, Henrik Thunman and Fredrik Lind. A scale-up project for operating a 115 MW<sub>th</sub> biomass-fired CFB boiler with oxygen carriers as bed material. *5<sup>th</sup> International Conference on Chemical Looping*, 2018, Park City, Utah, USA.

# Contribution report

Angelica Gyllén (previously Corcoran) has contributed to the papers as follows:

- Paper I: Angelica is the principal author of Paper I, with the main responsibility for the experimental work, evaluation and writing.
- Paper II: Angelica co-authored the paper and contributed to the experimental work, the theoretical evaluation and to the discussions.
- Paper III: Angelica is the main author with main responsibility for experimental work, analyses, evaluation, writing and editing of the paper.
- Paper IV: Angelica is the main author with main responsibility for experimental work, analyses, evaluation, writing and editing of the paper.
- Paper V: Angelica is co-author and supported with knowledge on the parts of the paper that deals with ash interaction with bed material. Angelica contributed to the experimental work, evaluation and was responsible for writing parts of the paper that deals with ash accumulation and hollow ash particles.
- Paper VI: Angelica is the main author with main responsibility for experimental work, analyses, evaluation, writing and editing of the paper.
- Paper VII: Angelica is co-author and contributed with the experimental work, discussions and editing of the paper.
- Paper VIII: Angelica is co-author and contributed with the experimental work, discussions and editing of the paper.

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*Angelica Gyllén, Mölndal 2019*



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# CHAPTER 1

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## INTRODUCTION

The growing demand for energy has led to an increase in the levels of greenhouse gas (GHG) emissions, as the global production of heat and power is mainly generated by combustion of fossil fuels [1]. Released GHG accumulate in the atmosphere and are associated with an increase in the average global temperature and climate change [2]. It is well admitted that emissions of GHG will have to be reduced to meet the targets set by the Paris Agreement in 2015 [3]. A prerequisite for a sustainable future energy mix is that it has a low impact on the environment. Biomass is considered a neutral resource regarding emissions of GHG [4]. Used in combination with carbon capture and storage (CCS), biomass has the potential to yield net negative GHG emissions [5]. Furthermore, urbanization with ever-increasing production and consumption of products have resulted in significant augmentation of solid waste volumes. Worldwide, municipal solid waste (MSW) is principally deposited in landfill, of which open dumps predominate, causing pollution to air, land and water [6]. MSW is a feasible addition to today's energy mix as a noteworthy part is made up of biomass, and as there is a need to process waste volumes in society.

A common characteristic of biomass and solid waste is that they often come in irregular shapes and sizes. Additionally, they contain variable levels of moisture and ash-components, which is further described in Chapter 2. Because of this, they are considered difficult to combust [7]. The main technologies utilized for combusting biomass and waste are grate-fired and fluidized-bed (FB) boilers. Grate-fired boilers are used on smaller scale (10-100MW) while fluidized bed boilers are used on a larger scale (>50MW). In FB boilers, small particles of a chosen material, termed "bed material", are accelerated to a state of fluidization by combustion air and at occasion

also recirculated flue gases. An even distribution of temperature is achieved throughout the reactor as the bed material transfers the heat released by combustion to the heat-transfer surfaces. Depending on the rate of gas flow through the bed, FBs are defined as either bubbling fluidized-beds (BFB) or circulating fluidized-beds (CFB). In BFB the bed remains stationary during fluidization while in CFB the rate of gas flow is higher, which causes bed material to be entrained with the gas.

### 1.1 Circulating fluidized bed combustion

Apart from providing sufficient conditions for fluidization, the main function of the bed material in a CFB is to store and distribute heat in the reactor volume. During coal combustion, the bed material is made up of the inherent ash. Biomass, however, does not possess suitable ash, resulting in the need for addition of bed material to the system. Similarly, as MSW is inconsistent in its composition and contains large pieces, supplementation of bed material is required to preserve satisfactory fluidization properties. Further description of the fuels is provided in Chapter 2. Conventionally, the bed material utilized in biomass and waste fired CFB boilers is quartz sand with the main phase  $\text{SiO}_2$ , as it is a low-cost material with high mechanical resistance.

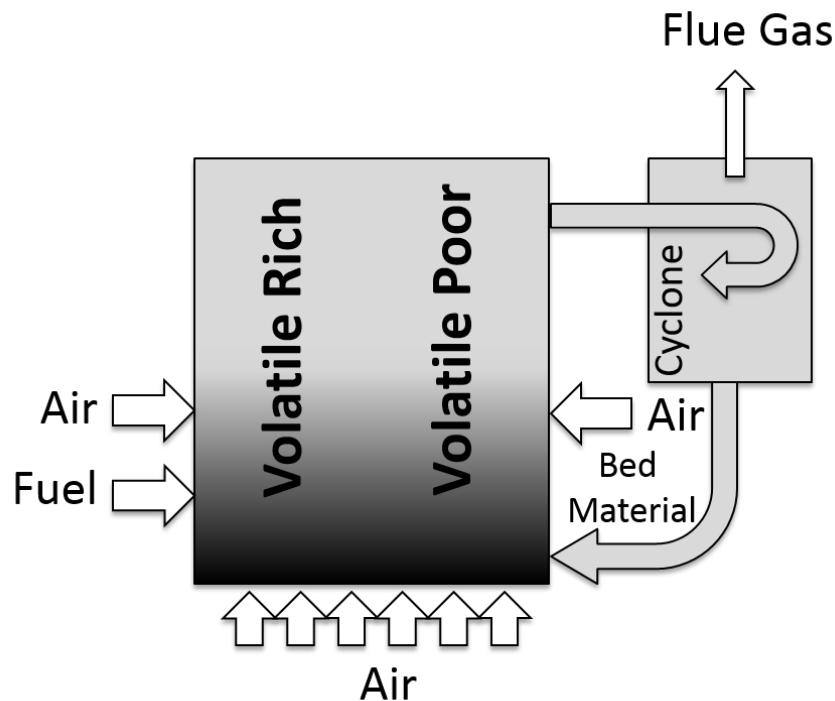


Figure 1.1: Principal distribution of fuel, air and bed material in a CFB boiler, where the intensity of the grey color illustrates an increase in the available bed material.

Primary combustion air is introduced at the bottom of the combustion chamber. The velocity of air causes fluidization of the bed and a considerable flow of bed material is carried away from the dense bottom bed. Thus, bed material is found throughout the volume of the combustion chamber, with a density declining upwards. The solids are exposed to both reducing and oxidizing conditions as they meet combustible gases and air, respectively. During the upward transport, internal recirculation occurs where part of the material is carried continuously to the walls and falls back to the bottom of the combustor. Bed material that does not fall back inside the furnace follows the flue gas and enters an adjacent cyclone with high velocity. The cyclone is well-mixed and allows for burnout of remaining combustible fractions of the fuel. In the cyclone, solids and gases are separated. The gases leave for the convection path and stack at the top of the cyclone, while solids are drained at the bottom. The solids are transported back to the combustion chamber through a loop-seal, maintaining the bottom bed by external recirculation. [8]

During combustion of solid fuels, three stages for reduction of mass takes place: drying, devolatilization and char combustion. The steps of drying and devolatilization occur rapidly and mainly take place close to the fuel inlet. Fuel is commonly fed on top of the dense bed, inserted through the walls. Depending on the size of the combustor, fuel can be fed from one or several positions. Furthermore, the lateral mixing in a CFB boiler is counteracted by the vertical transport of bed material. This causes an increased concentration of volatiles at locations where the fuel is introduced [8, 9]. The phenomenon results in volatile-rich and volatile-poor regions in the combustor, depicted in Figure 1.1. Insufficient mixing between the regions allows for oxygen-rich gas streams, which may cause local variations in temperature with a vast increase where char particles encounter the oxygen-rich passages. Moreover, insufficient mixing between the zones results in loss of combustion efficiency.

For complete combustion to take place, the achievement of adequate mixing of fuel and oxygen is decisive [8]. To avoid emissions of unburned species and loss of efficiency, the adopted measures have been to improve the contact between fuel and oxygen. However, predicting how the fuel meets oxygen is difficult and inadequate mixing is usually counteracted by increasing the amount of air fed to the system [8]. The primary air is distributed through nozzles evenly distributed across the bottom part of the chamber, while the secondary (and tertiary) air is injected through nozzles mounted in the furnace wall at higher positions.

Thunman et al. [10] proposed an innovative concept to improve the distribution of oxygen in FB units. The authors replaced part of the bed inventory with an oxygen carrying mineral. Thereby, the distribution of oxygen was evened out in space and time. The concept is referred to as oxygen carrier aided combustion (OCAC) and targets the combustion of heterogeneous fuels, such as biomass and waste. OCAC is

essentially a technical adjustment of a conventional FB boiler and is described in detail in Section 1.2.

Oxygen carriers were proposed, already in the 1950's to produce syngas or pure CO<sub>2</sub> from carbonaceous fuels [11]. Later, the method was developed and proposed as an option for combustion with CO<sub>2</sub> capture, whereby the term chemical-looping combustion (CLC) was introduced [12, 13]. In the early 2000's, the field of CLC optimized this concept through the use of two interconnected FB boilers [14, 15]. Since then, research on CLC has expanded and the knowledge gained has been vast. Apart from testing a wide spectrum of oxygen carriers, a range of fuels in gaseous, liquid and solid form have been used during CLC experiments [16]. Furthermore, the operation of a CLC unit with biomass as fuel and subsequent storage of CO<sub>2</sub>, provides net negative emissions [17, 18].

## 1.2 Oxygen Carrier Aided Combustion

The rationale of OCAC is to replace the inert bed material in a conventional CFB boiler with an oxygen carrier. Thus, the existing features of the technology are taken advantage of, and the presented challenges can be met in an innovative manner. An oxygen carrier is a transient material, often a metal-oxide that can undergo oxidation and reduction at the conditions present in the combustion chamber. Thereby, oxygen is absorbed and released where it occurs in abundance or in deficit, respectively. The reduced form (Me) is oxidized according to reaction (1.1) when it encounters the combustion air. The bound oxygen is converted through reactions with volatiles, as described in reaction (1.2) to CO<sub>2</sub> and water, either in the emulsion phase or during the upward transport through the combustion chamber. The reduced oxygen carrier is subsequently recirculated to the dense bed, where it is oxidized again.

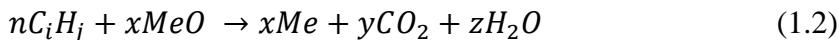


Figure 1.2 illustrates the path and reactions for the oxygen carrier in the CFB boiler. In this manner, advantage is taken of the solid bed material's good mixing properties to improve the contact between oxygen and fuel. Hence, the use of excess air can be decreased and boiler efficiency increased. As oxygen availability is improved both temporally and spatially, OCAC is an innovative approach for managing heterogeneous fuels, such as biomass and waste.

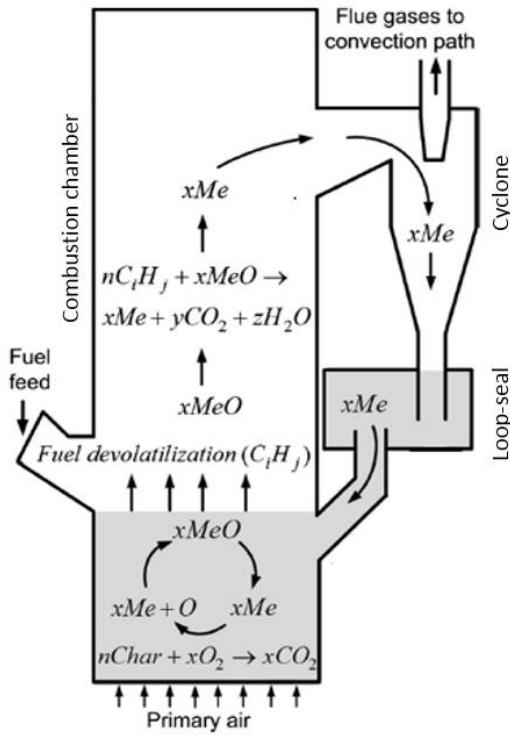


Figure 1.2: Schematic representation of the boiler and the chemical reactions therein, involving fuel and oxygen carriers.

### 1.3 Implementation of a new concept

Implementation of a new concept, such as OCAC, is a process that follows several important stages. For an implementation to be recognized and applied to industrial scale, several criteria need to be met: 1) The cost during initial implementation should be minimized and further kept low in comparison to the potential gains that may be achieved by the concept. 2) Safety measures should be applied during implementation to minimize risk of operational failures and accidents. 3) It is necessary for the concept to be proven effective on industrial scale where long-term effects of the new materials need to be benign.

Due to the complexity of the fuel, CFB boilers used for combustion of both biomass and waste require an extensive amount of bed material when they are scaled up. When quartz sand is used, the bed inventory is regenerated excessively to mitigate the risk for agglomeration (a result of ash interaction that will be further described in Chapter 4). Thus, several tons of bed material pass through the system daily, only to be put in landfill. Disposal to landfill requires the used bed material to be environmentally benign, or else the bed material is required to be managed as hazardous waste, which leads to increased cost.

Without convincing proof that the theoretical predictions of the concept apply to reality, the cost and risk associated with initial trials for implementation can easily be regarded as too high. Accordingly, a validation of the concept is imperative, where it is established that reactions postulated in theory occur at the prevailing conditions in an industrial CFB boiler. The oxygen carrying capabilities of the bed material need to account for beneficial outputs to the process. Furthermore, the interaction with fuel ash should not inhibit the material from functioning as oxygen carrier. For the industry to be able to plan their material management, knowledge of how the material is affected during operation is fundamental. Both mechanical and chemical properties of the material are included, as the ash interaction and decomposition affect the lifetime of bed materials.

To apply oxygen carriers to the current energy system, the material needs to be economically feasible in comparison to when quartz sand is used. Currently, the price for potential oxygen carriers is higher than the price for quartz sand. Thus, the potential benefits need to outweigh the increased cost. Apart from providing the system with favorable combustion conditions, the lifetime of the oxygen carrier should be sufficient. As the material at end of life is put in landfill, extending its lifetime simultaneously reduces the volumes of waste leaving the process. Figure 1.3 illustrates factors that impact particle lifetime. Namely, the particle should retain oxygen transfer capabilities as long as possible and not be impaired by ash interactions and be resistant to mechanical stress.

A notable advantage for the prosperity of OCAC is the already existing field of CLC, which has covered numerous types of oxygen carriers. The research and findings on oxygen carriers used for CLC has been an advantage for the progress of OCAC, as requirements for the materials are similar. Although the research on potential oxygen carriers is extensive, literature only slightly covers the aspect of ash interaction and long-term operation of oxygen carriers. Therefore, the development of OCAC can potentially bring further insight to the CLC process regarding characteristics of oxygen carriers in large scale settings with complex fuels.

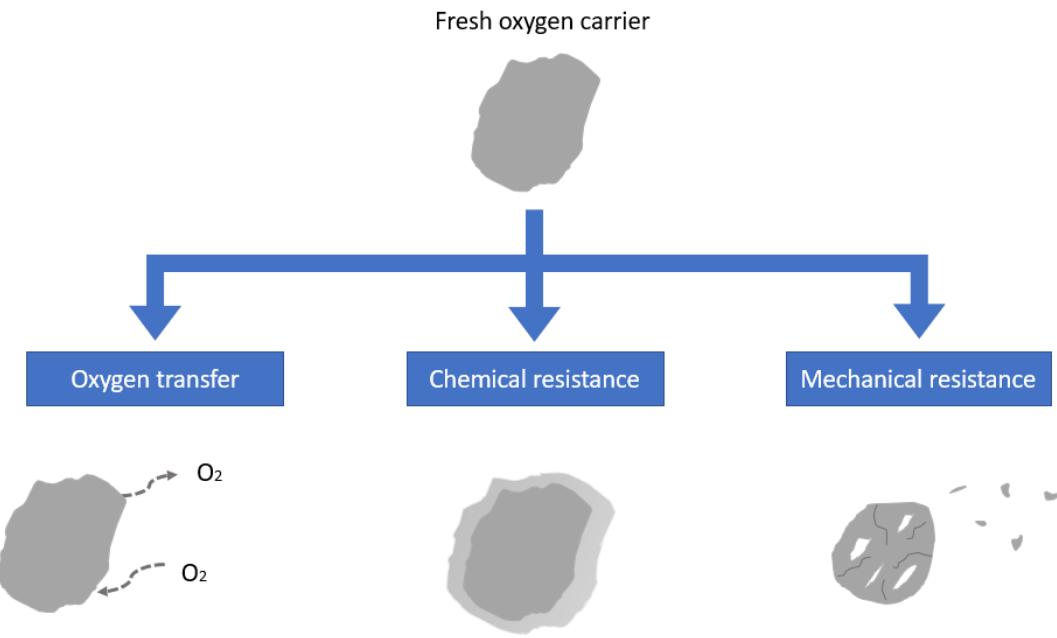


Figure 1.3: Illustration of the demands set for an oxygen carrier to be used as bed material during OCAC.

## 1.4 Aim and objective

The overall aim of this thesis is to describe the implementation process of a new concept, where oxygen carriers have been applied to existing industrial settings. The ambition is to map how the material develops in order to understand which parameters affect its lifetime under the prevailing conditions. Furthermore, investigations have been made to distinguish the possibility to optimize the concept. For these purposes, experimental work has been carried out on a broad set of scales. Materials have been investigated on laboratory, semi- full industrial scales, detailed further in Chapter 2. Samples from the industrial experiments have been extracted and, apart from being analyzed as is, they have been used on laboratory scale to achieve further understanding of how the material develops in large scale conditions. The focus of this thesis can be organized into four main research questions:

- 1) Can oxygen carriers be applied to existing industrial settings without significant changes to the process?
- 2) What parameters affect the lifetime of an oxygen carrier used for OCAC?
- 3) Are there any ways for optimizing the utilization of the material?
- 4) Are the presented benefits promising enough to propose the concept?

### 1.4.1 Outline of papers

Figure 1.4 illustrates how the papers included in this thesis connect to the research and the information they provide. To validate the concept, dedicated experiments were performed to evaluate the oxygen carrying properties of ilmenite, presented in **Paper II**. This paper gives a comprehensive picture of the oxygen transferring ability of ilmenite during OCAC. **Papers I** and **V** present the first experience of new materials tested for the concept, where ilmenite and manganese ore are reported in the respective papers. **Papers I** and **IV** present the detailed mechanisms of ash interactions as well as how the inherent elements in the material propagate with time in the semi-industrial boiler. Furthermore, **Paper III** details the structural development of two different ilmenites used for OCAC. **Papers VII** and **VIII** show that the concept is applicable at full industrial scale. Here, the concept was demonstrated on industrial scales at 115MW<sub>th</sub> and 75MW<sub>th</sub>. The fuels used here were waste wood and MSW, which are both complex fuels to combust. These papers provide the opportunity to study industrially relevant issues. **Paper VI** combines all scales that are included in this work and provides insight into possible optimization methods, together with **Paper VIII**. **Papers I, III, IV and VI** provide insight into the lifetime of ilmenite as an oxygen carrier in OCAC of biomass. Together, all papers contribute to a more complete understanding as to whether the benefits are satisfactory enough for the concept to be utilized.

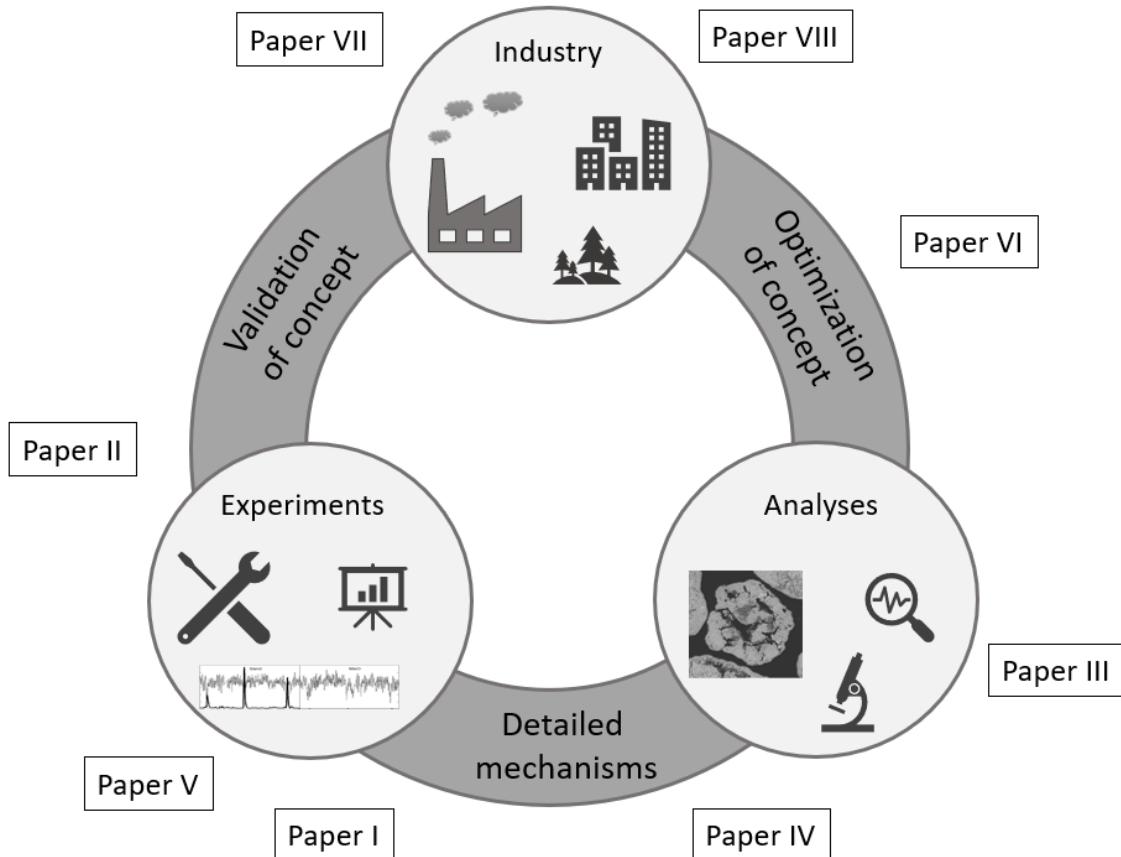


Figure 1.4: Illustration of which areas the papers included in this thesis approach.

#### 1.4.2 Structure of thesis

To provide an understanding of how the experimental work of this thesis has been conducted, the experimental facilities and analysis methods are described in Chapter 2. Here, the materials used are presented as well. Furthermore, Chapter 2 provides a matrix that comprises the experimental campaigns included and to which papers and research questions they are connected. Chapter 3 discusses the activity of oxygen carriers. As introduction it provides a background to active materials used for thermal conversion and focuses on activity of oxygen carriers. Here, the findings coupled to activity of oxygen carriers in this work are presented. In Chapter 4, a brief review of ash interactions with bed materials in general is given. Further, this chapter focuses on ash interactions with oxygen carriers. In Chapter 5, the work covering ageing of oxygen carriers is presented. The ageing is discussed regarding oxygen transferring capacity and the chemical and mechanical resistance of the materials. Chapter 6 presents the process of application to industry and the findings from the work connected to full industrial scale. Finally, Chapter 7 summarizes the main findings and Chapter 8 presents the conclusions and outlook of the work.



# CHAPTER 2

## EXPERIMENTAL

The papers included in this thesis are based on experimental work carried out on three scales: laboratory scale, semi-industrial scale and full industrial scale.

The unique opportunity to integrate the work between the scales, as illustrated in Figure 2.1, is a key factor for the success and rapid understanding of the concept and its implementation to industry. The semi-industrial scale provides an intermediate step, allowing to test the concept at industrial scale without the economic risk associated with full industrial scale.

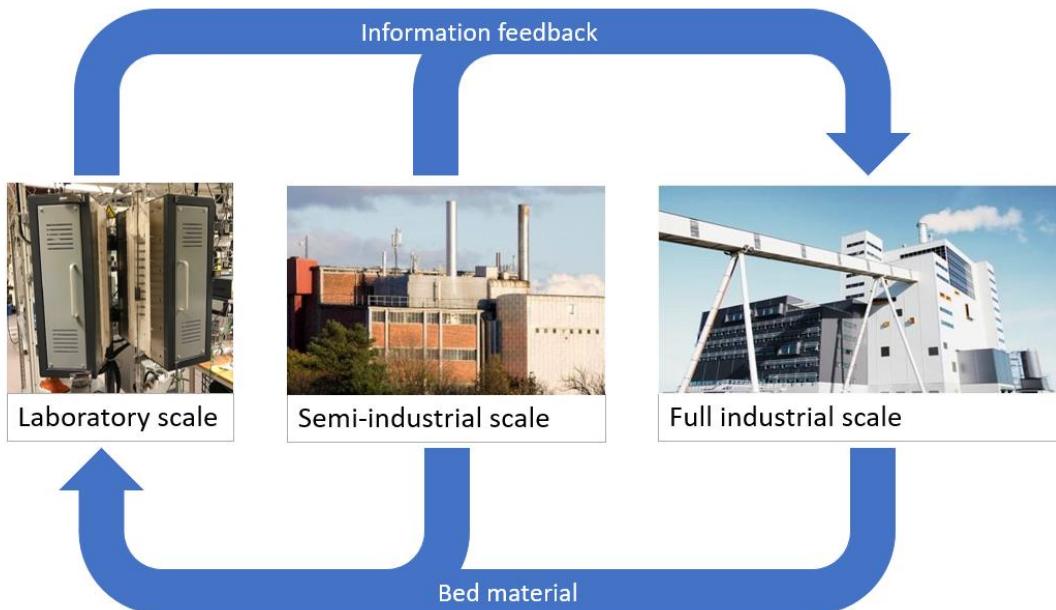


Figure 2.1: Integration of experimental scales. Bed material is extracted from semi- and full industrial scale to be evaluated on laboratory scale. The laboratory and semi-industrial scale provide information that can be implemented in industry.

Bed material extracted from the industrial units were analyzed and run through the laboratory scaled reactor, providing important information on how the material develops on large scale. The laboratory and semi-industrial scales provided information feedback, used for a more rapid scale up of the concept. In this manner, the research questions postulated in Section 1.4 can be approached in an effective way. The laboratory and semi-industrial experiments were carried out at Chalmers facilities, while full industrial experiments were carried out in EON's and Kraftringen's facilities. The details of the experimental settings included in this thesis are presented in this chapter. Furthermore, this chapter presents the analysis methods and materials included in this thesis.

## 2.1 Laboratory scale

Measurements in a laboratory scaled reactor were conducted to determine the chemical performance of oxygen carriers. In the experiments, syngas was used as fuel and the oxygen transfer capacity of the material was established by the conversion of carbon monoxide. The system has been used frequently for evaluation of oxygen carriers for CLC and is depicted in Figure 2.2 [19-21]. The reactor consisted of a quartz glass tube with an inner diameter of 22 mm and a height of 820 mm. At a height of 370 mm, a porous quartz plate was placed as support for the bed material to be evaluated. As the plate holds the solid material, it allows for gas to penetrate through. The gas was supplied from the bottom of the reactor and, thus, fluidized the bed material as it passed through the reactor. For each batch, 15 g of oxygen carrier was used.

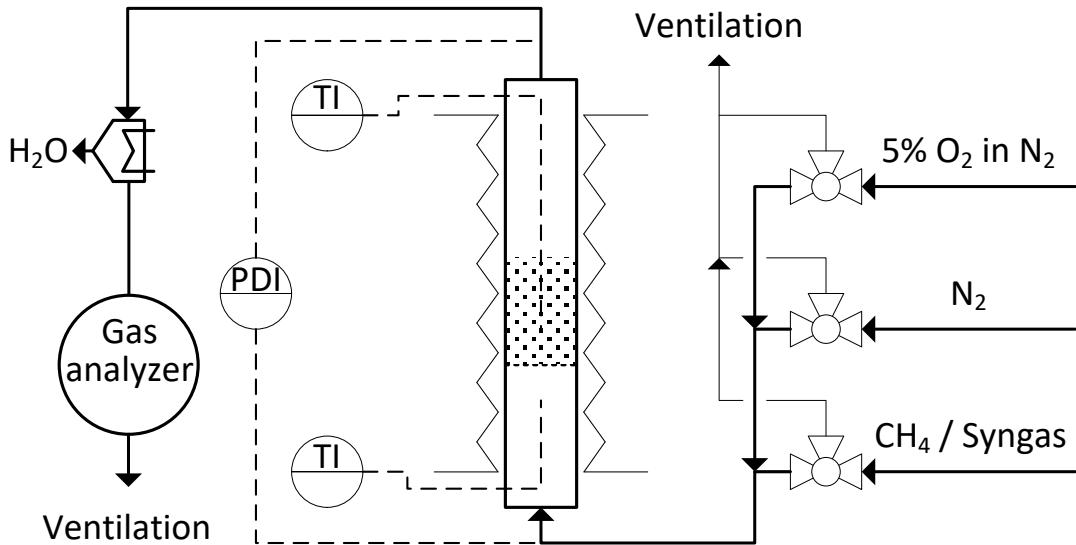


Figure 2.2. Schematic overview of the laboratory fluidized bed batch reactor system used for oxygen transfer testing of the chosen materials. TI denotes the placement of thermocouples and PDI is the location of pressure measurement.

After leaving the reactor at the top, the flue gases were then cooled to condense the contained steam. The dry gas was analyzed in a Rosemount NGA 2000 instrument equipped with thermal conductivity and paramagnetic gas sensors for hydrogen and oxygen determination. CO, CO<sub>2</sub> and CH<sub>4</sub> were analyzed with nondispersive infrared detectors. The temperature was measured by a thermocouple of type K enclosed by a quartz shell above and below the bed, as seen in Figure 2.2. Continuous fluidization was ensured by monitoring pressure changes over the bed. A Honeywell pressure transducer with a frequency of 20 Hz was used to measure the pressure at the top and bottom of the quartz reactor.

To investigate the oxygen transferring capacity of the oxygen carrier, it was subjected to alternately reducing and oxidizing conditions at different temperatures. As mixing of reducing and oxidizing gases would influence the results, the reactor was purged with an inert gas (N<sub>2</sub>) between the oxidation and the reduction periods. The experiments of the bed materials were performed in cycles, where every cycle was initiated by the bed sample being fully oxidized in oxidizing conditions, this was followed by reactor purge during an inert phase in N<sub>2</sub> and with subsequent reduction under reducing phase. Table 2.1 shows the conditions for the laboratory scale experiments included in this work.

Table 2.1: Operation parameters used for oxygen transfer testing of bed materials during labscale experiments

Test Phase	Gas mixture	Gas flow [ml <sub>N</sub> /min]	Temperature [°C]	Time [s]
<b>Oxidizing</b>	5% O <sub>2</sub> in N <sub>2</sub>	1000	800-950	900
<b>Inert</b>	100% N <sub>2</sub>	1000	800-950	180
<b>Reducing</b>	100% Syngas (50/50 CO/H <sub>2</sub> )	900	800-950	20

The materials evaluated in this reactor are presented in Table 2.5. Additionally, both fresh quartz sand and fresh oxygen carrier were tested in the reactor, to be used as reference. The fresh quartz sand was expected to be inert as an oxygen carrier, while the fresh oxygen carrier represents the materials initial oxygen transferring capabilities when introduced to a boiler. Thereby, combining the reference with used samples, an understanding of how the material develops can be obtained. During the experiments, gas concentrations, temperatures and pressure were logged during the entire operation every 2 s and the obtained data was then evaluated. To quantify the amount of converted gas, the gas yield of CO<sub>2</sub> ( $\gamma_{CO_2}$ ) was used in accordance with previous oxygen carrier tests [19].

$$\gamma_{CO_2} = \frac{x_{CO_2}}{x_{CO_2} + x_{CO}} \quad (2.1)$$

The CO<sub>2</sub> yield is defined as the fraction of CO<sub>2</sub> in the outgoing gas divided by the sum of the fractions of carbon containing gases, as presented in eq. (2.1). Thus, a  $\gamma_{CO_2}$  value of 0 corresponds to no conversion while 1 corresponds to total conversion of the fuel.

## 2.2 Semi-industrial scale

The experimental work conducted on semi-industrial scale was performed in Chalmers 12MW<sub>th</sub> CFB-boiler. The boiler produces hot water for district heating of the campus facilities from November through April. Ordinarily, the boiler is operated with a bed inventory consisting of 2 tons of quartz sand. A schematic of the system is shown in Figure 2.3. The furnace (1) has a square cross-sectional area of 2.25 m<sup>2</sup> and a height of 13.6 m, where the fuel is fed on top of the bed via a fuel chute (2).

The combustion chamber is equipped with several ports where bed material samples can be extracted through H1-3 and combustion gas samples through H4-13. The entrained bed material is separated from the flue gases in a water-cooled cyclone (4) and transported back to the boiler via a particle distributor (9). Heat is recovered from the separated flue gases in the convection path (5) where they can be extracted through port kh2, for analysis. Fine particulates are separated from the flue gas by a secondary cyclone (6) followed by a textile filter (7).

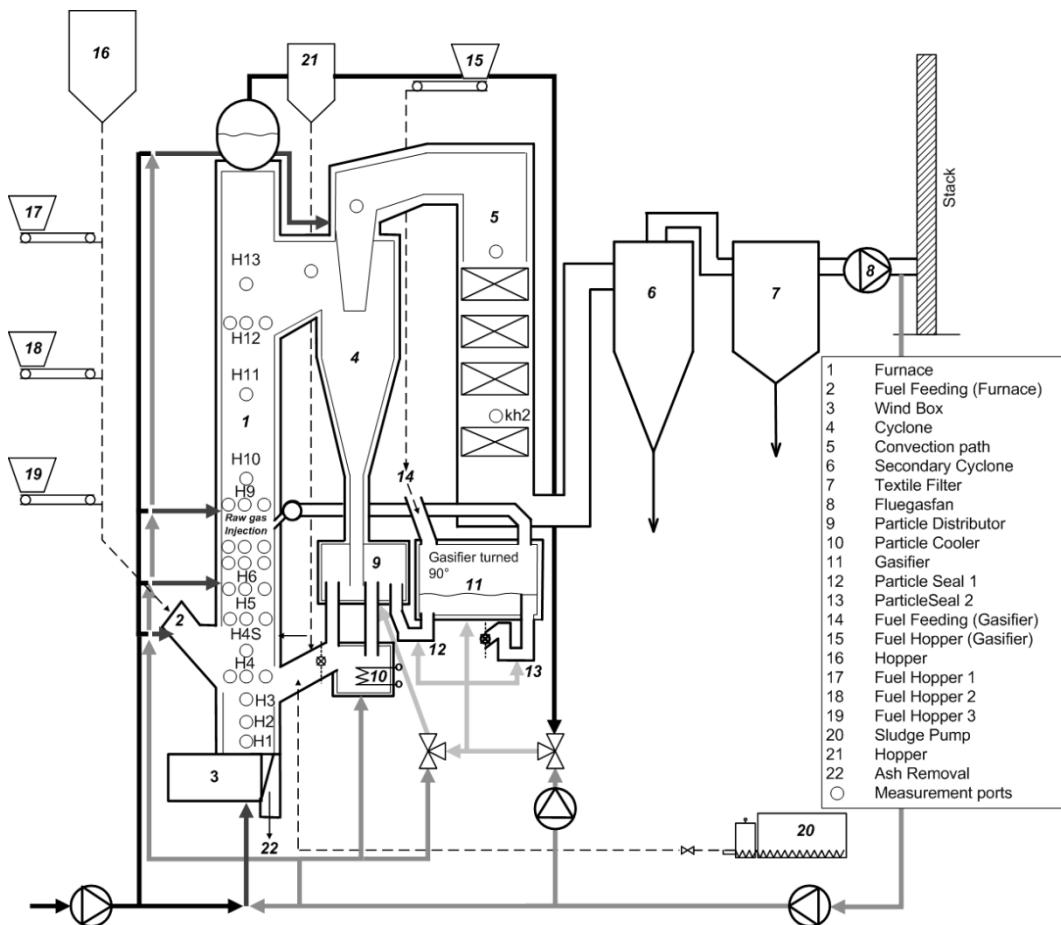


Figure 2.3: Schematic representation of Chalmers 12MW<sub>th</sub> CFB-boiler system.

In order to obtain satisfactory operation of the plant, it is necessary to maintain consistent pressure drop over the bed. As fine fractions of the bed material are entrained with the flue gases, fresh material needs to be added continuously to the system during the test periods. The OCAC campaigns conducted in this unit included sand and rock ilmenite, a mixture of rock ilmenite and quartz sand and a manganese ore. Specifications of the trials are summarized in Table 2.5.

All bed material and bottom ash samples from the semi-industrial unit investigated in this work have been extracted with a water-cooled suction probe through port H2. Moreover, a gas probe was immersed in sampling port kh2 in the convection path during the experimental campaigns. The gas probe was a heated Teflon tube (6 mm in outer diameter) with a length of 15 m and further transported the gases to a cooler for condensation of steam before entering the gas analyzers. The CO concentration was measured by an online Non-Dispersive Infrared (NDIR) analyzer (0-1000 ppm). Oxygen was analyzed with an online paramagnetic analyzer (0-21 mol%).

## 2.3 Full industrial scale

### 2.3.1 Kraftringen's 115 MW<sub>th</sub> – waste wood

Kraftringen's CFB-boiler is located in the south of Sweden and consists of a biomass-fired CHP cycle (112 bar, 540 °C) with a nominal thermal capacity of 115 MW<sub>th</sub>. The turbine and flue gas condensers supply heat to the local district-heating grid. The amount of bed material in the system is about 60 tons under normal operation. The bed material is separated from the flue gases in two parallel gas–solid separators and then returned to the furnace via two separate loop-seals. The cross-section of the furnace is 2.2 m x 8.8 m at the height of the fluidization nozzles and expands to 5.5 m x 8.8 mm in the upper part of the furnace. The height from the base of the furnace is 28.4 m. Furnace and separators are equipped with ammonia injection (SNCR) systems to reduce the emissions of NO<sub>x</sub>. The loop seals include submerged steam super-heaters, which are of the INTREX™ (integrated heat exchanger) type. Blower engines are used to fluidize the loop seals and provide a pressure between 30 kPa and 70 kPa (50 kPa in normal mode). The boiler is also equipped with flue gas recirculation to control the temperatures in the furnace and increase flexibility. After the flue gases are cooled in the convection path, remaining particles are separated using textile filters. The last available heat is then extracted via the flue gas condenser before the flue gases are released to the atmosphere via the stack. A schematic of the system is illustrated in Figure 2.4.

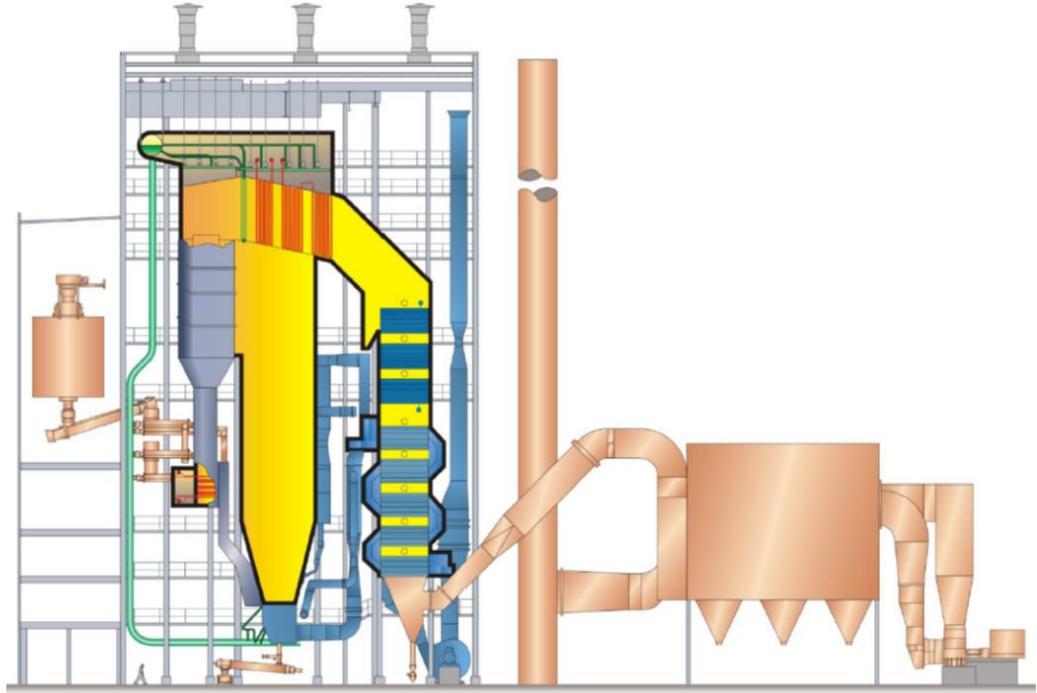


Figure 2.4: Schematic of Kraftringen's 115MWth CHP plant.

The boiler is normally operated with quartz sand as bed material and is equipped with a drum sieve for bed-material recovery. The recovered fraction is directly sent back to the furnace and the rejected stream is sent to ash containers. The oxygen concentration in the flue gases is used to control the boiler system, and it is measured before the economizer section in the convection pass. This position holds three O<sub>2</sub> sensors of the type ABB Zirconia Oxygen Analyzers AZ20. The emission monitoring in the CFB boiler is carried out in the stack position and is managed using the UV DOAS (AR600) and IR DOAS (AR650) analysis instrument from Opsis.

During the OCAC campaign, rock ilmenite successively replaced the quartz sand, and the fuel consisted of waste wood and to some extent wood chips. Bed samples were collected several times per day after the water-cooled bed ash extraction screw-feeders. Each sample was sieved, where the fraction below 710 µm was used for further analysis and the fraction above 710 µm (e.g. nails, small stones, hinges, etc.) was discarded. The ilmenite fraction in the samples below 710 µm was then separated by a rare earth roll belt magnet represented in Figure 2.5. This magnetic separation system has a capacity of approximately 700 kg/h and consists of a belt stretched across two horizontal cylinders [22]. The sample was fed evenly to the belt through a distributor on one end. On the other end, non-magnetic material left the apparatus in a trajectory parabola to the front of the separator, while the magnetic material followed the belt around the magnetic drum and fell from the belt behind the magnet.

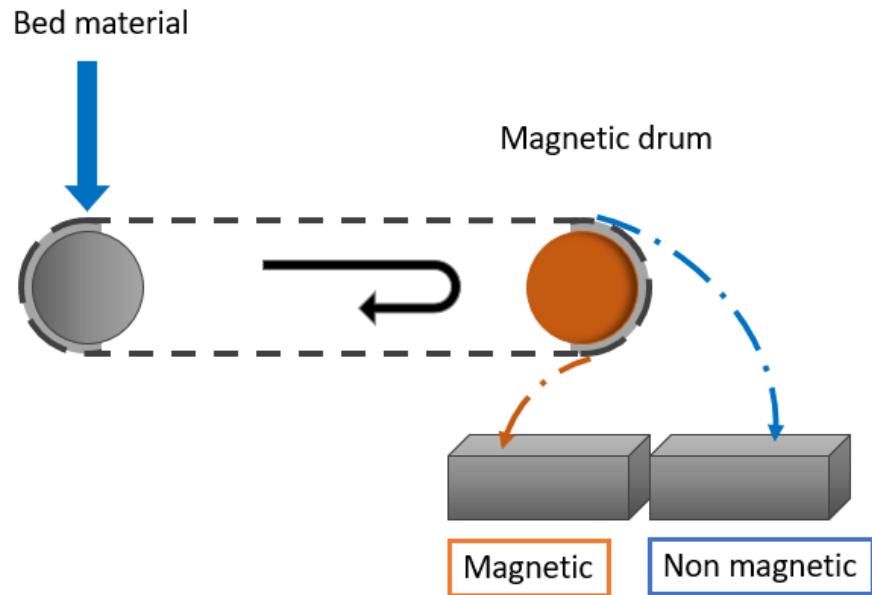


Figure 2.5: Schematic drawing of the roll belt magnetic separator used to separate the collected bed material in magnetic and non-magnetic fraction.

### 2.3.2 E.ON's 75 MW<sub>th</sub> – MSW

E.ON's 75MW<sub>th</sub> CFB-boiler provides heat to the district heating network in the city of Norrköping, electricity by a steam turbine and covers the steam demand for the production of ethanol from wheat in the adjacent industrial facility, Agroetanol, via an integrated steam pipeline. The boiler is normally operated with a steam pressure of 6.5 MPa and steam temperature of 450 °C. The base load fuel is MSW, but the design allows for combusting a wide range of different fuels including industrial waste, sewage sludge, rubber and demolition wood waste. The bed material ordinarily is composed of a mixture of quartz sand and inert material from the fuel, roughly amounting to 25 tons.

Figure 2.6 presents a simplified overview of boiler. The fuel is fed via three separate fuel feeding ports located at a height of 4 meters (1-3), where bed material is fed on top of the fuel. Air is fed in primary (4), secondary (5) and tertiary (6) registers. Inert materials originating from the fuel and bed material are continuously removed from the furnace through ports at the bottom of the furnace (7) with the help of two water-cooled screw conveyors. Large fractions are removed in a circular drum sieve, while finer fractions that are suitable as bed material are recirculated back to the furnace with an air-blown ash classifier.

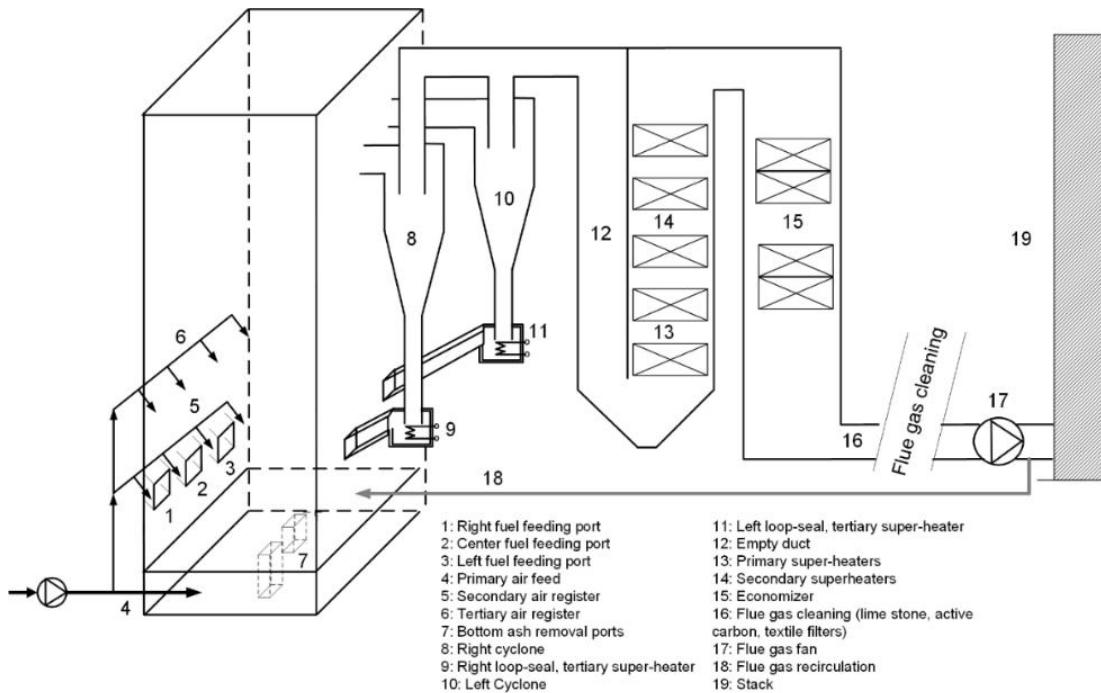


Figure 2.6: Schematic representation of E.ON's 75MWth CFB-boiler.

Fly ash and bed material entrained with the flue gases exit the furnace into two parallel cyclones (8, 10) where the bed material is separated and is deposited in the two respective loop-seals (9, 11). Here, the bed material is cooled by the tertiary super-heaters before being returned to the furnace. The flue gases leave the cyclones at the top and proceed through an empty duct (12), where they undergo initial cooling. Further cooling of the flue gases is achieved by two steps of super-heating (13, 14) and finally, by the economizer (15). After cooling, the flue gases are subjected to cleaning (16) by exposure to limestone and activated carbon, where all the remaining particles are removed by textile filters. The flue gases eventually reach the flue gas fan (17), after which they are either recirculated to the boiler (18) or emitted to the atmosphere through the stack (19).

The concentration of CO, NOx, SO<sub>2</sub>, HCl, NH<sub>3</sub> and water in the flue gas are measured in the stack with a fast fourier transform infrared spectrometer (FTIR). The concentration of oxygen is measured in the convection path by two lambda sensors and used for operational control. Further, the concentration of oxygen in outgoing flue gases is measured in the stack by a paramagnetic analyzer. During the OCAC trials, rock ilmenite was used as oxygen carrier and was supplied gradually by a separate feeding system. This measure was taken to secure that quartz sand would be accessible through the normal feeding system.

## 2.4 Materials and methods

Bed samples extracted from the experimental units described in Sections 2.1-2.4 were evaluated further by several analysis methods. These methods, as well as oxygen carriers and fuels used, are presented in this section.

### 2.4.1 Analysis methods

For the total elemental composition analysis, the collected bed samples were initially dissolved in LiBO<sub>2</sub> using a microwave digestion in several heat treatment steps. The obtained solutions were further analyzed using ICP-AES according to the EN 13656 standard. This procedure was conducted by the external company ALS Scandinavia.

Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS) was used for the morphological evaluation of the material, as well as for following the elemental distributions within the particles. Bed material was placed on carbon tape for examination of the particle surfaces. Samples were immobilized in epoxy resin, ground and polished to obtain a flat cross-section of particles. Tabletop Phenom ProX and Quanta 200FEG equipped with an Oxford EDS were the systems of choice for the evaluations. Both systems were used in low-vacuum mode and with charge reduction. For imaging, back-scattered electron signal was used. During the EDS analysis, point analyses and elemental intensity maps were used to derive the elemental distributions.

To determine the crystal phase of the materials, they were analyzed by powder X-ray diffraction (XRD). The materials were ground to powder prior to analysis, where a Siemens D5000 diffractometer with Cu K $\alpha$  characteristic radiation was used. The extracted profiles took place with a capturing angle between 10° and 90° (2 $\theta$ ) and a step size of 2°.

The attrition resistance was measured on 5g of material in a customized jet-cup rig. The apparatus and methodology used is constructed to simulate the mechanical stress that particles undergo in fluidized bed environment. The bed samples were sieved and particles in the size range of 125-180  $\mu\text{m}$  were collected for measurement of their mechanical stability. A filter collecting the fine material leaving the device at the top, was measured continuously, providing the rate of attrition caused on the bed material. The apparatus and methodology have been described in detail by Rydén et al. [23].

### 2.4.2 Oxygen carriers

All oxygen carriers used in the scope of this thesis were natural occurring ores, with different origins. Two types of ilmenites, a sand and a rock ilmenite, and one manganese are included. The sand ilmenite originated from Australia and was provided by Sibelco Nordic AB, while the rock ilmenite originated from Norway and was provided by Titania A/S. The main crystal phase identified in both ilmenites was FeTiO<sub>3</sub>. The manganese ore was supplied by Sibelco Nordic AB and had been calcined prior to delivery. The elemental compositions of the fresh materials are presented in Table 2.2.

Table 2.2: Elemental content of oxygen carriers as-received from the supplier

	<b>Sand Ilmenite</b>	<b>Rock Ilmenite</b>	<b>Manganese ore</b>
<b>Element</b>	wt.%	wt.%	wt.%
<b>Fe</b>	34.20	33.29	5.14
<b>Ti</b>	27.93	23.85	0.23
<b>Mg</b>	0.44	1.83	0.25
<b>Si</b>	0.15	0.94	3.71
<b>Al</b>	0.19	0.34	3.40
<b>Mn</b>	0.48	0.13	46.23
<b>Ca</b>	0.06	0.26	1.88
<b>K</b>	0.07	0.07	0.99
<b>Na</b>	0.04	0.08	0.05
<b>P</b>	<0.01	<0.01	0.10
<b>Ba</b>	<0.01	<0.01	0.23

Cross-sectional SEM micrographs of fresh sand ilmenite and rock ilmenite particles are shown in Figure 2.7 a) and b), respectively. The materials differ with respect to particle morphology, where the sand ilmenite particles have rounded edges and the rock ilmenite particles have sharp edges. The difference in particle shape is influenced by the origins of the materials, which are described further in Section 3.2. The sand ilmenite has prior to collection been exposed to natural weathering, erosion and attrition, causing the particles to obtain a rounded shape. In contrast, the rock ilmenite particles have been mined and ground, which results in the particles being sharp-edged. Analyses with SEM-EDX show that both materials have a homogeneous distribution of Fe and Ti over the cross-section, with no local enrichment of either of the elements.

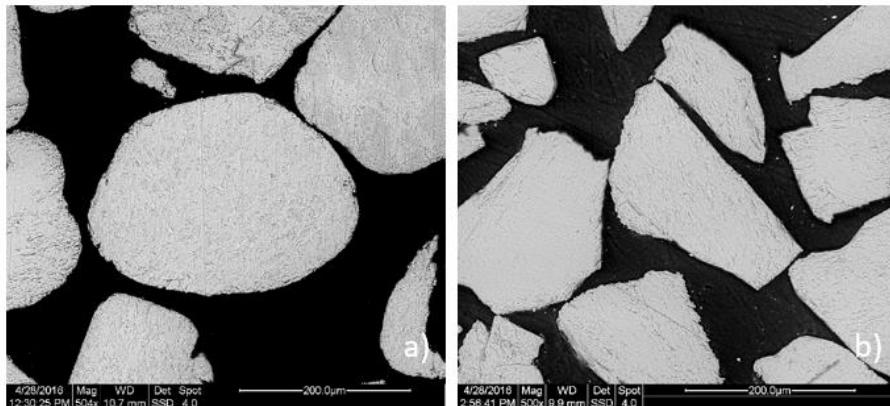


Figure 2.7: SEM micrographs of the cross-section of fresh bed material a) sand ilmenite; b) rock ilmenite.

#### 2.4.3 Fuels

The fuels used in this study vary widely in composition and complexity. On laboratory scale, synthetic gas (syngas) with a composition of 50/50 CO and H<sub>2</sub> was used. Chalmers semi-industrial CFB-boiler was operated with wood chips as base load fuel for all experiments. Wood pellets were used as compliment fuel for easier management of temperature. The main difference between wood chips and wood pellets is that wood

pellets contain significantly less moisture, as demonstrated in Table 2.3. Apart from moisture content, the fuels are similar and their ash composition is given in Table 2.4.

Table 2.3: Properties of wood chips and wood pellets (based on fuel as received)

	Wood chips	Wood pellets
Moisture wt.%	38.5 – 45.3	7.2 – 9.8
Volatiles wt.%	43.8 – 50.1	72.9 – 75.3
Ash wt.%	0.4 – 0.6	0.2 – 0.4
Lower Heating Value dry ash free MJ/kg	18.6	18.6

Table 2.4: Ash composition of wood chips/pellets obtained at 550°C.

Element	Ca	K	Mg	Si	P	Na	Mn	Al	Fe	Ba	Ti
Wt.%	23.60	14.60	3.36	2.07	1.68	0.64	1.07	0.46	0.43	0.23	<0.05

Kraftringen's 115MW<sub>th</sub> CFB plant was operated with a base load of waste wood, and partially by wood chips. Waste wood and wood chips are differentiated by that waste wood can contain painted or impregnated wood, as well as items like screws and hinges. Thus, the ash composition of waste wood does not only include elements originating from the wood, as is the case for wood chips and pellets. The most complex fuel included in this thesis is MSW, used at EON's 75MW<sub>th</sub> CFB boiler. MSW includes both waste from industries and households, whereby it is highly heterogenic with time. Large refractory items can be found in the ashes, such as ceramics, metals and glass. Even though it is chopped prior to introduction to the boiler, the fuel size and heat value is specifically difficult to control for MSW. Figure 2.8 illustrates the variation in complexity of the presented fuels.



Figure 2.8: Illustration of the complexity development and heterogeneity of the fuels used.

#### 2.4.4 Summary of experimental campaigns

The experimental campaigns conducted on semi- and full industrial scale are summarized in Table 2.5. Here, the length of each campaign and the corresponding base load fuel, scale of boiler and type of bed material are presented. Moreover, the table presents the type of measurements conducted during the campaigns that are used for this thesis. The table emphasizes which bed materials have been used in the laboratory scaled reactor, as illustrated in Figure 2.1. Additionally, the analysis methods used on bed samples are stated here. Furthermore, the table shows how each paper and research question connects to the experimental campaigns.

Table 2.5: Summary of experimental campaigns and corresponding analyses included in thesis

	Semi-industrial scale			Full industrial scale	
<b>Base load fuel</b>	Wood chips			Waste wood	MSW
<b>Scale of CFB-boiler</b>	12 MW <sub>th</sub>			115MW <sub>th</sub>	75MW <sub>th</sub>
<b>Bed material</b>	Sand ilmenite	Rock ilmenite	40wt% Rock ilmenite*	Manganese ore	Rock ilmenite
<b>Campaign duration (h)</b>	360	360	72	172	400
<b>Flue gas measurements<sup>1</sup></b>	x				x
<b>Temperature measurements</b>					x
<b>Operational experience</b>	x			x	x
<b>Oxygen transfer test<sup>2</sup></b>		x			x
<b>Elemental Analysis<sup>3</sup></b>	x	x	x	x	x
<b>SEM/EDX<sup>3</sup></b>	x	x	x	x	x
<b>XRD<sup>3</sup></b>	x	x	x		
<b>Attrition test<sup>3</sup></b>	x	x			
<b>Paper</b>	II, III, IV	III, VI	I	V	VI, VIII
<b>Research Questions<sup>4</sup></b>	1,2, 4	2, 4	2, 4	2, 4	1, 2, 3, 4
					1, 4

\*In quartz sand, \*\*As published in Paper VII, to date over 20 000 hours of operation have been accomplished, <sup>1</sup>With special emphasis on measuring the concentration of oxygen and carbon monoxide, <sup>2</sup>Conducted in the laboratory reactor presented in Section 2.1, <sup>3</sup>Method presented in Section 2.4.1, <sup>4</sup>Research questions are presented in Section 1.4

# CHAPTER 3

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## ACTIVITY OF OXYGEN CARRIERS

Active bed materials utilized in thermal conversion are materials that react with fuel in a manner that enhances the conversion. Bed materials that do not react in a preferred manner are often considered to be inert to the process. The differentiation between active and inert materials becomes more complicated when considering that inert materials may become activated during, for example, change in morphology and ash interactions [24]. Furthermore, bed material can be assigned as deactivated when affected in a manner that indicates they no longer are active in the preferred way [25]. This chapter presents the active bed materials utilized in different FB technologies and focuses on the activity of ilmenite. Based on **Papers II, VII and VIII**, a validation of the concept is presented. The progression of Fe in bed particles is presented based on **Papers I, IV and VI**. Additionally, **Paper VI** investigates how well the material functions as oxygen carrier at different sampling times and operational conditions. Thereby, insight to the lifetime of ilmenite as oxygen carrier is obtained. Properties of materials extracted from full scale experiments are presented, based on **Papers VI and VIII**.

### 3.1 Active bed materials

When quartz sand is used as bed material, it is most often referred to as inert. However, it could be argued that quartz sand is active in the context of ash removal. Notably, it reacts with alkali, the presence of which in the gaseous phase has negative impact on the thermal conversion, as will be discussed further in Chapters 4 and 5. Catalytically active bed materials can be used for optimization in gasification processes. In

gasification, bed materials are selected to increase the quality of the produced gas by facilitating fuel conversion and ensuring a low level of tar formation. Typical catalytically active bed materials used in gasification are olivine and dolomite [26].

In CLC, the activity of bed materials is referred to its oxygen transferring capacity. In the field of CLC, oxygen carriers have been studied widely and their suitability has been defined to include certain requirements. According to the stated requirements, oxygen carriers used in CLC should provide high conversion during the reduction stage, be resistant to mechanical and chemical stress, not agglomerate and be inexpensive and environmentally sound [14].

Oxygen carriers can be divided into natural and synthetic materials. Natural oxygen carriers include particles from materials that are found in nature not requiring extensive process treatment. Treatments in the category natural oxygen carriers include crushing and sieving of the material. Synthetic oxygen carriers include materials manufactured using raw derived oxides or natural minerals as raw materials. They also include oxygen carriers manufactured from natural materials but have undergone more extensive treatments, such as preheating or additives. A third category of oxygen carrier material that remains difficult to classify as either of the above, is waste materials.

A comprehensive study covering a wide range of oxygen carriers found that Cu, Fe and Mn oxides were suitable for CLC [27]. In general, transition metals have oxygen carrying capabilities, where Mn and Fe are considered as environmentally benign. The metal oxide can be combined with a binder, an inert material acting as a porous support providing increased surface area for reaction and which may increase the mechanical strength [28, 29]. Typical binders are Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub> and SiO<sub>2</sub> [28, 29].

The combustion process with an oxygen carrier differs depending on the fuel used. Gaseous fuels are likely the simplest type of fuel and can react directly with the oxygen carrier in a gas-solid reaction. The gaseous fuel can be used directly as the fluidizing agent and can consist of for example natural gas, syngas or refinery gas. Extensive studies on oxygen carriers for gaseous fuels have been carried out in the last two decades, summarized by Mattisson et al. [16]. During combustion of solid fuels, the volatile part of the fuel needs to be released and can then react in a gas-solid reaction with the oxygen carrier. The remaining char can be gasified and combusted by the oxygen carrier in the same manner.

As described in Section 2.4.3, solid fuels contain ash. Moreover, accumulation of ash and its composition can add complexity to the process, which will be discussed further in Chapter 4. Thereby, solids need to be removed continuously and valuable oxygen carrier material will inevitably be lost with bottom ash removal. Similar to when quartz is used as bed material, this gives rise to considerable waste material flows. Additionally, it raises the overall cost for the process, especially when oxygen carriers

are used as they are more cost intensive. Combined with the attempt to aim for commercial scaled processes, demand rises for extensive quantities of material. Thereby, it becomes important to find materials already existing as traded products in large quantities that are relatively inexpensive. Therefore, materials available at large quantity from a variety of sources are key features for the implementation of oxygen carriers to commercial scale. Ilmenite is a natural ore that fulfills both the main requirements for an oxygen carrier and is already available as a traded product, and has therefore been selected as oxygen carrier in this work.

### 3.2 Ilmenite as oxygen carrier

As mentioned in Section 2.4.2, ilmenite is an abundant naturally occurring mineral dominated by the compound  $\text{FeTiO}_3$ , with the same name. It is the most abundant source of Ti, where its main commercial use is for white pigment production [30], which stands for 94% of the market of ilmenite [31]. It exists naturally in two forms; hard rock ilmenite and sand ilmenite obtained from heavy mineral placer deposits [30]. The ore containing rock ilmenite is mined, ground and sieved to produce particles of desired size distribution. Sand ilmenite has been exposed to weathering, causing natural oxidation and erosion to the material. This process causes the sand ilmenite to obtain more rounded particles and higher content of  $\text{TiO}_2$  [30, 31].

In CLC, rock ilmenites are found to have higher oxygen transferring capacity than sand ilmenites, as they often contain more Fe [20]. Activity will be further discussed in Section 3.2.4. CLC has typically been conducted in the range of 1 to 10 kW, thus, OCAC presents the first experience of using oxygen carriers on industrial scale. Furthermore, the performance of ilmenite when used as oxygen carrier for OCAC has not been investigated previously.

#### 3.2.1 Validation of the OCAC concept

Although similar, the respective environments in CLC and OCAC subject the oxygen carrier to slightly different conditions. In OCAC the environment is not distinctly separated between oxidizing and reducing as in CLC, but rather a combination of both. Thus, the oxygen carrier is required to be reactive in an environment that changes rapidly. The initial experience of OCAC indicated that combustion burnout was enhanced as 40 wt% of the regular bed inventory (quartz sand) was replaced by ilmenite [10]. The effect of the oxygen carrier being underrepresented in the bed inventory is further discussed in Section 3.2.3.

The oxygen buffering ability of sand ilmenite was evaluated by comparison to quartz sand, where each material was investigated during two separate trials in which the respective material made up 100% of the bed inventory. The details of the study are presented in **Paper II**. A rapid increase of fuel load was introduced to the boiler after which the step responses of oxygen and CO were followed. As quartz sand is known

to be inert with regard to oxygen transfer, this study provides further understanding of the oxygen transfer capabilities of ilmenite.

The base load fuel during this study was wood chips, while the introduced fuel pulse consisted of wood pellets. Specifications of the fuels are presented in Tables 2.3 and 2.4. The wood pellets contained a relatively low moisture level, which resulted in a rapid release of volatiles upon introduction to the combustion chamber. Furthermore, as volatiles account for the major fraction of the combustibles in the fuel as seen from the proximate analysis [32], it also resulted in a rapid increase in load. The fuel pulse was selected to deliver an instantaneous pulse of such a magnitude that it could not be covered by inherent oxygen existing in the gas phase. The rationale for this is that the gaseous oxygen would prove not to be sufficient to cover the augmented fuel load. The fuel pulse was introduced on top of the base load and on nominal base. As volatiles are released instantaneously upon introduction of fuel [9], a volatile-rich zone was created near the fuel inlet as described in Section 1.1.

The pulse responses of the oxygen and carbon monoxide concentrations in the dry flue gases are presented in Figure 3.1, for the two trials. For both materials, the oxygen concentration decreased as the fuel pulse was introduced (dashed line, Figure 3.1). This response is explained by a rapid increase in the concentration of volatiles, which consume the oxygen present in the gas phase when combusted. The response of carbon monoxide, however, differ for the two materials. During operation with quartz sand, a constant background response and distinct elevations of carbon monoxide were observed subsequent to introduction of the fuel pulse (solid line, Figure 3.1). No background response was detected during operation with ilmenite, and only moderate elevations in the concentration of carbon monoxide were noted after the introduction of the fuel pulse.

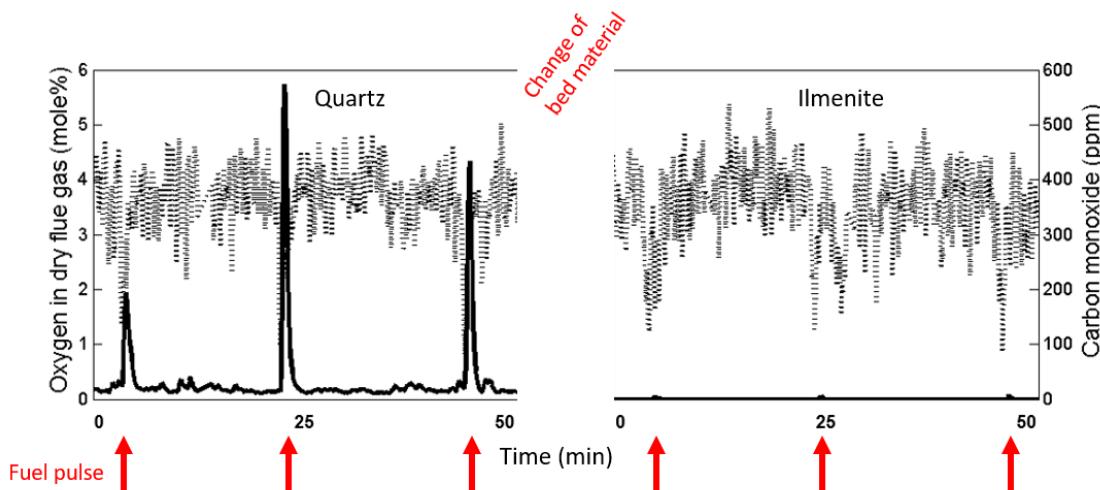


Figure 3.1: Response time of unburnt fuel (carbon monoxide (ppm), solid line) and oxygen (mole%, dashed line) in dry flue gases from Chalmers 12MWCFB boiler using quartz sand (left) and a ilmenite (right) as bed material. Red arrows show where the fuel pulses were introduced.

The peaks in carbon monoxide levels detected during operation of the boiler with quartz sand as well as the fact that the level of oxygen, albeit low, was detected in the flue gases during the decrease of carbon monoxide, implies that the mixing of fuel and oxidizing gas was insufficient. As the boiler was operated under equivalent conditions during the trials, the difference in carbon monoxide concentrations between the trials with quartz sand and ilmenite is attributed to the oxygen buffering and oxygen transporting properties of ilmenite. Thus, utilization of the oxygen stored in the ilmenite temporarily compensates for the oxygen deficit, which results in enhanced combustion in the volatile-rich zone.

In order to determine whether the experimental results could be fully coupled to the oxygen carrier, the system was evaluated by a global mass balance. In the theoretical mass balance, the bed material was separated into two fractions to account for the volatile-rich and volatile-poor zones as described in Section 1.1. The empirical data needed for the global mass balance was based on experimental findings. Thereby, the dominating patterns were identified and the amount of oxygen available through the bed material and by the gaseous phase were investigated. It was concluded that the excess oxygen found in the flue gas for both bed materials is a result of the limited mixing between the volatile-rich and volatile-poor zones. Further, results confirm that ilmenite functions as a buffer of oxygen and compensates for the insufficient mixing in the gaseous phase in space and time.

### 3.2.2 Oxidation forms of ilmenite

In ilmenite, Fe is the active oxygen transferring part while Ti acts as binder. The oxygen carrying ability is based on the transition between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . Three distinct oxidation levels of Fe in ilmenite that have been observed [19] are presented in Table 3.1. The most reduced form of these states is ilmenite,  $\text{FeTiO}_3$  ( $\text{FeO} + \text{TiO}_2$ ), while the most oxidized form is pseudobrookite,  $\text{Fe}_2\text{TiO}_5$  ( $\text{Fe}_2\text{O}_3 + \text{TiO}_2$ ) [ 19, 33]. Cuadrat et al. found that the oxidation step was limited by the supply of oxygen [34].

Table 3.1: Different forms of mixed Fe-Ti oxides obtained by oxidation of ilmenite, constructed from Leion et al. [19].

<b>Level of oxidation</b>	<b>Compound</b>	<b>Corresponding Fe/Ti compound</b>	<b>Added oxygen</b>
<b>0</b>	$\text{FeTiO}_3$	$\text{FeO} + \text{TiO}_2$	-
<b>1</b>	$1/3 \text{Fe}_3\text{Ti}_3\text{O}_{10}$	$1/3\text{Fe}_3\text{O}_4 + \text{TiO}_2$	$1/3$
<b>2</b>	$\frac{1}{2}\text{Fe}_2\text{TiO}_5 + \frac{1}{2}\text{TiO}_2$	$\frac{1}{2}\text{Fe}_2\text{O}_3 + \text{TiO}_2$	$1/2$

Although fresh ilmenite shows a rather low conversion, a gradual increase has been observed with increased reduction and oxidation cycles. The dependency on the number of redox cycles is widely acknowledged for ilmenite [19, 20, 33], and is referred to as an activation process. The conversion increases during the first cycles and then levels out when the materials are considered as “activated” [20]. Activation can be reached more rapidly if particles are reduced to greater extent in one cycle [33]. However, extensive reduction has been linked to agglomerative tendencies and defluidization [19, 34]. Calcination, which is a pre-oxidation of the material at elevated temperature, has shown to be beneficial to reach activation more rapidly while avoiding defluidization [33]. Another method for reaching activation faster while avoiding agglomeration and defluidization is to begin the activation process at a lower temperature [20]. Activation of ilmenite has also proven to be dependent on the reduction agent, where syngas provides more rapid activation than methane [33, 34]. A general observation for most oxygen carriers is that syngas is more easily converted than methane, which could be a reason for why it activates the material faster.

During the activation process, Adanez et al. observed the formation of free  $\text{Fe}_2\text{O}_3$  at the expense of  $\text{Fe}_2\text{TiO}_5$  [33]. In their study, Fe and Ti were uniformly distributed on fresh and calcined ilmenite, while activated ilmenite presented a Ti-enriched core and a Fe-enriched shell. The Fe-enriched shell was slightly separated from the rest of the particle, which had obtained a more porous core. Cuadrat et al. observed a similar phenomenon, where the slightly separated Fe-layer grew thicker with the number of cycles [34]. Segregation of Fe has been found in earlier studies on ilmenite [35, 36], and have been explained as the migration of  $\text{Fe}^{2+}$  ions through the solid lattice toward grain boundary during the oxidation step [36].

The phenomenon is important regarding the activity of ilmenite for several reasons. As the material is activated, Fe migrates to the surface and may affect the oxygen transferring capacity. When made accessible at the surface the conversion increases, as Fe is the active oxygen transferring part of ilmenite. In addition, increased porosity leads to a higher reaction surface area, which further increases the oxygen transferring capacity [33]. Cuadrat et al. found an increase in pore size and an overall increase in porosity from 1.2% for calcined ilmenite to 38% when ilmenite had been activated [34]. However, with more of the active part of the oxygen carrier at the surface, the bed material particles become more sensitive to attrition. Upon attrition, surface areas are primarily worn down. Thereby, the lifetime of the oxygen carrier can be reduced substantially as Fe-enriched fine particulates leave with the flue gas stream.

### 3.2.3 Pathways for iron migration

The chemical distribution of sand and rock ilmenite upon exposure to OCAC of biomass is described in **Paper I, IV and VI**, where Fe migration has been studied. This section presents the findings and conclusions drawn from these studies. The materials were used at different configurations, as described in Table 2.5. Rock ilmenite used as

40wt% of the bed inventory is expected to have been subjected to more distinct oxidizing and reducing conditions in the boiler, as there is less oxygen carrying material available.

**Sand ilmenite 100%.** Upon its initial exposure, Fe was found to migrate to the surface of sand ilmenite particles. With time, Fe-rich clusters were formed, which were prone to settle adjacent to cavities and cracks developed in the particle. A similar phenomenon has previously been reported on rock ilmenite by Knutsson and Linderholm [37]. The authors postulated that the cavities and cracks formed short passages for oxygen diffusion and thus, Fe-rich clusters would form near cavities due to the high oxygen potential. Accordingly, no cavities were found in the particle during the initial migration to the surfaces.

**Rock ilmenite 100%.** Rock ilmenite used as 100% bed material showed a migration of Fe to the surfaces. Thus, the migration of Fe in the rock ilmenite particles follows the mechanism commonly reported in literature [33, 34]. No cavities were detected in the rock ilmenite particles.

**Rock ilmenite 40%.** Shortly after exposure, rock ilmenite particles exhibit Fe migration to the surfaces and over time the layer of Fe persisted together with the existence of an Fe-rich core. In between the layer and the core, an increasing area with low amounts of Fe was detected. After longer exposure, an Fe-rich layer became prominent surrounding a core with low content of Fe. The migration of Fe is found in this case to be faster than when 100% of rock ilmenite was used. This difference could be due to the fact that a lower concentration of oxygen carrier, used at the same load, will undergo a higher degree of redox-cycles, which is the driving force for Fe-migration.

For all materials, Fe is found to migrate to the accessible environment with high oxygen potential. As cavities develop in the sand ilmenite, locations with high oxygen potential are made disposable in the particle and Fe is migrated there. For rock ilmenite, the nearest accessible location with high oxygen potential, is the environment surrounding the particle. The oxygen carrying ability of ilmenite is determined by the oxidation and reduction of Fe between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , and the access of the fuel to the Fe-oxides. In the case of rock ilmenite, these reactions occur at the surface of the particle, where the contact with combustible gases takes place. For sand ilmenite, these reactions partly occur inside the particle. Consequently, two distinct pathways for Fe migration have been identified for ilmenite used as oxygen carrier for OCAC, where both mechanisms are driven by the accessible locations with high oxygen potential. The schematic presented in Figure 3.2 illustrates the mechanism progression with increasing time of exposure. The SEM-EDX images are of particles with different lengths of exposure and are selected for illustrative purpose only.

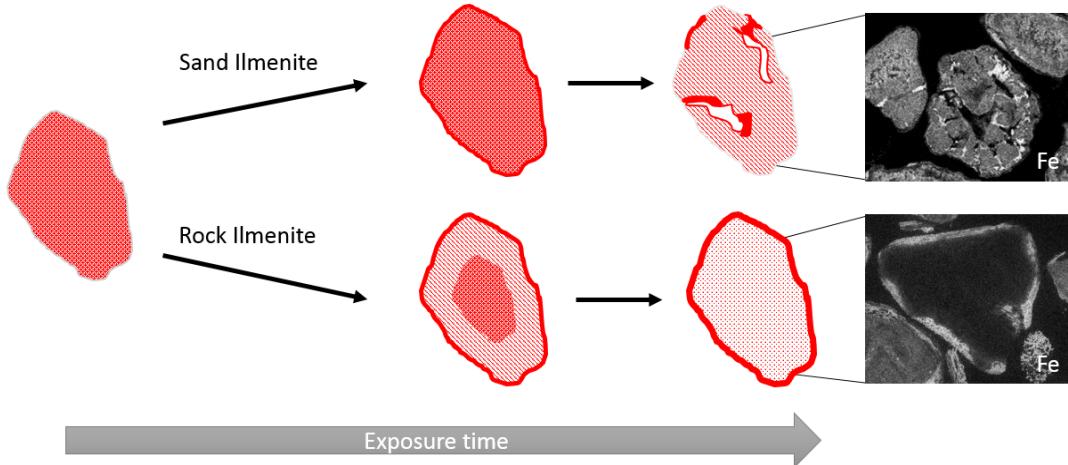


Figure 3.2: Pathways for Fe migration during OCAC exposure, where Fe is illustrated in red, and a SEM-EDX intensity mapping of Fe on sand ilmenite (above), and rock ilmenite (below).

### 3.2.4 Activity of ilmenite

A selection of rock ilmenite samples from the OCAC campaign in Chalmers 12MW<sub>th</sub> and Kraftverkens 115MW<sub>th</sub> CFB-boiler were tested for their oxygen transferring capacity in the laboratory system described in Section 2.1. Figure 3.3 summarizes the results from the Chalmers boiler, including fresh materials. Quartz sand, which is inert with regard to oxygen transfer, is presented as a reference and has insignificant conversion of syngas. Fresh rock ilmenite shows the lowest conversion of the ilmenite samples evaluated. The CO<sub>2</sub> yield increases for used samples with residence time in the boiler, except for the sample with longest residence time (322h), which shows a slight decrease in conversion. These results confirm that the activation process reported during CLC exposure (presented in Section 3.2.2) is also needed for ilmenite used for OCAC operation. Furthermore, the decrease in conversion of the sample with longest residence time indicates that the material has a limited lifetime as oxygen carrier, which will be further discussed in Chapter 5.

Depending on which phase the material obtains, its magnetic susceptibility differs. Hematite is antiferromagnetic, while ilmenite is paramagnetic and magnetite is naturally ferromagnetic [31, 38]. The magnetic susceptibility of ilmenite increases with higher Fe content [39], whereby rock ilmenite has been found to be more strongly paramagnetic than weathered ilmenite [31]. This feature opens for magnetic separation and subsequent recirculation of the material to the boiler. Reusing the oxygen carrier would significantly reduce the cost, and thereby make the concept more feasible.

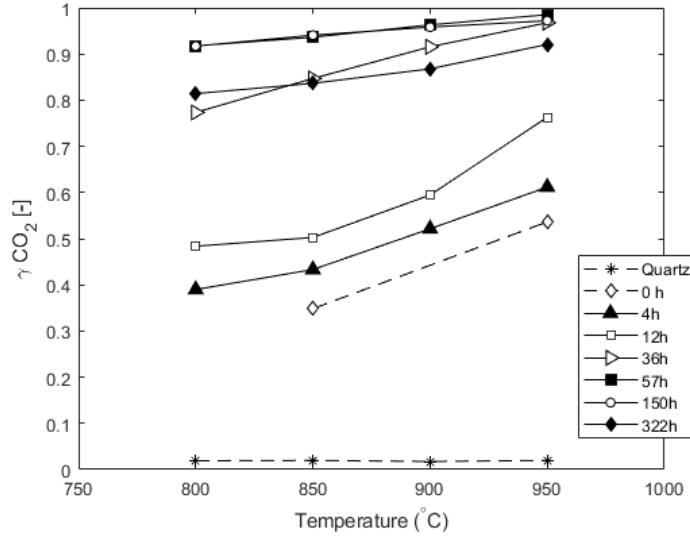


Figure 3.3: Results from bench scale experiments with syngas. Solid lines denote materials obtained from the 12MWth CFB-boiler, while dashed lines represent fresh materials.

Previous research has shown that ilmenite that has been heated could be separated by a magnet [10, 30]. A magnetic separator was installed in the industrial setting at Kraftringen (**Paper VIII**), as described and illustrated in Section 2.3.1. A sample, with the mean residence time of 202h, was chosen for analysis and the total elemental analyses of its fractions are presented in Table 3.2. Both Fe and Ti content are significantly higher in the fraction accepted by the magnet, while the Si content is significantly higher in the rejected fraction. By visual inspection, the material accepted by the magnet showed ilmenite particles as usually encountered after operation in OCAC, while material rejected showed accumulated ash and quartz sand.

Table 3.2: Elemental analysis of a bed sample from Kraftringen's 115MWth CFB boiler, divided by the magnet. The ilmenite in the sample has a mean residence time of 202h.

	Magnetic Accept	Magnetic Reject
	wt.%	wt. %
<b>Fe</b>	19,09	1,53
<b>Ti</b>	14,14	1,32
<b>Ca</b>	13,58	10,22
<b>Si</b>	4,17	23,51
<b>Mg</b>	2,62	1,02
<b>K</b>	2,22	5,25
<b>Al</b>	1,14	3,37
<b>P</b>	0,71	0,48
<b>Mn</b>	0,61	0,22
<b>Na</b>	0,58	1,18

The magnetic and non-magnetic fractions were tested separately for their activity in the laboratory reactor during experiments with syngas as fuel. The results are plotted together with results from the Chalmers boiler for comparison, in Figure 3.4. The fraction accepted by the magnet results in a CO<sub>2</sub> yield comparable to the 322h sample from the Chalmers boiler. This can be explained by that the mean residence time of the ilmenite in the material accepted by the magnet is 202h, which is relatively close to an operational time of 322h. Furthermore, the conversion obtained by the non-magnetic sample is low, amounting to 20-35%. These results indicate that magnetic separation is a feasible way to optimize the usage of ilmenite as oxygen carrier. Additionally, less material is put in landfill, reducing the cost for the company and reducing the generated waste streams in society.

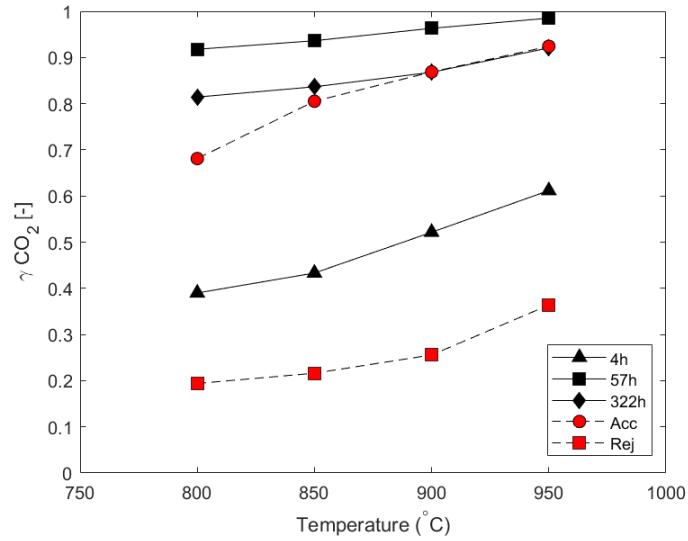


Figure 3.4: Conversion of syngas as a function of temperature. Black markers represent material obtained from the 12MW<sub>th</sub> CFB-boiler. The red markers represent the industrial bed sample extracted from the 115MW<sub>th</sub> boiler, where ilmenite has the mean residence time of 202h. Circles denote material accepted by the magnet and squares represent the non-magnetic material.

# CHAPTER 4

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## ASH INTERACTION

**D**uring combustion, ash contained in the fuel is released and found in the system. In FB boilers, the ash may interact with bed material particles. This chapter addresses the problems caused by ash in FB boiler systems, and specifically describes the interaction of ash with bed material. Based on the findings in **Papers I and IV**, this chapter describes the ash interaction that occurs when ilmenite is used as bed material. Thereby, the chemical resistance of ilmenite is further understood, which is an aspect that impacts the lifetime of the oxygen carrier.

As described in Chapter 2, biomass is a complex fuel containing a heterogeneous mixture of organic matter and to lesser extent inorganic matter. The term biomass includes all organic materials originating from plants, such as wood, crops and algae. The ash-forming matter is the solid residue that results after the combustion and varies depending on the type and origin of biomass. The content of ash depends on fuel type and can be less than 1wt% for woody biomass, while ranging up to a couple of percentages for herbaceous biomass [40, 41]. In general, the main elements found in biomass can be arranged in decreasing order of abundance as follows; C, O, H, N, Ca, K, Si, Mg, Al, S, Fe, P, Cl, Na including Mn, Ti and other minor trace elements [40]. Woody biomasses are dominated by Ca and K, as can be seen in Table 2.4. Most ash-forming elements are nutrients and have essential biological function to the plant. However, during thermal conversion they can cause problems in FB systems such as sintering, fouling and corrosion [41, 42].

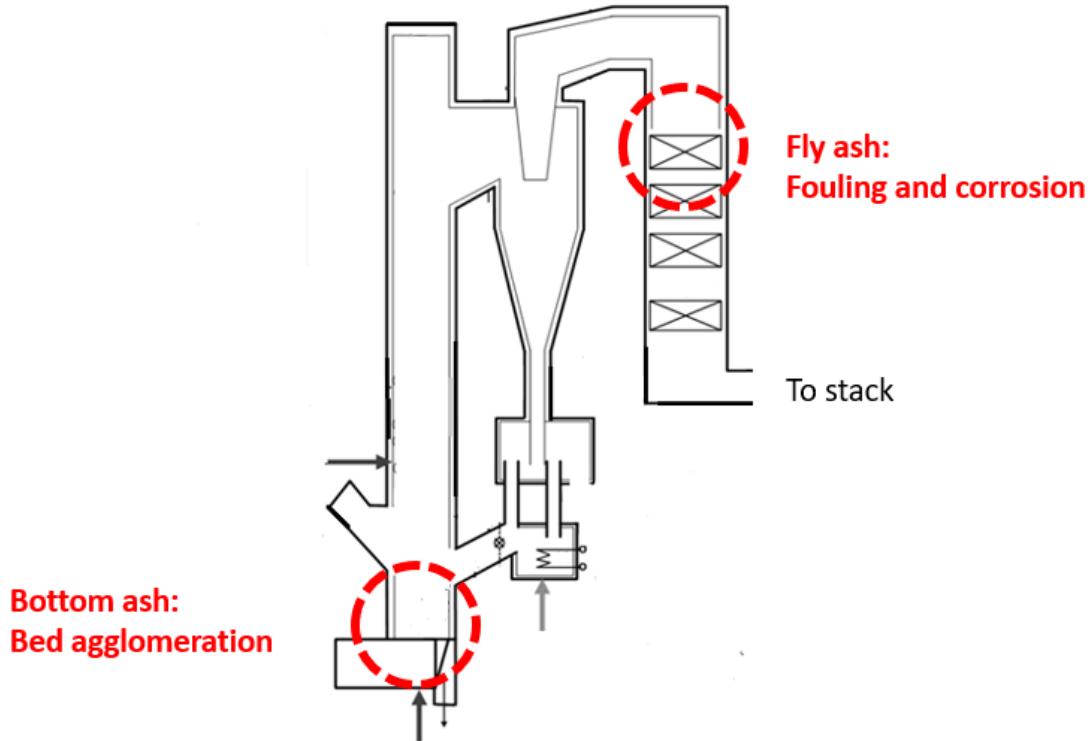


Figure 4.1: Simplified illustration highlighting areas where biomass ash cause disturbances to a CFB system.

The problems connected to ash-forming matter in a CFB boiler are distributed over the system, where the ash ends up as either fly ash or bottom ash. Fly ash is made up of fine particulates entrained by the fluidizing gas that are later collected downstream in the system. Bottom ash is made up of the bed material and ash that ends up in the dense part of the bed. Figure 4.1 illustrates at which locations in a CFB system these respective ash fractions cause issues. As mentioned in Section 1.1, solid material entrained with the flue gases is separated by a cyclone and recirculated back to the bed. There, fly ash passes through the cyclone with the flue gas. As the stream is cooled down over the subsequent superheater and economizer, fly ash may deposit on the heat transfer surfaces [43-45]. Thereby, deposits contribute to fouling and corrosion, causing shortened lifetime of the equipment as heat transfer surfaces deteriorate [42, 45, 46]. Deposit formation is largely dependent on the properties of ash, where compounds with low melting points are known to form sticky melts already at 750°C and are specifically problematic to the process [47]. Ash-forming elements located in the bottom ash may interact with the bed material. During combustion, alkali in the biomass and waste ash is partly converted to the gaseous phase in the reactor [48, 49]. To mitigate corrosion and fouling, Si-based materials have been used deliberately to remove alkali from the gaseous phase [50]. Thus, apart from having high mechanical

strength, quartz sand provides the possibility to absorb alkali metals, preventing them from causing further problems by deposition on heat transfer surfaces [7]. During the absorption stage, a melt of alkali silicate is formed that can cause the bed particles to coalesce [51, 52]. When extensive, this phenomenon is referred to as agglomeration and can cause defluidization of the entire bed, followed by an unplanned shutdown of the plant. To avoid agglomeration, the bed material is regenerated continuously, i.e., used material and ashes are successively replaced by fresh bed material. When the used quartz sand is removed, it is deposited in landfill and, thus, not utilized subsequently.

#### 4.1 Bed agglomeration

Bed agglomeration is caused by sintering and may lead to defluidization, which can be described as a collapse of the entire bed to a solid mass. Consequently, defluidization can cause unplanned shut down of the plant, with loss of revenue as a result. The rate of sintering is increased at elevated temperatures causing more rapid and stronger bonding of bed particles [53]. Thus, operation of FB boilers is limited by agglomeration at higher temperatures.

Most studies cover quartz sand, as it is the regularly used bed material during combustion of fuels with difficult ash composition. Different theories exist behind the formation of agglomerates and can be divided into melt-induced and coat-induced agglomeration [43]. Melt-induced agglomeration is characterized by the formation of a molten phase on bed particles. As burning char may reach significantly higher temperature than the surrounding gas [54, 55], ash-forming matter is proposed to melt upon collision with the burning char particles [56-58]. As the char burns away, the melt is cooled down and solidified, whereby a hollow agglomerate remains [58, 59]. The route for agglomeration may also depend on the fuel used, where low density fuels are more likely to form melt-induced agglomerates [57-59]. Accordingly, coat-induced agglomerates have mainly been found during combustion of more dense fuels [60, 61]. According to Öhman et al. [61] coat-induced agglomeration is initiated by ash deposition on the bed particle via i) attachment of small particles, ii) condensation of gaseous alkali species or iii) chemical reaction at the surface. This is followed by sintering and homogenization, finally resulting in partial melting, agglomeration and defluidization.

## 4.2 Layer formation

Coat-induced agglomeration is characterized by a coating on bed particles, also referred to as layer formation. Elements found in layers mainly originate from the bed material itself or the fuel used [61]. The composition of layers on quartz sand are invariant for woody biomass and three mechanisms for their formation have been proposed [60]:

- 1) Layer grows outward onto the particle, bed particle is inert carrier for the layer material. All elements in layer originate from the fuel
- 2) Layer grows inward onto the particle. Reactive elements may react with the bed particle. (In 1 and 2 growth is limited by either erosion of layer or diffusion limitation or both).
- 3) A combination of 1 and 2.

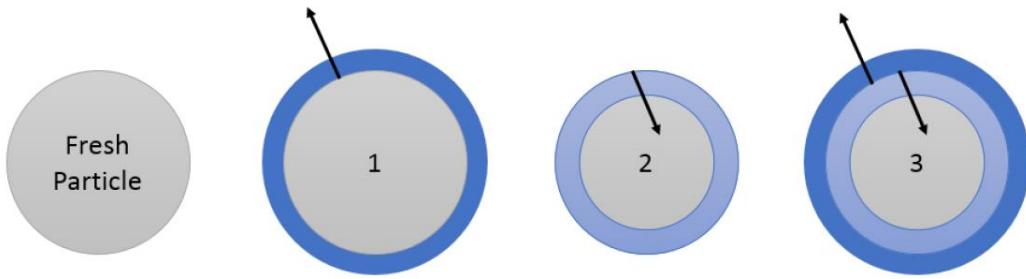


Figure 4.2: Illustration of the different mechanisms for ash layer formation on bed particles.

Figure 4.2 depicts an illustration of the stated mechanisms. Several research groups have investigated layer formation on bed materials during conversion of biomass, and a common result is that mechanism 3) is the most encountered one [60, 62-64]. It should be mentioned that no major differences in layer formation have been found between bed materials used for combustion and gasification [65]. Thus, studies on layer formation generated from gasification are of interest to combustion processes, and vice versa.

Many studies covering both quartz and olivine as bed material have reported on the formation of an outer more heterogeneous and an inner more homogeneous layer [60-63, 66-68]. The heterogeneous layer resembles the fly ash in composition and grows outward on the bed particle. The inner layer is found to contain less variations and is often dominated by Ca and/or K. The inner layer is formed by inward diffusion and subsequent reaction of Ca and K with the bed material itself.

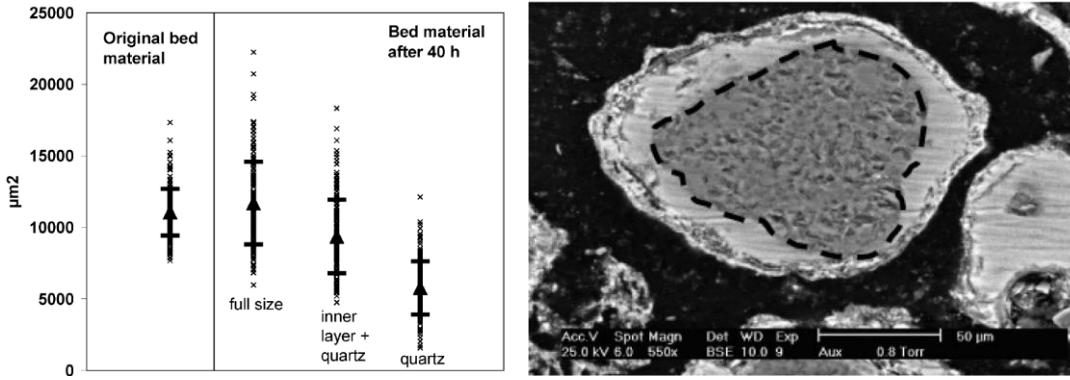


Figure 4.3: Progression of ash coatings elaborated by Brus et al. [62].

The initial step of layer formation has been appointed K-silicates, which form a sticky melt on the particle surface [60, 67]. Coarse fly ash including CaO and MgO can then be trapped in the sticky melt. Brus et al. [62] investigated the growth of ash layers and showed that reactive ash components dissolved in the quartz phase of the bed particle, extending the inner layer toward the center of the particle. The growth outward in combination with this inward attack resulted in increased particle size simultaneously as a shrinking core of unreacted bed occurred, represented in Figure 4.3. Bed material subjected to longer operational times in combination with fuels rich in K have resulted in an “inner-inner” layer [43, 67]. However, sufficient growth of the Ca-rich inner layer appeared to prevent further interaction with K.

Gatternig and Karl [59] proposed that during inward diffusion, ash components react with the bed by invading the highly ordered  $\text{SiO}_2$  lattice. According to the authors, Ca tends to replace Si atoms, while K occupies interstitial spaces within the lattice. This inflicts stress upon the Si-O bonds and decreases the energy necessary for bond breakage, effectively lowering the melting point. Incorporation of  $\text{Ca}^{2+}$  to the initial structure of bed material has also been found on olivine and K-feldspar. For olivine, ion substitution of  $\text{Ca}^{2+}$  with  $\text{Mg}^{2+}$  or  $\text{Fe}^{2+}$  occurs, where the exchange with  $\text{Fe}^{2+}$  is more likely [66, 69]. In K-feldspar  $\text{Ca}^{2+}$  has been found to substitute  $\text{K}^+$  [70]. Thus, there is a tendency over a range of bed materials for  $\text{Ca}^{2+}$  to be incorporated in the bed particle structure during layer formation.

#### 4.3 Ash interaction on ilmenite

Although the research covering ash interaction with bed materials is substantial, it almost exclusively considers Si-based materials. Knowledge on alternative bed materials and their ash interaction is scarce. The limited research on ash interaction and oxygen carriers has mainly covered coal ash, which has been reported to have a negative impact on the conversion [71-73]. However, if Ca content is high, a positive effect can be observed on conversion. A correlation between composition of ash was proposed by Bao et al. to effect conversion, where high content of Ca has a positive, and high content of Si has a negative impact on conversion [72]. This correlation was

confirmed for biomass ash by Gu et al., who studied its interaction on an iron ore [74]. Needless to say, it is of great importance to the field if alternative bed materials are to replace quartz in existing systems. **Paper I** and **IV** included in this thesis cover the ash interaction and mechanism for layer growth on ilmenite used for OCAC. The mechanism for ash interaction on ilmenite is consistent for both sand and rock ilmenite and is therefore presented and discussed together.

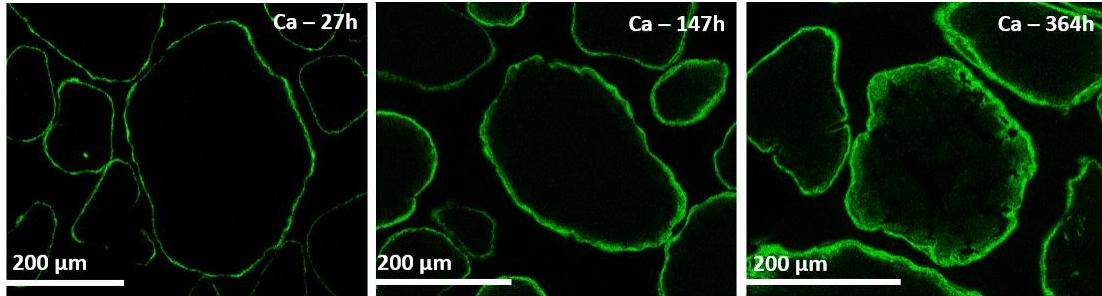


Figure 4.4: EDS intensity maps of Ca on a particle extracted at a) 27h, b) 147h and c) 364h.

The propagation of Ca on ilmenite is illustrated by its EDS intensity maps on cross-sections of ilmenite particles in Figure 4.4. The Ca is enriched in surface layers, which become thicker with time of exposure to OCAC of biomass. The Fe-rich layer described in Section 3.2.3, was found to be enclosed by an ash layer rich in Ca. This evidence, thereby, suggests that the migration of Fe to the surfaces follows a pathway through the Ca-rich layer surrounding the particles.

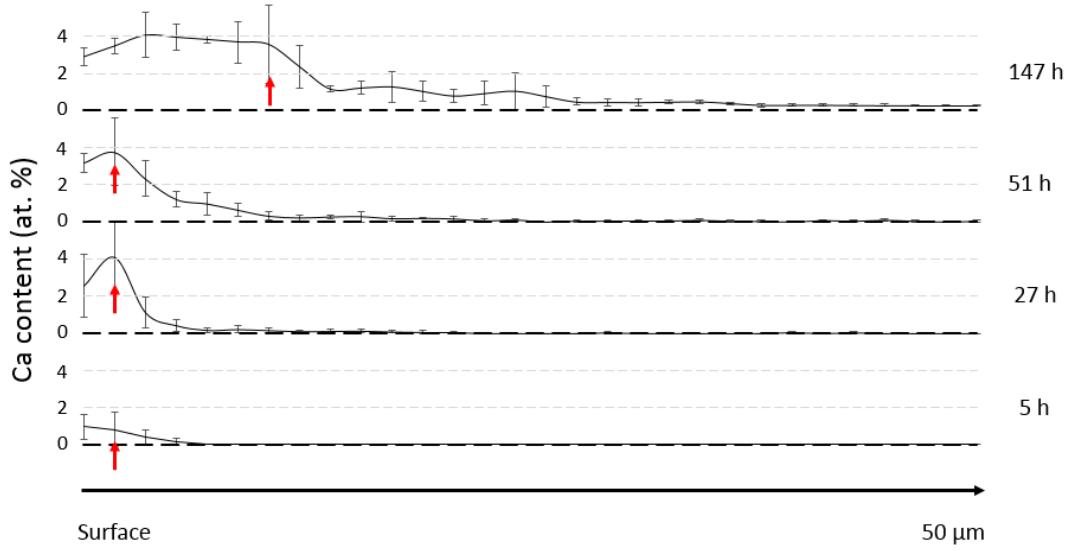


Figure 4.5: Ca deposit and migration into the particle, the figures show the outer 50 μm from surface inward from left to right. The figure shows the weight percentage of Ca in particles extracted after 5h, 27h, c) 51h and 147h.

With further investigation of the ash layers, the presence of Ca could be divided into two parts, similar to the heterogeneous outer layer and homogeneous inner layer described in Section 4.2. Point analyses reveal that the outer part increases in depth rather than in concentration. The depth is marked by a red arrow in Figure 4.5. In the outer part, Ca was found to coexist with other ash elements such as Si and P. Furthermore, a low concentration (roughly 1 at.% or less) of Ca was detected, forming an inner layer on the particles. The inner layer was found to be more homogeneous and propagated inwards on the particle over time.

A heterogeneous layer is formed after deposition of ash elements on the surface of particles from which Ca migrates inward on the particle forming a more heterogeneous inner layer. Thus, the Ca-rich layer is suggested to be built up according to mechanism (3), presented in Section 4.2 [60]. The compound formed is confirmed by XRD to be a Ca-titanate, where the dominating phase is  $\text{CaTiO}_3$  for sand ilmenite and  $\text{Ca}(\text{Ti}_{0.7}\text{Fe}_{0.3})\text{O}_{2.85}$  for rock ilmenite. Thus, the mechanism on ilmenite is similar to findings on other bed materials, and the diffusion inward is a result of incorporation of  $\text{Ca}^{2+}$  to the ilmenite structure.

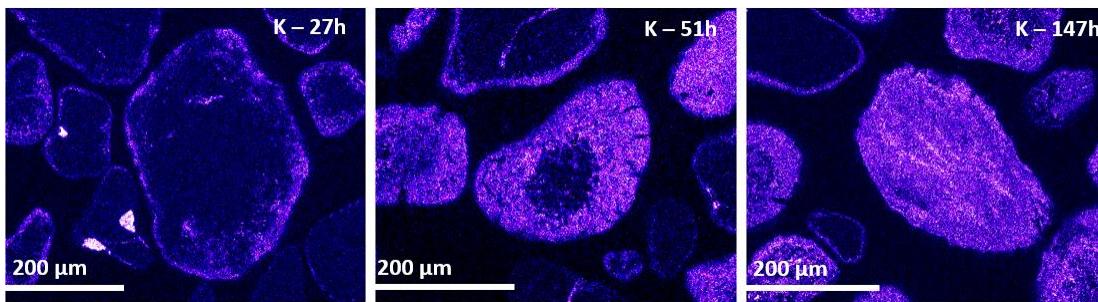


Figure 4.6: EDS intensity maps of K of the cross sections of particles extracted at a) 27h, b) 51h and c) 147h

A successive diffusion of K inward on ilmenite particles occurs as they are exposed to OCAC of biomass, as shown in Figure 4.6. From left to right, K can be seen to initially be found at outer parts and then diffuse inward until the entire cross-section is covered. The propagation is visualized quantitatively in Figure 4.7, where the amount of K appears to increase to an upper limit of around 2 at.%. By comparing Figure 4.7 to Figure 4.5, K can be noted to be more or less absent in the heterogeneous outer layer and occurs further in on the particle than the inner Ca-layer. Thereby, reaction of K could be surpassed at locations where Ca-titanates have already formed, as reported for Si-based materials. Also, the rate of diffusion for K is faster than for Ca, causing the “inner-inner” layer, inside the homogeneous layer containing Ca.

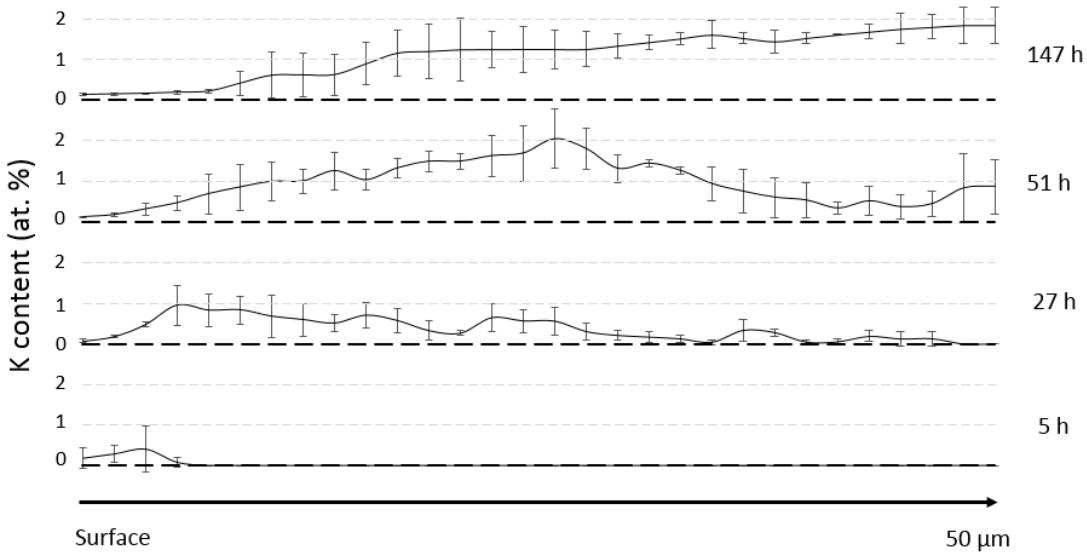


Figure 4.7: K migration into the particle, the figures show the outer 50  $\mu\text{m}$  from surface inward. The weight percentage of K is shown in particles extracted after a) 5h, b) 27h and c) 51h.

A K-titanate phase,  $\text{KTi}_8\text{O}_{16.5}$ , was found to be formed by XRD, which is a mixed oxide crystal structure of  $\text{K}_2\text{O}$  and  $\text{TiO}_2$  at the molar ratio of 1:8. To reach available  $\text{TiO}_2$ , K is required to diffuse through the Ca-rich ash layers and through the  $\text{KTi}_8\text{O}_{16.5}$  that is already formed in the crystal structure. Similar inclusions of K in titanate structures have been reported in literature [75-77]. During observation of K release from various fuels, it was noted that the discharge of K from fiberboard was significantly low [75, 76]. Fiberboard contains  $\text{TiO}_2$ , due to pigmentation and it was suggested that K was incorporated in the titanate structure, remaining stable up to 1150°C. This was confirmed by Wiinikka et al. [77], who studied the vaporization of K from straw during  $\text{TiO}_2$  addition to the fuel. The authors found that  $\text{KTi}_8\text{O}_{16}$  was formed, and proposed  $\text{TiO}_2$  as a suitable additive to reduce vaporization of alkali during combustion.

Migration of K inwards occurs at a higher rate than the migration of Ca and when captured, K is encapsulated by the formed ash layer and will have limited options. In a study on K-Feldspar,  $\text{Ca}^{2+}$  was shown to replace  $\text{K}^+$  in the silicate structure [70]. Similarly,  $\text{K}^+$  could be replaced by  $\text{Ca}^{2+}$  in the titanate structure here. K would then be outmatched and either proceed into the titanate structure by a diffusion-controlled inclusion or be devolatilized. Thus, the presence of Ca could promote the observed mobility of K.

#### 4.4 Consequences of ash interaction to oxygen carrier function

The distinctive feature as alkali-capturer provides another advantage to ilmenite as bed material. Exposed samples of rock ilmenite were leached for the purpose of understanding whether K could be extracted from the bed material. If rendered possible, leached ilmenite could be re-used for further capture of alkali. The results reported in **Paper I** showed that K in the formed titanate is stable in the crystal structure and not leachable by water at ambient conditions. However, it should be mentioned that the limit for saturation of K in ilmenite has not been investigated.

The main purpose of an oxygen carrier as bed material is to distribute oxygen in the combustion chamber more efficiently. Therefore, it is important that ash interactions do not inhibit the oxygen transferring capabilities of this material. Ash interaction over time and its effect on activity is discussed in more detail in Chapter 5.



# CHAPTER 5

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## AGEING OF OXYGEN CARRIERS

If no prior treatment has been exerted on bed materials upon introduction to the combustion chamber, they are referred to as fresh materials. To avoid operational issues, used material is continuously replaced by fresh material through regeneration of the bed inventory. The purged stream leaving the system contains a blend of bed material with a variation of obtained residence time. As the material gains increased residence time, it will undergo certain physiochemical changes. This process is referred to as ageing of the bed material. Ilmenite has already been discussed in this thesis in terms of the physiochemical changes it undergoes. In Chapter 3 the distribution and migration of Fe was treated, whereas the formation of ash layers was considered in Chapter 4. This chapter deals with how the collected aspects of ageing, presented in Figure 1.3, affect the lifetime of the material. It is based on **Paper IV**, which covers how the ash layers build up over time and **Paper VI** which deals with how ash layers affect the oxygen transferring capacity of the material. Thus, connecting to the oxygen carrier capabilities and the chemical resistance. The mechanical resistance is treated, based on **Paper III** where the structural development of both sand and rock ilmenite are mapped out. Finally, this chapter presents the findings of when ash is accumulated in the system, connecting to **Papers V** and **VI**.

Ageing of bed material is ascribed to several typical signs during thermal conversion of biomass. Indications of ageing can be the thickness of ash layers, rounded shape or development of pores, cracks and cavities [37, 63, 78]. In the context of this thesis, the age of bed material is defined as the residence time it has obtained in the respective boiler. This is possible as the experiments with ilmenite on semi-industrial scale were performed after the total bed inventory was fresh material at the start of the campaign. As new material was partly added to the system during the campaign, the most aged

particles were always chosen for inspection upon analysis. The method for choosing aged particles is described in more detail in Section 5.2.

## 5.1 Ash and activity

Apart from their ability to transfer heat, bed materials are also chosen for their catalytic activity, as described in Chapter 3. Addition of inorganic compounds containing Ca and K have been shown to improve catalytic performance of the bed materials [24, 79-81]. Moreover, the increased catalytic performance has been attributed to ash layers formed on the bed material [68]. Specifically, the Ca-rich layer has been ascribed to promote the water-gas-shift reaction and reduce tars in the produced gas [82]. In fact, a study of quartz sand with developed ash layers showed that, the otherwise non-catalytic material, obtained catalytic abilities higher than for fresh olivine [24]. As bed material is aged, formed layers containing Ca and K compounds originating from the fuel have also shown to increase the catalytic ability [25, 81].

### 5.1.1 Potassium as CO oxidation inhibitor

Although K has been shown to be catalytic during gasification, Marinkovic et al. [25] revealed that K can act as a strong inhibitor of CO oxidation. In the dual fluidized bed (DFB) gasifier studied, the authors observed high emissions of CO in the combustion unit. In a similar study, using manganese ore as bed material, high CO emissions were observed [83]. In fact, using Mn ore as the bed material resulted in higher CO emissions than for quartz sand, which is a significant result as Mn is considered an oxygen carrier and should improve combustion [83]. The fresh Mn ore contained an amount of roughly 1% of K and as no further absorption occurred, it was assumed to already be saturated with K.

In both studies, two methods were found to be effective for deactivating the inhibitory effect that K had on the CO oxidation. Namely, quartz sand or S addition, in which the S addition was found to be most effective in both cases. These results emphasize the impact of K during thermal conversion. Interaction between K and bed material, despite causing risk for agglomeration, may be essential to reach adequate conditions during combustion of K-rich fuels, since accumulation of K in the gaseous phase may inhibit the oxidation of CO. Thus, regardless of which bed material is used, the ability to capture alkali in the bottom ashes is of great importance.

## 5.2 Ageing of ilmenite

During the OCAC experiments with ilmenite at semi-industrial scale, the boiler was operated for over 300 hours without any discharge of bed material. Bed material samples were extracted on a daily basis, which provided insight into the ageing of the bed material. Fresh ilmenite was, however, added to the system to maintain safe operating conditions of the boiler. Therefore, the sampled particles could be of different residence time and needed to be appreciated accurately. A useful indication of particle

age was the thickness of the formed ash layers, where thicker layers denoted particles with longer residence time. Furthermore, rounded shape and formation of pores, cavities and cracks were indicators for more aged particles. The ageing of ilmenite is discussed in terms of ash layers, activity and its structural development.

### 5.2.1 Buildup of ash layers

Ash layers are found on ilmenite used for OCAC, where the two main elements discussed in this thesis are Ca and K. In Chapter 4 it was presented that Ca builds up through diffusion inward and grows outward, while K interaction occurs through diffusion inward. The propagation of the two elements over time can be observed in Figure 5.1.

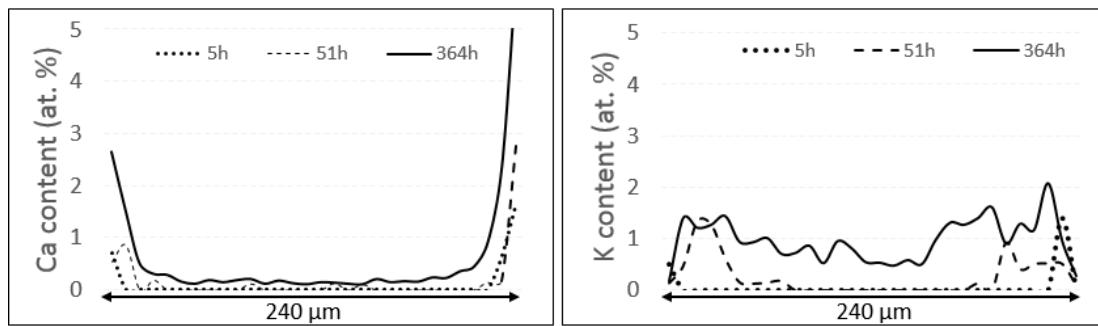


Figure 5.1: Line scan analysis of the cross section of a particle from surface-to-surface. The figure shows the weight percentage of Ca (to the left) and K (to the right).

In Figure 4.6 it was observed that the diffusion of K inward continues until it covers the entire cross-section. The diffusion rate of K was found to be linear and full coverage was estimated to occur after 83 hours, or approximately 3.5 days, as presented in Figure 5.2. The concentration of K is around 1.5-2 at.% throughout the propagation inward, and has not been found to accumulate further at the investigated conditions. This could indicate that the particles are saturated with K, or that inclusion of Ca hinders further incorporation of K.

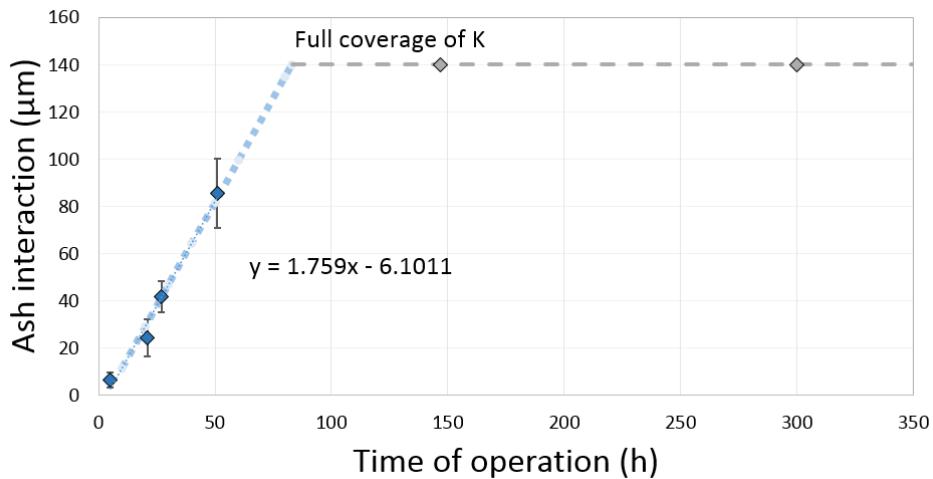


Figure 5.2: Coverage of K, followed as the thickness of the K-layer found on ilmenite particles. The error bars show that the uncertainty increases with time except for when the particles are fully covered by K.

The total accumulation of ash elements in the bottom ash can be observed in Figure 5.3. As the content of Si and Ca continue to increase with time, K evens out after around 50 hours of operation. As a result, this confirms that no further inclusion of K occurs after full coverage of the particles is obtained. A general decline of Fe and Ti occurs simultaneously with a general increase of ash elements. Consequently, an investigation to determine whether activity and oxygen carrying capacity are affected by ageing is called for.

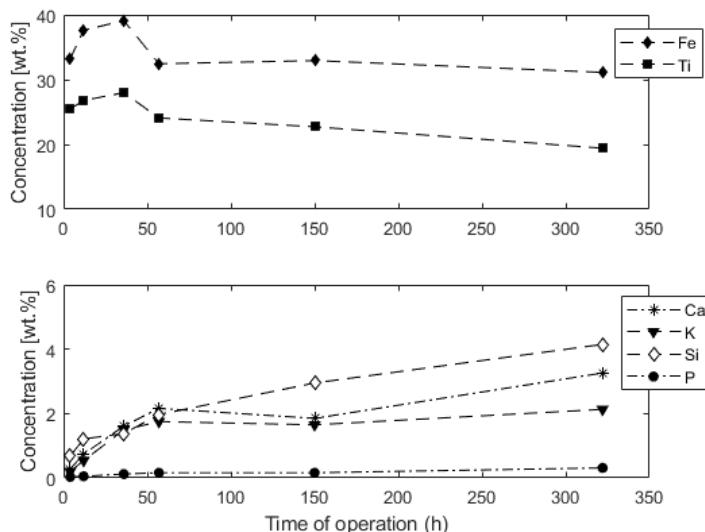


Figure 5.3: Total elemental analysis of bed samples. Above is the content of inherent ilmenite components (Fe and Ti), and below the major ash constituents are presented. All results presented in wt.-%.

### 5.2.2 Activity dependence on ash layers

The activity of ash-coated ilmenite was identified by studying the conversion of syngas in the laboratory reactor, described in Section 2.1. A detailed discussion on the activity was provided in Section 3.2.4 and will be further considered regarding its dependence on ageing. The CO<sub>2</sub> yield of ilmenite from the semi-industrial boiler as a function of time is presented in Figure 5.4. The lower conversion for samples with low operational time are due to the activation process needed for ilmenite. The material could be considered activated after around 36 hours (or 1.5 days) in the system. Optimal conversion was observed at 50 hours (2 days), after which the conversion was found to decrease with remaining operational time. However, it should be noted that samples extracted after more than 300 hours still resulted in relatively high conversion. The decrease in CO<sub>2</sub> yield with longer exposure could be a result of the decreasing amount of Fe in the material. However, this hypothesis is contradicted by that the Fe content is consistent between the most aged sample, 322h, and the sample with highest conversion, 57h (Figure 5.3). A correlation can instead be seen where ash content increased simultaneously as the conversion decreased. As the thickness of ash-layers increase, the availability of Fe-oxides at the surface is decreased and, thereby, also the conversion.

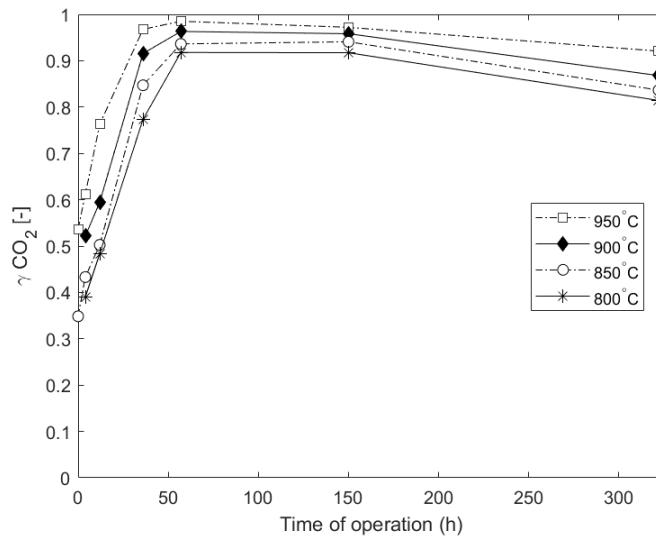


Figure 5.4: CO<sub>2</sub> yield of ilmenite with increased residence time from the semi-industrial CFB boiler.  
The conversion is tested at different temperatures with syngas as fuel.

### 5.2.3 Structural development

Evaluation of how sand and rock ilmenite particles were affected by mechanical stress during long-term exposure of OCAC was presented in **Paper III**. SEM images depicting the cross-section of exposed particles provided visual understanding of the structural evolution. As described in Section 3.2.3, small cavities were formed within the sand ilmenite particles. These cavities were found to increase in size and quantity with residence time. In rock ilmenite, distinct cracks were formed inside the particles. The cracks were found to extend along the inner parts and eventually lead to splitting of the particles. The mechanical resistance was measured by attrition tests. It was shown that the fresh materials were similar in their mechanical resistance, where sand ilmenite showed slightly higher stability. Upon exposure, the sand ilmenite became more sensitive to attrition. Its mechanical resistance was, however, not drastically altered with time. The rock ilmenite was initially sensitive to mechanical stress but became more resistant with time.

Even though the mechanical strength of both sand and rock ilmenite is weakened by exposure, the materials were found to follow different paths of degradation. The suggested mechanisms are illustrated in Figure 5.5. It is proposed that the sand ilmenite is held together by the ash layer that encloses it. When it can no longer be held together by the ash layer, it is shattered into fine particulates. The accumulated stress in the sand ilmenite is constant as the cavities are formed simultaneously over time as the ash layer builds up. As a result, the fragile core is stabilized by the ash layer. The cracks formed in the rock ilmenite are results of the inherent stress the material retains from its preparatory stages during mining. As the cracks expand they finally cause splitting of the particles. The inherent stress is released early during exposure and results in the splitting apart of the particles. Thereafter, these particles will become more resistant for further mechanical stress.

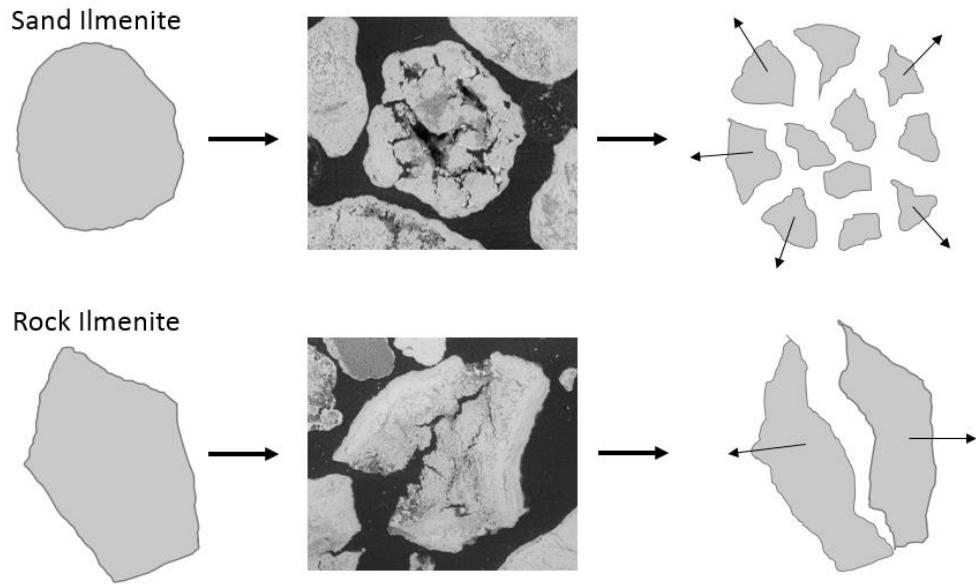


Figure 5.5: Mechanism for the structural decay of sand (above) and rock (below) ilmenite.

### 5.3 Long-term accumulation of ash

In the full industrial boiler Kraftringen, described in Chapter 2, the ilmenite used as oxygen carrier was separated after extraction by a magnet. Analyses of the material showed that the non-magnetic fraction was less reactive and almost exclusively contained elements originating from ash (Chapter 3). **Paper VI** showed that two main particle types were identified in this fraction, namely, quartz sand particles and hollow particles consisting of ash elements. An illustration of the hollow particles is presented in Figure 5.6, which includes the EDS intensity maps of Fe, Ti, Si, Ca and K. The crust of these hollow ash particles contains mainly Ca and Si, but other fly ash elements were also observed, including Fe and Ti. These ash particles are considered to form by collision of the fly ash with burning char, according to the melt-induced theory described in Chapter 4. It should be noted that these particles were observed when the boiler had been operated employing a low rate of regeneration for several days (**Paper VIII**). As a result, their formation may be caused by an accumulation of ash in the system.

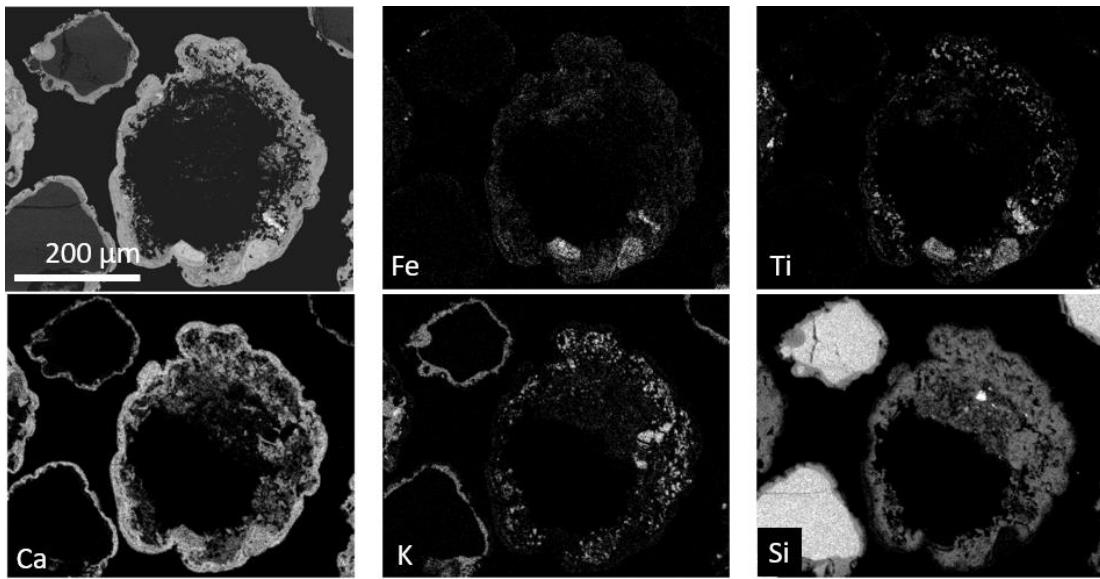


Figure 5.6: SEM micrograph and EDS maps of Fe, Ti, Ca, K and Si on a particle from material rejected by the magnet at the full industrial experiments at Kraftringen.

A similar phenomenon was observed when the Chalmers boiler was operated with a manganese ore as oxygen carrier (**Paper V**). Figure 5.7 shows an example where a probable melt of K, Si and S is observable beside the hollow structure. The melt and hollow part are enclosed by a Ca and Si-rich crust also containing fine parts of Mn and other fly ash elements. Although these hollow structures have been found upon accumulation of ash during OCAC, there has not been any indication that they disturb the operation in a negative way.

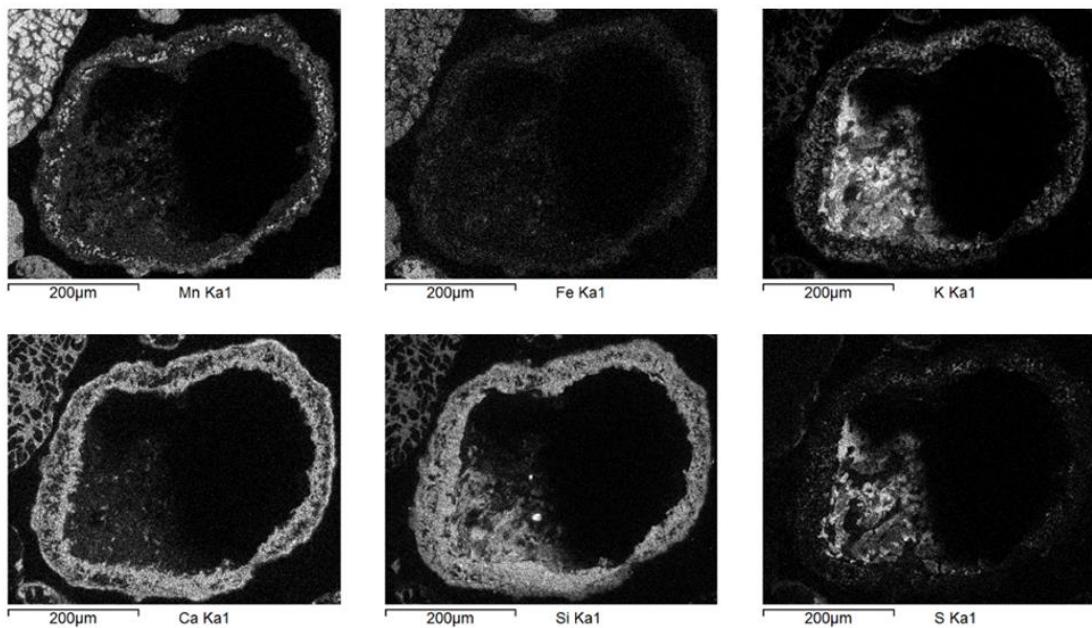


Figure 5.7: EDS maps of Mn, Fe, K, Ca, Si and S showing a hollow particle from the sample taken after 172 h of operation with manganese ore in the semi-industrial CFB boiler.

# CHAPTER 6

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## APPLICATION TO INDUSTRY

A prerequisite for full industrial scale-up of the OCAC concept required validation of the concept on semi-industrial scale. The validation was discussed in Chapter 3, and a more detailed description is found in **Paper II**. The main purpose of this validation was to confirm the concept on large scale and show that oxygen carriers are applicable to industrial settings without any operational disturbances. With this confirmation, the initial full-scale experiments with an oxygen carrier as the material was performed at E.ON's 75MW<sub>th</sub> CFB-boiler fired with MSW (**Paper VII**). Subsequently, the concept has been tested in Kraftverk's 115MW<sub>th</sub> CFB-boiler fired with waste wood (**Paper VIII**), where several optimization attempts were made. This chapter presents the obtained industrial experience and possible optimization measures. Furthermore, the efficacy of the concept is discussed.

### 6.1 Initial industrial experience

During the initial experimental campaign at E.ON's 75MW<sub>th</sub> CFB boiler, safety measures were implemented by adding the oxygen carrier through a separate silo. In that manner, quartz sand could be fed at high rate to the boiler if anything should have gone wrong. Ilmenite was added successively to the bed inventory during a constant boiler load. Concurrently, the temperature measured in the top section of the combustion chamber was increased slightly, while the temperature at the cyclone outlet was significantly decreased. High temperatures at the cyclone outlet are associated with combustion taking place in the well-mixed cyclone. Thus, it was shown that a more extensive burnout was achieved in the combustion furnace with ilmenite included in the bed inventory. Furthermore, a lower excess of air and considerably lower emissions of carbon monoxide were achieved with ilmenite as bed material. The collected experience was presented after 12,000 hours of operation in **Paper VII**. Furthermore,

the study showed that the boiler was operated smoothly, and logistics were manageable with the new bed material. These features are important for implementation of the concept. In conclusion, **Paper VII** showed that the concept was implemented to full industrial scale without making any adjustments to the existing system.

## 6.2 Optimization measures

Considering all costs, including transport, ilmenite is around 6-10 times more expensive than quartz sand, of which the raw material is found in the range of 200-300 SEK/ton (Sweden, April 2019). Thus, optimization aspects are important to increase the feasibility of the concept. The optimization methods, decreased bed regeneration and magnetic separation were evaluated in **Paper VIII** and are presented in this section.

### 6.2.1 Decreased bed regeneration

For quartz sand, a rule of thumb is that the bed material consumed is roughly 3 kg/MWh for biomass combustion and 6 kg/MWh for combustion of MSW. The consumption of bed material during combustion of waste wood is assumed to fall in between these values. For Kraftringen's 115MW<sub>th</sub> CFB-boiler, this corresponds to a regeneration rate of 8-16 ton/day. During the campaign at this boiler, the initial feeding rate for ilmenite was held at 15 ton/day for 220 hours after which it was successively reduced to 8, 4 and finally 2 ton/day, as presented in **Paper VIII**. The final rate corresponds to approximately 0.72 kg/MWh, which is exceptionally low even for biomass combustion. The trial was performed without any disturbances coupled to the decreased rate of regeneration.

### 6.2.2 Magnetic separation

As described in Chapter 3, ilmenite becomes magnetically separable after being exposed to OCAC conditions. Lind et al. [22] presented the possibility for magnetic separation of ilmenite in large scale waste fired units. The magnetic separation was trialed at Kraftringen's 115MW<sub>th</sub> unit, and subsequently installed at E.ON's 75MW<sub>th</sub> unit. Analyses of the fractions obtained, presented in Table 3.2, show that the method is effective to separate still active material from non-reactive material. Thus, by magnetically separating the material with remaining oxygen carrying capabilities, the possibility to reuse the material arises. Thereby, the operational costs can be brought down additionally.

## 6.3 General discussion

The industrial experience shows that combustion is enhanced on full scale with particularly complex fuels when OCAC has been implemented. Rock ilmenite can be integrated to current logistics. Even though ilmenite is more expensive than quartz sand, this work shows that the exchange of bed inventory can be reduced significantly, lowering both the initial cost at purchase and cost for disposal of the material. Additionally, in Section 3.2.4 it was shown that ilmenite is relatively effective as

oxygen carrier after long term exposure, despite the ash layers that build up on the particles (Section 5.2.2). Thus, the further utilization of material enabled by magnetic separation (Sections 3.2.4 and 6.2.2). Without any discussion about cost in absolute terms, the collective assessment is that OCAC is a viable concept for combustion of complex fuels on full industrial scale.



# CHAPTER 7

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## SUMMARY OF MAIN FINDINGS

In the present thesis work, oxygen carriers have been applied to existing industrial settings in a successful manner. Rapid scale-up of OCAC has been possible through integration of scales. Thereby, a loop of bed material and information feedback was achieved, as explained in Chapter 2. This thesis work presents the implementation process of OCAC to existing industry with the main objectives to describe the parameters affecting the lifetime of an oxygen carrier under these conditions and evaluate potential optimization efforts. Several oxygen carriers, including two types of ilmenite and one manganese ore have been investigated. The focus has been on ilmenite and the specific configurations are summarized in Table 2.5.

The concept OCAC was validated through dedicated experiments on semi-industrial scale, as reported in **Paper II**. The oxygen transferring capacity and buffering ability of ilmenite was demonstrated, confirming that oxygen is made more accessible in space and time by using an oxygen carrier as bed material. The oxygen transferring capacity of ilmenite is attributed to its Fe content. This work shows that Fe migrates through the ilmenite particles through different pathways (**Papers I, IV and VI**). Sand ilmenite develops cavities, to which Fe migrates, whereas for rock ilmenite, Fe migrates to the surface of particles. For both materials, the migration occurs toward locations with high oxygen potential. Furthermore, this work confirms that ilmenite requires to be activated before the material reaches its full potential, as presented in **Paper VI**.

Ash interactions with ilmenite used for OCAC with biomass as fuel were investigated in **Papers I and IV**. This work proposed that ash components including Ca and K interact in a similar mechanism as other bed materials used for conversion of biomass,

as was described in Chapter 4. Specifically, a mixed mechanism including a heterogeneous layer growing outward and a homogeneous layer propagating inward on particles, was proposed.

The ageing of ilmenite was followed in **Papers III, IV and VI**. Different structural developments were found for sand and rock ilmenite. The work shows that the cavities found in sand ilmenite eventually causes the particles to shatter into numerous small pieces. On the other hand, rock ilmenite is decomposed by the development of cracks which subsequently split the particles. Furthermore, it was found that buildup of ash layers may improve the mechanical stability of particles.

The formation of ash layers was not found to directly inhibit the oxygen transferring capability. However, as the ash layers were built up over time and became thicker, a slight decline in conversion was observed. In combination with the activation required for ilmenite, this implies that an optimal window of bed material lifetime exists. Specifically, the material needs to be retained in the system long enough to obtain optimal conversion, and then utilized further until it is impaired by chemical and mechanical resistance.

Upon accumulation of ash in the system, **Papers V and VI** presented that when sufficient bed material was not available to react with the ash, hollow ash particles were formed. These particles consisted mainly of Si and Ca and did not prove to be problematic with regard to operation.

During the first industrial trials, presented in **Paper VII**, the regularly used bed material could gradually be replaced by an oxygen carrier, which was introduced through a separate system. This provided additional security and a speed of transition that could be regulated by the operators. **Papers VII and VIII** demonstrate that the OCAC concept is applicable to combustion of waste wood and MSW. Increased fuel conversion spatially and temporally, as well as increased boiler efficiency was obtained. Moreover, it was shown that stable continuous conditions can be achieved during long-term operation of OCAC at full industrial scale. The potential of operating a boiler at full industrial scale with a drastically decreased regeneration of bed material was presented in **Paper VIII**. Additionally, it was shown that magnetic separation provides the opportunity to reuse material that is still active as oxygen carrier.

Based on the work presented in this thesis, it can be established that oxygen carriers have already been accepted and applied to existing industry. The lifetime of oxygen carriers is affected by both its chemical and mechanical resistance. The formation of ash layers may prolong the lifetime of particles as it improves their mechanical stability. However, buildup of thick layers can impair the oxygen transferring capabilities of ilmenite. The feasibility of OCAC is increased by optimization measures including to reduce and reuse bed material in the system, as described in Chapter 6. In conclusion, OCAC is an approach that can be used to improve the conversion of complex fuels.

# CHAPTER 8

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## CONCLUSION AND OUTLOOK

This thesis presents the first comprehensive exploration of the concept OCAC. It has been demonstrated that OCAC is a feasible technology providing enhanced combustion to existing CFB units. The concept has been validated on semi-industrial scale with biomass in a 12 MW<sub>th</sub> CFB-boiler and shown to be viable on full industrial scale in two CFB-boilers at 115 and 75 MW<sub>th</sub>, fired with waste wood and MSW respectively. Several oxygen carrier configurations, including sand and rock ilmenite and a manganese ore were used on semi-industrial scale. Further investigations on full industrial scale were carried out with rock ilmenite.

Bed material extractions during the experimental campaigns allowed for a comprehensive evaluation of the oxygen carrier. The focus of this work was to study the biomass interaction as well as the chemical and mechanical development of ilmenite used during OCAC. Ilmenite undergoes several changes when used as bed material, where iron migrates to locations with high oxygen potential simultaneously as ash layers are built up on the particles. The buildup of ash layers is not directly inhibitory to the activity of the material. However, thick layers occur after long operational time and may cause a decrease in oxygen transfer capacity. The layers may prolong the lifetime of particles as they become more resistant to mechanical stress. If ash accumulates in the system but is not absorbed by the oxygen carrier, hollow ash particles can form.

Full scale OCAC operation with waste fuels has shown to be possible without making changes to the existing equipment. The full scaled projects were successful regarding logistics and the boilers were operated with lower surpluses of air. Furthermore, magnetic separation is proposed as a method to ensure sufficient activity in the bed. By these means, not only non-reactive ash compounds but also oxygen carriers that are no

longer active are removed from the system. Lessons are learned from OCAC on possibilities to optimize the utilization of oxygen carriers in industry.

Further research may include continued improvement to the concept, management of ash streams and development of other processes:

- Different configurations of bed materials could be evaluated further. Mixtures of different oxygen carriers could be used to take advantage of their specific qualities. If sufficient oxygen availability is obtained by a lesser amount of oxygen carrier, quartz sand could be used in the mixture to reduce cost.
- Management of ash streams is another topic that demands further investigation. Both the inherent elements in ilmenite and ash elements could possibly be recovered from the ash. For example, if extracted, Ti could either be recycled to the system for further capture of K. If separated from the ash, nutrients like Ca and K could be utilized by being recycled back to nature in a controlled manner.
- Separation of Ti could open for secondary use of the spent bed material, where it could be used for white pigment production. Furthermore, the knowledge gained through this thesis can be used in the continued development of CLC. The aspects concerning the lifetime of oxygen carriers when used with complex fuels on large scale to great extent can be applied to CLC, as the reactions and fluidization properties are similar. Furthermore, this work provides the first experiments where oxygen carriers have been introduced to industrial settings. The acceptance and logistics implemented can be helpful to pave the way for CLC in the future.

# NOMENCLATURE

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GHG	Greenhouse gas
CCS	Carbon capture and storage
MSW	Municipal solid waste
FB	Fluidized bed
BFB	Bubbling fluidized bed
CFB	Circulating fluidized bed
OCAC	Oxygen carrier aided combustion
CLC	Chemical looping combustion
FTIR	Fourier transform infrared spectrometer
SEM-EDS	Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy
XRD	X-ray diffraction
DFB	Dual fluidized bed



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