An analysis of ilmenite particles used as bed material for combustion of biomass in a CFB boiler

Master's Thesis in Sustainable Energy Systems

ANGELICA CORCORAN

Department of Energy Technology
Energy and Environment
Chalmers University of Technology
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Abstract

Combustion of biomass in a fluidized bed boiler with silica sand as bed material is related to problems such as agglomeration of bed material and corrosion of the heat transfer surfaces, where potassium plays a major role in both issues. In the autumn of 2011 the Chalmers 12 MW_{th} CFB boiler was run with 40% of the natural ore ilmenite and 60 % silica sand as bed material.

The purpose of this thesis has been to study the possibilities of ilmenite to be used as bed material, considering physical and chemical changes which the material undergoes. Except for an investigation on how the ash layers are formed, the ilmenite was leached and investigated as a potassium capturer.

A segregation of iron to the surfaces and an enrichment of titanium in the particle core of ilmenite takes place when it is used as bed material in a CFB boiler fired with biomass. The ashes form a double layer on the particle, consisting of $Ca(Ti_{0.7}Fe_{0.3})O_{2.85}$, as well as a diffusion of potassium into the particle core forming KTi_8O_{16}. The potassium and calcium can be leached out 32 and 7 ppm respectively from the used ilmenite.

The diffusion of potassium into the core of ilmenite would be of great value for the chemistry in the boiler if it reduces both agglomeration and corrosion issues. Theoretically potassium could be captured at 5.7 wt% in ilmenite. Since the potassium is only leachable at a small extent, the possibilities to leach out potassium for further capture through regeneration of ilmenite are restricted. However, further studies are needed to appreciate the industrial implementation of ilmenite as a potassium capturer.

Acknowledgements

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Nomenclature

CFB	Circulating Fluidized Boiler
CLC	Chemical-Looping Combustion
SEM	Scanning Electron Microscopy
EDX	Energy Dispersive X-Ray
XRD	X-Ray Diffraction
ICP-OES	Inductive Coupled Plasma Optic Emission Spectroscopy
SP	SP Sveriges Tekniska Forskningsinstitut

Contents

1

Introduction

As the awareness of climate change is continuously growing, the research towards energy sources with lower climate impact is of importance. Biomass is considered to be a CO_2 neutral energy source but has a high fuel variability which makes its thermal conversion problematic. The high variability affects the properties of biomass such as moisture, structural components and inorganic constituents. An extensive overview of biomass including a classification of composition show that the major elements in biomass are, in decreasing order of abundance; C, O, N, Ca, K, Si, Mg, Al, S, Fe, P, Cl and Na [1]. Biomass is often, because of its high variety, commercially burned in a fluidized bed boiler which is a combustion technology with high fuel flexibility [2].

Combustion of biomass in a fluidized bed combustor is associated with problems such as agglomeration and sintering of bed material [2, 3, 4, 5]. If agglomeration becomes extensive it could lead to defluidization of the bed which inevitably results in a shut down of the process. Silica sand, which is the commercially used bed material, needs to be regenerated to large extent in order to avoid agglomeration of sand particles.

The main contributors to agglomeration of bed materials are temperature and the content and composition of ashes. The adhesive tendency of bed particles which causes them to agglomerate increases with increasing temperatures [3] and thereby amounts of melted ashes. Ashes containing potassium are considered to be especially demanding regarding agglomeration of sand because of the eutectic mixture with low melting point they form with silica [4]. High potassium content in the ash may also lead to severe fouling and corrosion of the heat transfer equipment. Corrosion of heat transfer areas will shorten the lifetime of the equipment and is either caused by gas phase species, deposits or a combination of them. In both cases, potassium is one of the driving forces of the processes causing corrosion. [6]

Another challenge for a fluidized bed combustor is the distribution of oxygen. Oxygen should preferably be evenly distributed over the boiler to reach stoichiometric combustion and an even release of heat inside the boiler. In a fluidized bed boiler the oxygen is supplied as air from the lower parts of the combustor. This design promotes combustion in the lower parts and may leave unburned gases at the upper parts of the boiler. The common way to obtain better combustion in a fluidized bed boiler is to increase the flow of secondary air and hence achieve a better mixing throughout the boiler. An excess of air will, however, cause a decrease in boiler efficiency and an uneven heat release in the combustion chamber. Uneven heat release causes temperature gradients in the boiler where melting of ashes can take place at hot spots [7]. Melting of ashes is, as mentioned above, one of the reasons for agglomeration of bed material. As an excess of oxygen in form of air promotes the formation of NO_x, which is related to costs of emissions, there is an additional incentive to find another way to obtain better mixing of oxygen in the combustor.

In order to deal with the challenges associated with the combustion of biomass in a fluidized bed boiler, different types of bed materials have been investigated. Both natural ores such as olivine, ilmenite and alumina sand as well as various synthetic materials have been tested [8, 9, 10]. An attractive bed material should not only have a high oxygen-carrying capacity and low agglomerative tendencies, it should also be environmentally harmless, highly reactive with fuel and found at a low cost. Synthetic materials can be expensive to manufacture and harmful to the environment at disposal while natural ores can be both a cheaper and an easier solution.

An option which has been tested for CLC (Chemical-Looping Combustion) is the use of oxygen-carrying bed materials [11]. Oxygen-carrying bed materials have the ability to absorb and release oxygen during the combustion process and thereby make oxygen accessible throughout the boiler. With oxygen accessible throughout the boiler, temperature gradients could be smoothed out reducing the risk for hot spots. In CLC studies evaluating different types of oxygen-carrying materials, the naturally occurring ore ilmenite ($FeTiO_3$) has shown preferable characteristics considering oxygen-carrying capacity and being comparable to silica sand in bulk price [12].

1.1 Aim and objective

The purpose of this thesis is to study the possibility of ilmenite to be used as bed material for biomass combustion in a CFB boiler. This study will investigate which physical and chemical changes that ilmenite undergoes during combustion when used as bed material. Focus will be put on ash layers of ash components formed on ilmenite during the combustion of biomass, because of the complications associated with layer formation causing agglomeration on silica sand.

The main objectives are to investigate;
1) how ashes interact with ilmenite during combustion of biomass and how these ashes form layers on the surfaces of ilmenite.
2) what leaching possibilities there may be for used ilmenite.

1.2 Scope

The study was initiated by an analysis of electron microscopic images taken of bed samples from a project in 2011, described further in chapter 3, where ilmenite was co-used with silica sand as bed material in Chalmers 12-MW$_{th}$ CFB boiler. The findings from this analysis, which are described in the result section of this report, were used as a basis for determining the experimental part of this thesis.

The experimental part will consider both leaching experiments where the aim is to investigate possibilities to leach potassium from the ilmenite and oven experiments where the layer of used ilmenite is investigated.

2

Theory

The aim of this chapter is to provide the theoretical background necessary for this thesis. The three analytical methods used, SEM with EDX (Scanning Electron Microscopy with Energy Dispersive X-ray analysis), XRD (X-Ray Diffraction) and ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry), will be described in this chapter. The mechanisms behind layer formation on a particle during combustion will be discussed based on the literature available.

2.1 Analytical methods

SEM with EDX was used to reveal the elemental composition of the particle cross-section, XRD was used to understand how the chemical composition of ilmenite changed from fresh ilmenite to used ilmenite and to see the changes that occurred after leaching the material. The last method ICP-OES was used to find which elements were leached out from the used ilmenite.

2.1.1 Scanning Electron Microscopy

SEM is a method where an electron beam is scanned over a surface of a sample placed in a vacuum chamber. The electrons from the beam are accelerated towards the surface. As the beam of electrons meets the surface secondary electrons or backscattered electrons are emitted from the surface. Secondary electrons are low-energy electrons and give information about the topography and surface variation of the sample. Backscattered electrons are high-energy electrons which are emitted when an electron from the beam is elastically scattered at the core of the atom. This collision gives information about the elemental composition of the surface [13]. A detector transforms the emissions into a signal which is used to create an image of the sample. Figure 2.1 illustrates a SEM image of an ilmenite particle which has been used as bed material for 24 hours in Chalmers CFB boiler combusted with biomass.

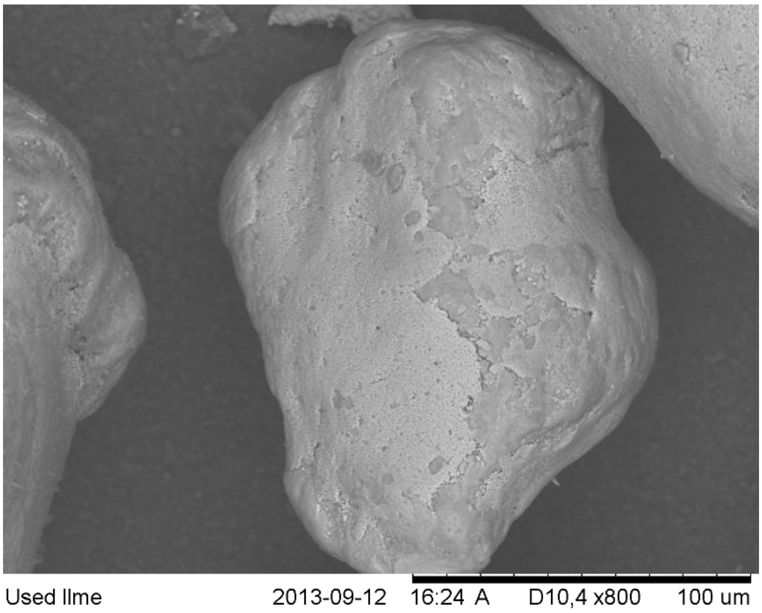


Figure 2.1: SEM image of an ilmenite particle from the combustion chamber

SEM with EDX

By combining the SEM with EDX it is possible to attain the elemental distribution over the sample. When an electron from the beam strikes out an electron from the inner shell of the atom, another electron from the valence shell drops down to fill out the emptied space. As a result of the difference, energy is released as X-ray emission, and since every atom has specific characteristics the energies compensated by the X-ray will reveal which element it is. [14]

When SEM is combined with EDX an image is created for every element present in the sample examined. The element is shown as the colored part of the image while the rest of the picture is dark. Most of the SEM/EDX images in this thesis are black and white where the white presents the element, but there is as well some images with other colors presenting the element observed.

2.1.2 X-Ray Diffraction

XRD is an analysis method for determining the structure of solid crystalline samples. By knowing the exact positions of the atoms, the binding length and the angle between the bindings of the substance can be revealed. Every crystal gives rise to unique diffraction pattern. This diffraction pattern is matched to a reference database and thereby the compounds in the sample are determined. The pattern depends on the size of the unit cell and how the unit cells are packed. The main components in the XRD-set are the X-ray radiation source, the rotation device which holds the sample and the detector. Detected rays are the ones that cause constructive interference, which satisfy Bragg's equation:

$$n\lambda = 2d_{hkl}\sin(\theta) \tag{2.1}$$

where n is the number of atom layers, λ is the wavelength of the used X-rays, d_{hkl} is the distance between the crystal planes and θ is the angle to the plane. The Bragg's condition for constructive interference results in only some angles being strong enough for detection.

The intensity of the detected pattern is depending on how many crystal planes the X-ray can be reflected against and create a constructive interference. In order to irradiate crystal planes on a deeper level the sample, the incoming rays are rotated synchronized with the detector to vary the angle. The result is a diagram which describes at which 2θ angles the sample gives constructive interference. This diagram is manually compared to a reference database to find the ingoing compounds. The results given by the reference database must be considered plausible. [16]

2.1.3 ICP-OES

ICP-OES is an analytical method that is used to determine the ion concentration of a solution. It uses Argon as plasma in which electrons are accelerated and collide with atoms. Some of the atoms are then excited to a higher state and when they later return to the ground state they emit characteristic wavelengths revealing which element it is. [15]

2.2 Layer Formation

Agglomeration of bed material, which is a major cause for defluidization, is initiated by the formation of layers on the bed material particles. Several studies [4, 5, 17] show that potassium compounds are most probably initiating the formation of layers on silica sand when it is used as bed material. The low melting points of potassium compounds, such as salts found in the fuel, allow them to evaporate at an early stage of the combustion. The evaporated salts form an eutectic mixture of potassium silicates with low melting point, which are melted on the surfaces of sand particles. The potassium silicates are sticky and accelerate the process of coating including forming of different compounds on the sticky surfaces.

An explanation of the mechanism of layer formation and an overview of which layers are formed on different types of bed materials is given in order to comprehend how other bed materials can be of advantage compared to silica sand.

According to Zevenhoven-Onderwater et al. [5] there are three ways for a layer to form:

1) The bed particle is considered to be inert and only acts as a carrier of the layer. In this case the layer grows outward of the particle and consists of elements originating from the fuel.
2) The formation is caused by a reaction between the bed particle and elements from

the fuel or additives. Here the layer grows inwards into the particle.
3) The layer can also be formed by a combination of (1) and (2).

The example is defined for a case where silica sand is used as bed material but can be applied for any material used. For all cases the authors conclude that the formation is limited by erosion of the layer and/or diffusion possibilities.

Below follows a description of layers found in studies where olivine and ilmenite are used as bed material in different types of fluidizing technologies.

2.2.1 The Iron layer

A migration of iron to the surfaces of particles has been found in bed materials naturally containing iron during CLC and gasification processes. In an attempt to study the catalytic activity of olivine in a fluidized bed biomass gasifier, iron rich areas were found at the surface of the particles after calcination. The migration observed was non-uniform and increased with the calcination time up to 10 hours where the content was as much as 34 wt % in some positions. [18]

In a CLC study by Cuadrat et. al. [11] a migration of iron was not found when ilmenite was calcined for 24 hours. The same batch of an activated ilmenite showed an iron layer and titanium enrichment in the core of the particle. The segregation increased with the number of redox cycles which was noted by the increase of free TiO_2 in the particle core. This is confirmed by Adánez et. al. [19] in a similar study with ilmenite.

The performance of ilmenite as an oxygen carrier was tested in a lab scale fluidized bed reactor by Azis et. al. [20] with addition of two different ash types separately. The iron layer was observed, but only for one of the ash types. The ashes used was Chinese bituminous coal ash and German lignite coal ash. The bituminous ash which contained SiO_2 and an iron oxide caused a segregation of iron to the surfaces of the ilmenite particle. The lignite ash similarly consisted of SiO_2 and an iron oxide, but in addition it also contained CaO, $CaSO_4$, $CaFe_3O_5$, $Ca_3Al_2O_6$ and MgO. The addition of lignite ash did, however, not form an iron layer on the ilmenite [20].

Summarizing, the iron layer has been observed on calcined olivine, activated ilmenite and activated ilmenite with the addition of ashes containing SiO_2 and an iron oxide. The iron layer has, however, not been observed on calcined ilmenite and activated ilmenite with the addition of ashes containing SiO_2, an iron oxide and several calcium compounds.

2.2.2 The Calcium Layer

Two calcium rich layers were found when olivine was used as bed material in a dual fluidized bed steam gasification plant. The inner layer was more homogenous while the outer layer had a composition containing elements usually found in the fly ashes of biomass ash. It was also noticed that the core of the particle showed an increase of potassium. According to Kirnbauer and Hofbauer [8] the layer formation follows the third mechanism described above. The homogeneous layer with a constant thickness is formed by the reaction of components where a layer is grown into the particle. The outer layer, on contrary, is inhomogeneous and does not have constant thickness which implies that it has grown outwards from the particle surface. [8]

A similar double layer of calcium on olivine was observed by Grimm et. al. [17] when studying the agglomeration characteristics of olivine. They also found the inner layer to be more homogenous while the outer layer was granular and similar to the fly ash. [17]

A notation worth mentioning during this literature study is that no iron layer has formed in combination with the calcium layer described.

3

Experimental

THE EXPERIMENTAL PART of this thesis is mainly constituted by analyses of bed material samples from either the Chalmers biomass-fired 12 MW$_{th}$ CFB boiler and from a lab-scale fluidized reactor. In addition to this, lab-scale experiments were conducted in a horizontal furnace to further investigate the properties of ilmenite in a controlled environment.

3.1 Chalmers 12-MWth CFB boiler

The 12-MW$_{th}$ biomass-fired CFB boiler at Chalmers University of Technology produces hot water for district heating and is operated on full load from november to april. The district heating from the boiler is predominantly used by Chalmers facilities. The combustion chamber has a cross-section of 2.25 m^2 and a height of 13.6 m and is fed with fuel from the top of the furnace via the fuel feed chute, shown as (2) in figure 3.1 [7].

Ordinarily the boiler is operated with 2000 kg silica sand as bed material. In the autumn of 2011 a project was run at Chalmers University of Technology where ilmenite was co-used up to 40% with silica sand as bed material in the boiler. The fuel used in the CFB boiler during this project was woodchips with a composition on dry basis shown in table 3.1 and the ash composition shown in table 3.2. Ilmenite was chosen as bed material because of its oxygen-carrying capacity in combination with its bulk price which is comparable with that of silica sand. In order for ilmenite to be competitive with silica sand the bed material should be able to reduce the extent of regeneration and thus have a long functional

Table 3.1: Composition of woodchips on dry basis

	wt. % dry basis
C	49.7
O	44
H	5.9
N	0.12
S	<0.02
Cl	<0.01
Ash	0.5

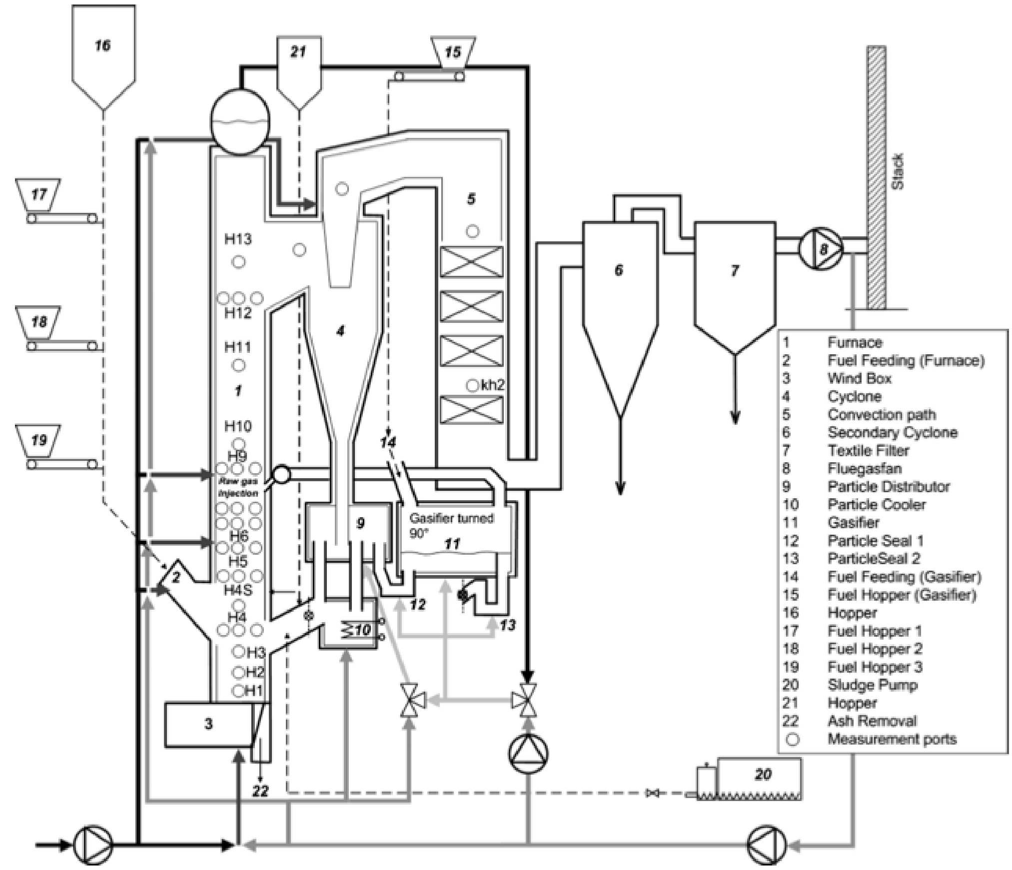


Figure 3.1: The 12-MWth CFB boiler at Chalmers University of Technology. (1) combustion chamber; (2) fuel feed chute; (3) air plenum; (4) secondary air inlet at 2.1m; (5) secondary air inlet at 3.7m; (6) secondary air inlet at 5.4m; (7) secondary air inlet into cyclone exit duct; (8) cyclone exit duct (9) hot primary cyclone; (10) particle return leg; (11) particle seal; (12) particle cooler; (13) measurement hole cr1; (14) measurement hole cr2; (15) measurement hole after convection pass; (16) cold secondary cyclone; (17) bag house filter; lime bin; (18) gas-extraction probe for emission monitoring; (19) flue gas fan; (20) sand bin; (21) lime bin; (22) hydrated lime bin; (23) fuel bunkers; (25) air fan; (26) flue gas recirculation fan; (27) IACM instrument; (28) ammonium sulfate injection point. [7]

lifetime. The absolute functional lifetime of ilmenite has not yet been fully decided, but from studies it was shown that it is a competitive alternative to silica sand [12]. The batch of ilmenite that was used in the experiments run in the project 2011 was supplied by Titania A/S (Norway). It was a naturally occurring ore with the composition; 40% ilmenite, 37% plagiclase, 8.6% ortopyroxene, 6.5% klinopyroxene, 4.2% biotite and some other minor phases [7].

The project aimed to investigate the advantages of using ilmenite as oxygen carrying bed material such as low emissions of unburned species in the exhaust gases and an even distribution of unburned species throughout the combustion furnace. It was concluded that the distribution of oxygen over the combustion furnace was improved. Not only was the temperature profile over the cyclone (6) in figure 3.1 reduced which implies a reduction of combustion in the cyclone, the concentration of both CO and NO had decreased in the exhaust gases. [7]

Ilmenite was added to the boiler at two occasions during the experiment. At the first addition the ilmenite represented 20% of the total bed material and at the second batch, which was added 24 hours after the first, the ilmenite was enhanced to 40%. There was a regeneration of silica sand to avoid agglomeration between the additions of ilmenite. The regeneration included both the supply of fresh silica sand and the removal of used bed material. [7]

Table 3.2: Ash composition of woodchips

	wt. % in ash obtained at 550 °C
Ca	26.0
K	12.3
Mg	3.69
Si	2.05
P	2.01
Na	0.79
Mn	0.78
Al	0.44
Fe	0.34
Ba	0.23
Ti	0.04

3.1.1 Extractions of bed material from the boiler

Four samples of bed material were extracted from the bed of the boiler at different times for the purpose of this thesis. The first sample was extracted after 1 hour. The second was extracted after 24 hours and before the second addition of ilmenite and the third extraction was 48 hours after the startup. The sample from 48 hours therefore contains a mixture of ilmenite that has been in the boiler for 48 and 24 hours. The last sample was extracted after 72 hours. The ilmenite used as bed material showed magnetic properties and was therefore separated from the ashes and the rest of the bed material with simple magnets [7].

A sample of fresh ilmenite together with the three first extractions; 1, 48 and 72 hours were sent to SP Sveriges Tekniska Forskningsinstitut for analyses. Fly ash samples extracted after 1, 24, 28 and 48 hours from the secondary cyclone, (6) in figure 3.1, were also sent to SP for analyses.

3.2 Sample preparation for analysis

Samples analyzed with SEM were mounted in epoxy resin and left to harden for approximately 24 hours. The mounted particles were grinded in order to obtain a flat surface cross-section. This procedure was conducted during a continuous supply of ethanol in order to avoid a temperature rise from the friction. The prepared samples were then examined by SEM (FEI Quanta 200 Field Emission Gun ESEM) with EDX (Oxford Inca EDX system for chemical analysis) in order to observe physical and chemical changes that have occurred.

In order to determine the compositional changes of the ilmenite exposed to the combustion chamber, both fresh ilmenite and used ilmenite were analysed by XRD (Siemens D5000, Grazing indidence with energy selective detector). The samples were grinded and placed on the sample holder. They were then pressed down vertically with a glass plate to assure a flat surface. The diffractometer was collected of angles 20 - 80 ° and the spectra obtained was compared to a reference database.

3.3 Lab-scale experiments

With the ambition to understand the formation of the double layer observed in the ilmenite used as bed material in the CFB boiler, a lab-scale experiment was conducted. The experiment was reconstructed in a lab-scaled fluidized bed reactor.

In this thesis experiments have been performed in a lab-furnace to understand the layer formation of ilmenite in the presence of Ca containing compounds. However, samples were also supplied from experiments performed in a lab-scaled fluidized reactor by co-workers at the department of Chemical and Biological Engineering at Chalmers University of Technology.

3.3.1 Lab-scale fluidized bed reactor

Bed material samples were tested for oxygen transport capacity and catalytic activity in a batch fluidized bed quartz glass reactor. The reactor had an inner diameter of 22 mm and a height of 870 mm. The even gas distribution was assured by a porous quartz plate at the bottom of the reactor on which the bed material is placed.

The experimental setup can be seen in figure 3.2. The fluidizing gases which consisted of 10 volume percent oxygen (O_2) in nitrogen (N_2) were applied from the bottom of the reactor and maintained under constant flow at 900 ml/min. The gas flow was controlled by automatic valves and mass flow regulators which can be seen in figure 3.2. The experiment was conducted during redox conditions, a reduction period and an oxidation period, where the reactor was flushed with inert nitrogen between the periods.

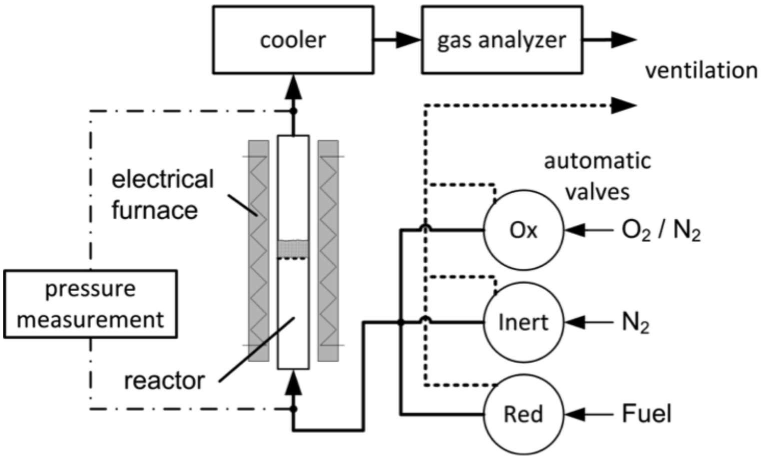


Figure 3.2: Setup of batch fluidized bed quartz glass reactor

Addition of CaO

Four grams of ilmenite and six grams of silica sand were mixed with calcium oxide and placed on the porous plate of the batch fluidized reactor. The reactor was heated to 850 °C and then staged to 950 °C under fluidizing and redox conditions.

Addition of K_2CO_3

Four grams of ilmenite and six grams of silica sand were soaked with K_2CO_3 and placed on the porous plate of the batch reactor. The reactor was then heated to 700 °C under fluidizing and redox conditions.

3.3.2 Lab-scale oven

Calcium carbonate (10 wt%) was mixed mechanically with fresh ilmenite (90 wt%). The mixture was heated to 840 °C in a cylinder oven. Two sets of samples were prepared, the first was treated for one hour and the second for 24 hours. For both samples a reference case wasused where only fresh ilmenite was heated to the same temperature and time. Only two samples were placed in the middle of the oven in order to avoid too large temperature differences due to stretched out locations of the samples.

3.4 Leaching experiments

Since potassium is described as the major cause to agglomeration considering silica sand, it is of great interest to investigate how it relates to ilmenite as bed material. A leaching experiment was conducted in order to evaluate the possibility or lack of possibility to extract eventual potassium from the used ilmenite. In a first experiment deionized water was used as the leaching agent to explore if leaching would even be possible. All samples (1h, 24h, 48h and 72h) were leached for 72 hours. Fresh ilmenite was leached as a reference sample. Two replicas were prepared for each sample, hence there was a total of 12 samples leached. All samples of ilmenite were prepared as 1 gram sample was dissolved in 10 grams of deionized water in a plastic container. After preparation all samples were placed on a shaking table for 72 hours. After the leaching test was completed the leachat was extracted and analyzed with ICP-OES. The rest of the sample was dried and analyzed by XRD.

4

Results

The chapter of results will be divided into three main sections. The first section will consider the change in elemental composition of the ilmenite used as bed material in Chalmers CFB boiler in 2011 with the time of sampling. It will also provide a comparison between the ilmenite and sand samples collected. The second section will present the findings from the experiments where the used ilmenite from the same project have been leached in deionized water. The third section will consider the results from several lab scale experiments investigating the elemental composition of used ilmenite in different experimental set-ups.

4.1 Elemental composition

A sample of fresh ilmenite together with three samples extracted from the boiler after 1h, 48h and 72h were sent to SP for elemental analysis. The total weight composition of the samples were evaluated by SP and part of the results are presented in table 4.1, the

Table 4.1: Weight percentages of elements in bed samples, representing bottom ashes

Element	**Fresh** wt %	**1 h** wt %	**48 h** wt %	**72 h** wt %
Iron, Fe	36	34	29	21
Titanium, Ti	28	27	25	27
Calcium, Ca	0.22	0.92	4.3	5.7
Potassium, K	<0.05	0.87	3.7	4.0
Silica, Si	0.67	2.3	1.3	3.5

Table 4.2: Weight percentages of elements in samples from the secondary cyclone, representing fly ashes

Element	**1 h** wt %	**24 h** wt %	**28 h** wt %	**48 h** wt %
Iron, Fe	5.66	15.6	17.5	13.3
Titanium, Ti	3.09	4.95	10.9	6.65
Potassium, K	4.24	3.10	3.11	4.18
Calcium, Ca	10.8	14.3	7.2	10.9
Silica, Si	24.5	14.0	15.5	17.2

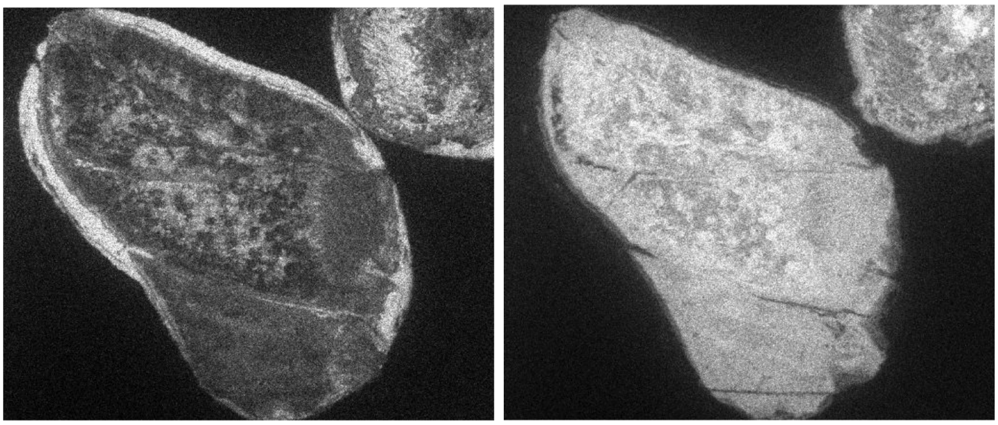
complete results are presented in Appendix A. The weight percentage of iron in ilmenite used as bed material decreases over time while the weight percentage of titanium is kept fairly constant. Both potassium and calcium increases in the ilmenite over time in the boiler.

Except from the bed samples, SP also analyzed four samples extracted from the secondary cyclone, hence representing fly ashes in the boiler. The results are partly presented in table 4.2 and the complete results are presented in Appendix A. In the result table the time is given as time of extraction after ilmenite was added as bed material. It should be noted that the project started up with a boiler full of sand that had been used, during regeneration, for a couple of weeks. Hence, the sand and also the fly ashes may have some unknown history to it. The results show that iron increased from 1 h to 20 hours and longer in the ashes. Titanium also shows a fairly increasing tendency, although, not as distinct as iron. Both potassium and calcium are fluctuating but still fairly constant in the fly ashes.

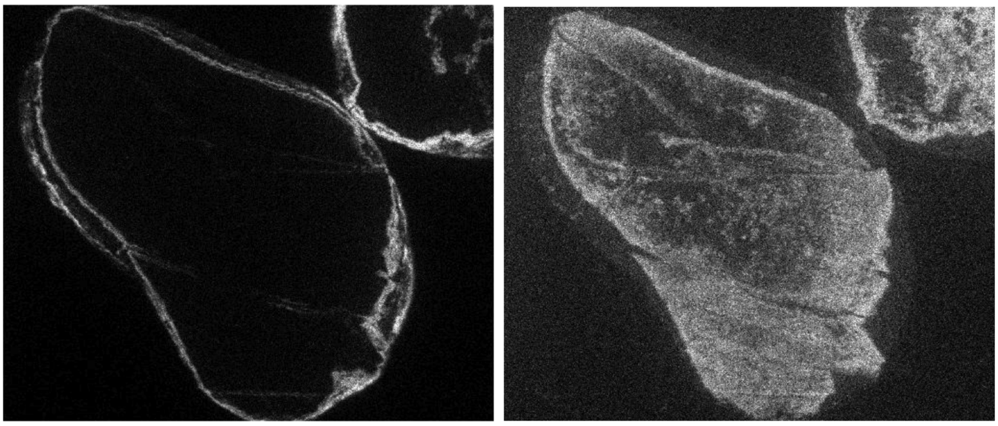
Although a number of elements were found in both fresh and used ilmenite, this thesis has focused on the composition and properties of iron, titanium, potassium and calcium. The characteristics of these four elements are described individually in this section and their dependence on each other will be discussed further in the next chapter.

After one hour in the CFB boiler the samples analyzed with SEM-EDX show a migration of iron to the surfaces of the particle which becomes more prominent after 24 and up to 72 hours which can be seen in figure B.1 in Appendix B. The layer of iron formed, which is thicker at some locations and absent at others, is non-homogeneous. As the segregation of iron takes place, titanium is enriched in the particle core which can be seen in figure B.2. The enrichment is homogeneous over the core, inside the formed iron layer. Both calcium and potassium are not present in the fresh ilmenite but occurs first after 1 hour and is the consistently found in the SEM/EDX images which can be seen in figures B.3 and B.4.

A thin irregular layer of calcium is formed after one hour, on the outside of the titanium but on the inside of the iron. After 24 hours the calcium layer has grown



(a) Fe mapping (b) Ti mapping

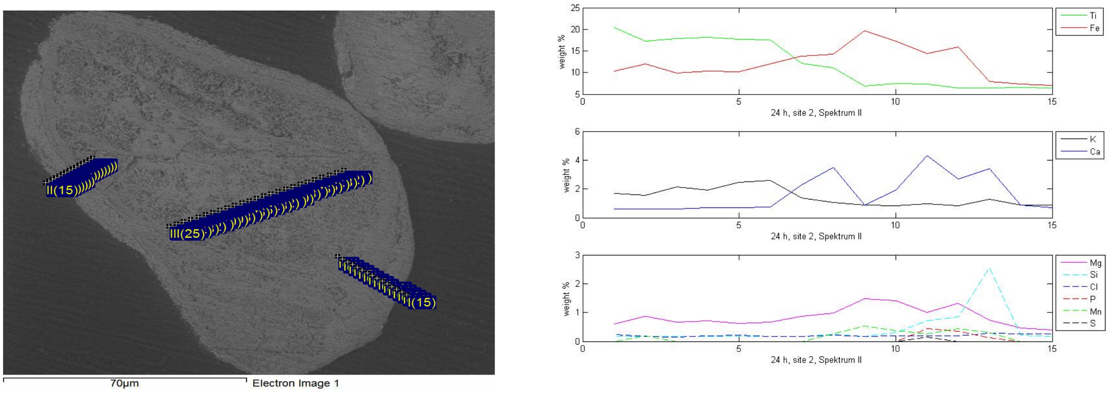


(c) Ca mapping (d) K mapping

Figure 4.1: SEM with EDX mapping of an ilmenite particle

thicker on the inside of the iron layer and in some places another calcium rich layer has formed on the outside of the iron layer. The double layer of calcium is consistent in all samples that have been exposed for 24 hours or more. In similarity with calcium, potassium forms a thin layer on the outside of titanium but on the inside of iron after one hour in the combustor. Their similarities, however, diverge after 24 hours. As calcium forms the double layer, potassium is found in the core of the particle. The images indicate that potassium has spread homogeneously over the parts where titanium is detected.

Figure 4.1 show SEM/EDX mapping of the four elements discussed above after 24 hours in the boiler. The trends explained above can all be seen in figure 4.1; iron is migrated to the surfaces of the ilmenite particle while titanium is enriched in the core. Calcium forms a double layer, with a layer on each side of the iron layer, while potassium is found in the core.



(a) The upper left spectrum is plotted

(b) Plot of spectrum analysis

Figure 4.2: Plot of the spectrum analysis of the layer

4.1.1 Structure of layer on ilmenite

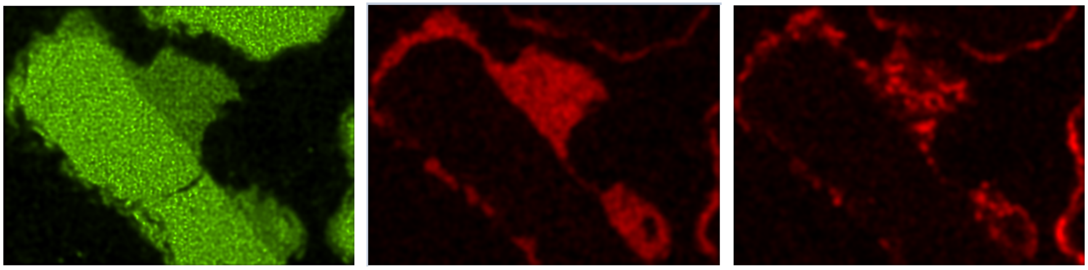
Linescans of the particles cross-sections was done and the results are presented in figure 4.2(a) and the results in weight percentages are plotted in figure 4.2(b) to visualize the structure of the layer formed on ilmenite after 24 hours. The upper subfigure of 4.2(b) shows the relation between iron and titanium. It can be seen that titanium is the dominating element at internal parts of the particle while iron levels increase and titanium levels decrease at the surface. The middle subfigure shows the relations between calcium and potassium. Calcium has two peaks which are placed before and after the peak of iron in the first subfigure. Potassium on the other hand follows the levels of titanium, with higher levels at the inner parts and lower at the layer. In the lower subfigure the trace elements found in the particle are plotted, where most of them seem to have rising levels where the layer has formed.

4.1.2 Comparison between Ilmenite and sand

SEM images with EDX were taken of silica sand that had been used as bed material in Chalmers 12 MW_{th} boiler when fired with biomass. The sand was exposed under similar conditions as the ilmenite in the project 2011.

Samples were taken from the bottom bed at times of exposure in the boiler corresponding to the samples of ilmenite reviewed from the project in 2011. These images were taken to use as a reference case to the ilmenite particles and can be seen in figures C.1, C.2 and C.3 in Appendix C.

The images show that the inner core of the sand particle is entirely dominated by silica. As can be seen in Appendix C both potassium and calcium has started to build a layer on the sand particle after one hour which grows thicker after 24 and 72 hours. In figure 4.3 the images from 24 hours are presented, where the layer which is dominated by potassium and to lesser extent calcium is illustrated.



(a) Silica mapping (b) Potassium mapping (c) Calcium mapping

Figure 4.3: SEM/EDX mapping of a sand particle used as bed material for biomass combustion in Chalmers 12 MW_{th} fluidized bed boiler

4.2 Leaching experiments

The fresh, used and leached ilmenite were analysed by XRD and the results are presented in table 4.3 in order to compare how the chemical composition of the samples changed with time. The fresh ilmenite contained two different compounds of iron titanium oxides as well as some impurities which can be expected from a mineral ore.

Table 4.3: XRD results of fresh, used and leached ilmenite

Fresh Ilmenite	**Used Ilmenite**	**Leached Ilmenite**
$FeTiO_3$	KTi_8O_{16}	KTi_8O_{16}
$Fe_{1.04}Ti_{0.96}O_3$	$Ca(Ti_{0.7}Fe_{0.3})O_{2.85}$	$Ca(Ti_{0.7}Fe_{0.3})O_{2.85}$
	$Fe(Fe_{1.04}Ti_{0.67})O_4$	$Fe(Fe_{1.04}Ti_{0.67})O_4$

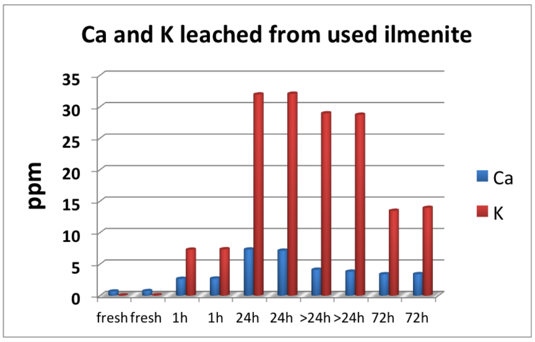
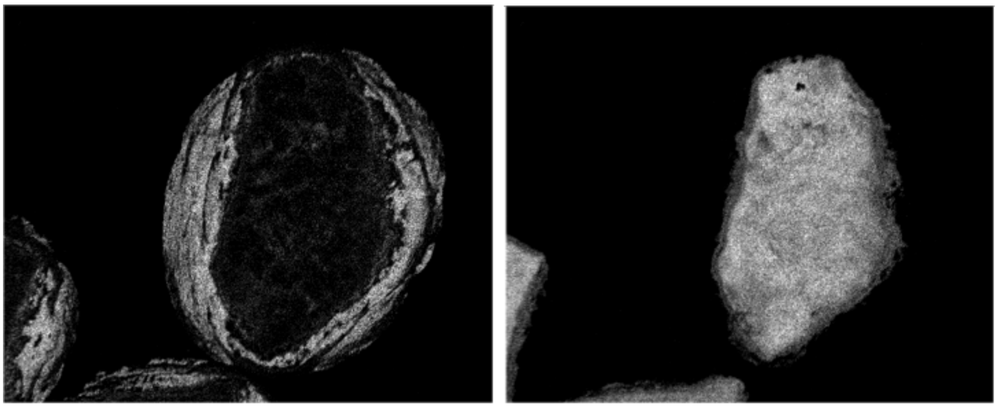


Figure 4.4: Leached elements in ppm

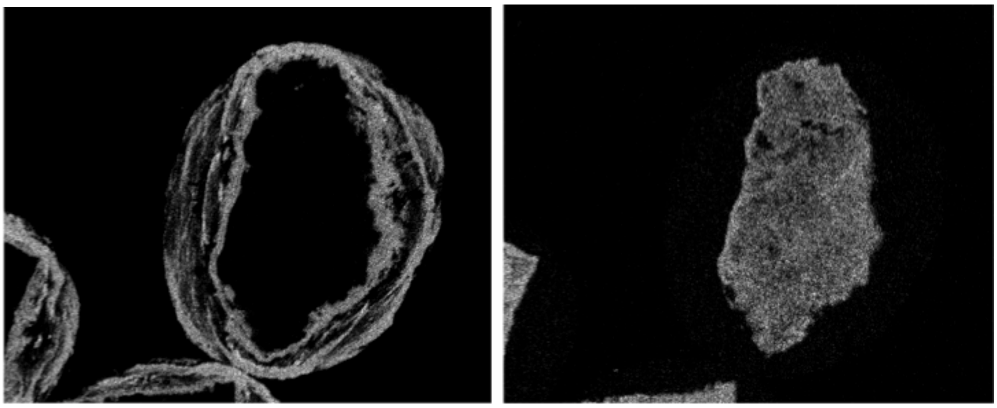
The used ilmenite, which in table 4.3 represents the sample extracted after 72 hours in the boiler, also contained iron titanium oxide. In addition, potassium titanium oxide, KTi_8O_{16} and a calcium iron titanium oxide, $Ca(Ti_{0.7}Fe_{0.3})O_{2.5}$ were also found in this sample. In studies where TiO_2 was added to biomass during combustion under fixed beds, the vaporization of potassium was reduced and the compound KTi_8O_{16} was formed [21].

The leached ilmenite in table 4.3 corresponds to the used ilmenite extracted from the boiler after 72 hours after it was leached for 72 hours. The leached ilmenite revealed the same composition as the used ilmenite in the analysis. In the study all the extracted samples were analyzed by XRD before and after leaching them. The samples presented in table 4.3 are representative for all results.

The results from the ICP-OES analysis of the leachate is presented in figure 4.4. It shows that highest amount of potassium, which was found in the leachate from the samples that had been in the boiler for 24 hours, is 32 ppm. The highest calcium content is found in the same samples as 7 ppm. Except from these results, small amounts of sulphur were also found in the leachate. The levels of sulphur found in the leachate were higher than those of calcium but lower than those of potassium.



(a) Fe mapping (b) Ti mapping



(c) Ca mapping (d) K mapping

Figure 4.5: SEM with EDX mapping of a leached ilmenite particle

Samples from 24 hours and 72 hours were analyzed with SEM/EDX in order to investigate how the elemental composition of the particle changed after being leached where the latter, representative for both, is presented in figure 4.5. The mapping of Fe, Ti, Ca and K in figure 4.5 compared to the mapping before leaching in figure 4.1 show that the elemental composition of used ilmenite has not changed during the leaching experiment. Potassium is enriched in the core of the particle at the same sites as titanium and there is a double layer of calcium on each side of the iron layer.

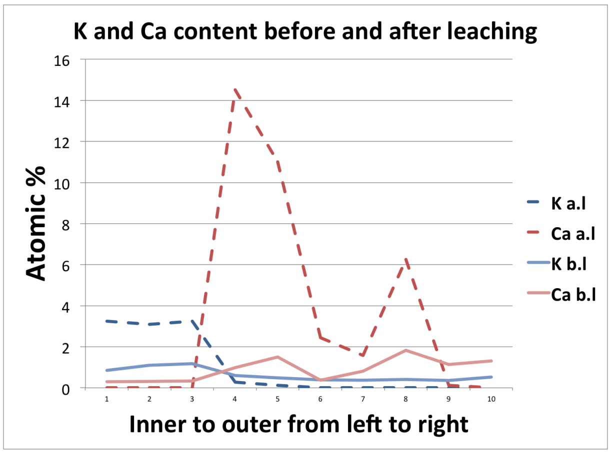
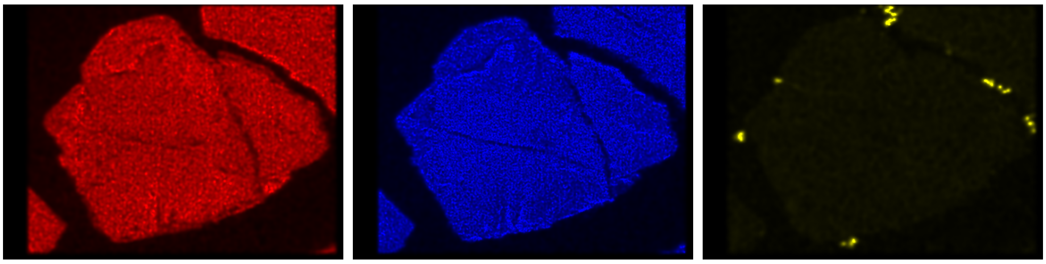


Figure 4.6: Content of K and Ca in atomic % on the surface of an ilmenite particle. Solid and dashed lines represent before and after leaching of ilmenite respectively.

The share of K and Ca, in atomic percentages, are plotted in figure 4.6. The figure shows a linescanned layer of ilmenite plotted before and after being leached. From left to right in figure 4.6 is the inner core moving out through the layer to the surface of the ilmenite particle. The levels of potassium are higher at the inner parts of the particle before and after leaching. The levels are, however, considerably higher after leaching, rising from about 1 to 3 atomic %. Similarly, the two calcium peaks in each sample are found at the edge of the particle where the leached particle has peaks almost ten times higher than the sample not leached. Another observation is that calcium has gone from a small share at the inner parts of the particle to no detection at all. Potassium has on the other hand gone from a small share at the surface, where the layer is, to no detection at all. It should be noted that it is not the exact same particle examined before and after leaching, and variations between particles remains as an uncertainty.

4.3 Investigation: Elemental composition

This section presents results from three lab scale experiments. In the first lab scale experiment, and the only one conducted within this thesis, fresh ilmenite was mixed



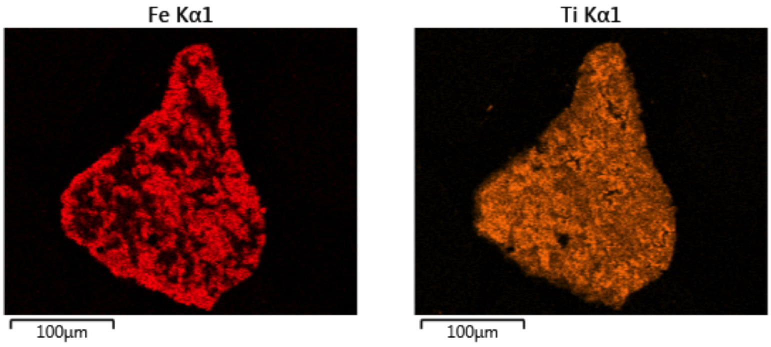
(a) Iron (b) Titanium (c) Calcium

Figure 4.7: SEM/EDX mapping of an ilmenite particle heated to 840 °C with $CaCO_3$

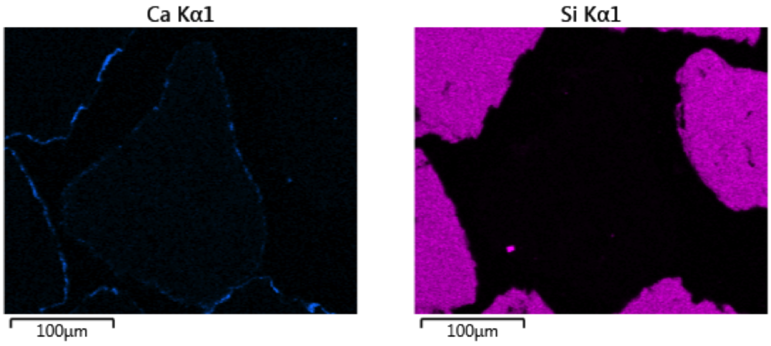
with $CaCO_3$ and heated to 840 °C in a horisontal furnace for 24 hours.

Figure 4.7 shows the mapping of Fe, Ti and Ca over an ilmenite particle from the experiment where ilmenite was heated with $CaCO_3$. There was no indication of reaction between $CaCO_3$ and ilmenite in any cases by the SEM-EDX images of the samples, as can be seen in figure 4.7(c). A slight segregation of both iron and titanium can be seen on some parts of the surface in figure 4.7(a) and 4.7(b).

The SEM/EDX images in figure 4.8 show Fe, Ti, Ca and Si mapping over an ilmenite particle surrounded by sand particles run through a lab scale fluidized bed reactor with CaO between 850 and 950 °C at redox conditions for 22 cycles. Figures 4.8(a) and 4.8(b) does neither show an indication of iron segregation to the surfaces nor enrichment of titanium in the core of the ilmenite particle. Figure 4.8(c), which is the mapping of calcium, barely shows any calcium around the ilmenite particle at all. The lightest parts illustrating calcium are found as a thin non-homogeneous layer on the sand particles surrounding the ilmenite particle.



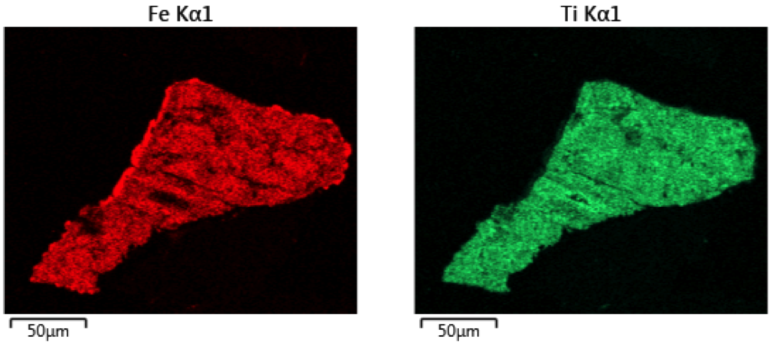
(a) Fe mapping (b) Ti mapping



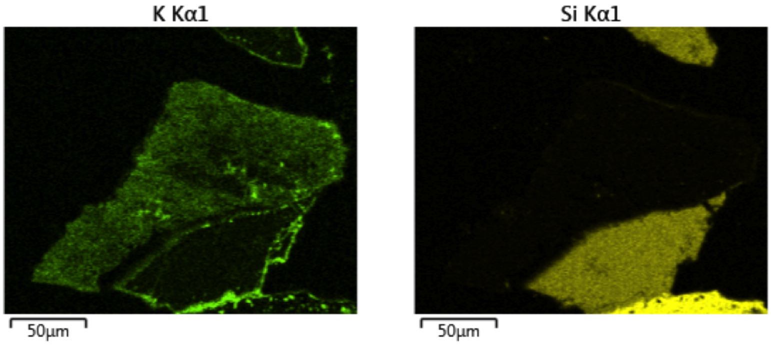
(c) Ca mapping (d) Si mapping

Figure 4.8: SEM/EDX mapping of an ilmenite particle from the lab scale fluidized bed reactor, heated with sand and CaO

Figure 4.9 illustrates the Fe, Ti, K and Si mapping of an ilmenite particle surrounded by sand particles. The particles are sampled from a batch where ilmenite and sand have been soaked in K_2CO_3 and run through a lab scale fluidized bed reactor. The mapping of iron shows a segregation of iron to the upper and left surfaces of the ilmenite particle. The ilmenite particle is surrounded by sand particles which can be seen in figure 4.9(d) where silica is mapped. The potassium is enriched in the core of the ilmenite particle while it forms a layer on the surfaces of the sand particles.



(a) Fe mapping (b) Ti mapping



(c) K mapping (d) Si mapping

Figure 4.9: SEM/EDX mapping of an ilmenite particle from the lab scale fluidized bed reactor, heated with sand and K_2CO_3

4.4 Potassium Capturer

Potassium is a problematic element in a CFB boiler both considering the role it plays in agglomeration and contributing to the corrosion of the heat transfer equipment. Potassium has shown to diffuse into the core of ilmenite and form the compound KTi_8O_{16}. Because of the issues related to K it is of interest to investigate the quantity possible to capture in the core of ilmenite and the time before the bed material reaches saturation.

Table 4.4: Experimental and theoretical values of how much K can be captured in ilmenite and how many hours the boiler could run with 2000 kg ilmenite as bed material before it reaches saturation.

	Theoretical	Experimental		
$K_{captured}$ (wt%)	5.7	1.0	2.0	2.5
$K_{captured}$ (kg)	64.4	20.0	40.0	50.0
$t_{saturation}$ (h)	52.4	16.3	32.5	40.6

In order to evaluate how much potassium could be captured, the saturation of ilmenite must be known. Except from a theoretical value, calculated in Appendix D, three experimental values based on linescans of ilmenite particles used as bed material for 24, 48 and 72 hours were used. The theoretical and experimental values express how much potassium can be bound in the core of ilmenite in weight percentages. Based on these values, the amount of K captured in ilmenite was calculated and is presented in table 4.4.

The amount of potassium supplied to the boiler was calculated in Appendix D to 1.23 kg_K/h. The calculations are based on the composition of the woodchips used as fuel, shown in tables 3.1 and 3.2, and the assumption that 2000kg fuel is supplied to the boiler each hour. Knowing the amount of K supplied to the boiler and the saturation of ilmenite, it is able to determine the number of hours until all the bed material has been saturated with K.

The results in table 4.4 show that it is theoretically possible to capture 64.4 kg of potassium in 2000 kg of ilmenite while the experimental values only capture between 20 and 50 kg potassium. Based on the experimental values it would take between approximately 16 and 40 hours before the bed material reaches a saturation of potassium while it theoretically would take 52 hours.

5

Discussion

The study of ilmenite particles, co-used as bed material in the 12-MW$_{th}$ CFB boiler fired with biomass showed a segregation of iron to the surfaces. The migration caused a formation of an iron layer and an enrichment of titanium in the core of the particle, two phenomena which have both been confirmed by literature [11, 19]. The study also revealed that ilmenite formed two calcium rich layers, one on the inside and one on the outside of the iron layer, and an enrichment of potassium in the particle core at the same sites as titanium. The literature reviewed in this thesis has shown that the segregation of iron is commonly known for activated ilmenite in CLC studies. An iron layer has in addition been found when an alternative bed material, olivine, was calcined. The literature also showed a calcium rich double layer on olivine used as bed material during combustion with biomass. These two layer types, the iron and double calcium layer, have in the covered literature not been found in combination, as they are in this study.

The results of SEM/EDX images in this study show that a segregation of iron is formed after one hour in the boiler where calcium and potassium have formed a layer on the inside of the iron layer. After 24 hours the iron layer becomes more prominent while the calcium has formed the double layer on each side of the iron as described above and the potassium has diffused in to the core of the ilmenite particle. The enrichment of titanium in the core also becomes prominent after 24 hours. Because of the lack of literature references on the calcium rich double layer and the enrichment of potassium in the particle core, they became the drivers of the experiments conducted in this thesis.

The results from the XRD analysis showed that KTi_8O_{16} as well as $Ca(Ti_{0.7}Fe_{0.3})O_{2.85}$ had formed after the ilmenite was used as bed material. As these were the only compounds found in the XRD analysis except for iron titanium oxides, which are the main constituents of fresh ilmenite, it is probable that KTi_8O_{16} is the compound dominating the core while $Ca(Ti_{0.7}Fe_{0.3})O_{2.85}$ is the dominating compound in the calcium rich layer.

The composition of the used ilmenite did not change by leaching the samples in deionized water for three days. Both potassium and calcium were leached to a very small extent, presented in figure 4.4, being 32 ppm and 7 ppm respectively at the most. A spectrum analysis over the layer and inner part of an ilmenite particle was plotted in figure 4.6. This plot shows that the atomic % of K and Ca changed dramatically after the leaching experiment. K is nonexistent in the layer after the leaching where it was, even though with lower levels than in the core, detected before the leaching. Ca on the other hand, increased its levels in the layer tenfold while it becomes nonexistent in the core after leaching. A reason for this trend may be that K is strongly bound to the compound it forms in the particle core, KTi_8O_{16}, and the K leached may be the K that has been situated in the layer. Similarly, Ca may be strongly bound to the compound it forms in the layer, $Ca(Ti_{0.7}Fe_{0.3})O_{2.85}$, and more easily leached from the core. The very high increase in Ca levels in the layer may be because other trace elements have been leached out from the layer, at small but contributing amounts.

The lab scale experiments with ilmenite and Ca compounds agree with the literature in the sense that neither an iron layer or a calcium layer is formed under either atmospheric or redox conditions. K acts in the same way in the lab scale test as it does in the CFB boiler fired with biomass containing potassium. According to the results of this thesis, potassium diffuses into the ilmenite particle when being the only additive as potassium carbonate, and the iron in the ilmenite is migrated to the surfaces during the process which can be seen in figure 4.9. These results may imply that calcium, when being the only additive, could be counteractive to the formation of an iron layer. Since both the iron layer and the double calcium layer as well as the diffusion of potassium into the particle core are formed when biomass is burned in the CFB boiler, there might be an interaction between K and Ca that causes this phenomena. This is however, difficult to conclude since the biomass used contains numerous elements that could all be interactive in the process.

The diffusion of potassium into the particle core might have a great value for the use of ilmenite as bed material in a CFB boiler. As the main reason for agglomeration of sand is the formation of sticky potassium silicates on the sufaces, agglomeration may be avoided by using ilmenite as bed material instead. When operating the Chalmers 12-MW_{th} CFB boiler with 40 % ilmenite and 60 % sand, less accumulation of deposits on the heat transfer surfaces were observed in comparison to 100 % sand [7]. This implies that ilmenite as bed material might not only cause less agglomeration, but also less corrosion in the boiler.

As potassium was found to diffuse into the ilmenite particle, the question if ilmenite could be used as a potassium capturer was raised. Calculations show that theoretically 64.4 kg of potassium could be stored in 2000 kg of ilmenite. These calculations assume that all titanium in 2000 kg of ilmenite form the compound KTi_8O_{16}. The experimental cases show a lower capturing capacity of potassium in 2000 kg of ilmenite, varying between 20 and 50 kg. The experimental cases do not consider the share of titanium in the bed material but are strictly based on the weight percentages of potassium found in ilmenite used as bed material in the Chalmers 12-MW_{th} CFB boiler. Neither the theoretical nor the experimental cases consider that parts of the ilmenite supplied as bed material could contain any impurities.

Based on the theoretical case, the boiler could run with 2000 kg of ilmenite as bed material for 52.4 hours before it reaches saturation of potassium. Based on the experimental cases, the boiler could not run as long before reaching saturation. If saturation is reached at 1 wt% of potassium in ilmenite, the boiler could only run for 16.3 hours before it is reached while it could run for 40.6 hours if the saturation is reached at 2.5 wt%.

Independent of how much K is possible to store in ilmenite as the compound KTi_8O_{16}, the leaching results of this thesis show that K in this is not leachable with deionized water from the core. It is therefore, once ilmenite is saturated with K, not possible to leach the ilmenite for regeneration and further capturing of K.

However, to obtain an accurate picture of how much potassium could be stored in ilmenite and how long the boiler could run before the bed material is saturated with potassium, further studies need to be done. These studies need to determine how much potassium is supplied to the boiler and how much is found in the bed material as well as in both bottom and fly ashes. They would also need to investigate further in the capture capacity of ilmenite, determining the amount of potassium that could be captured before the ilmenite is saturated.

6

Conclusions

When ilmenite is co-used with silica sand as bed material in a biomass fired CFB boiler some conclusions can be drawn about the elemental composition of an ilmenite particle exposed between 24 and 72 hours.

- A segregation takes place where iron is migrated to the surfaces of the particle and titanium is enriched in the particle core.
- Two calcium layers are formed, one on the inside of the iron layer and one on the outside. The calcium layer consists of the calcium iron titan oxide, $Ca(Ti_{0.7}Fe_{0.3})O_{2.85}$.
- Potassium diffuses into the particle homogeneously, forming the potassium titanate oxide, KTi_8O_{16}. This phenomenon makes ilmenite an attractive bed material with the potential to capture potassium during the combustion process.
- Although both potassium and calcium are leachable by 32 and 7 ppm respectively at the most, the composition of used ilmenite does not change by leaching it in deionized water. Thus, as potassium is only leached out at very low levels it is not possible to leach the ilmenite, once saturated with potassium, and regenerate for further capture.
- The diffusion of potassium into the particle core of ilmenite may be of great value for the use of ilmenite as bed material in a fluidized bed boiler. It could reduce both the agglomeration of bed material and corrosion of the heat transfer surfaces.
- Basic calculations show that between 20 and 64 kg of potassium could be stored in 2000 kg of ilmenite. The boiler could run with 2000 kg of ilmenite between about 16 and 52 hours before reaching saturation if woodchips are used as fuel and are supplied at 2000 kg per hour. In order to obtain an accurate picture of how ilmenite could be used as a potassium capturer in a CFB boiler further studies need to be conducted investigating both fuel, bed material and ashes extensively.

As results of separate experiments revealed:

- When a calcium compound, oxide or carbonate, is used as the only additive to ilmenite, no layer of calcium forms on the surfaces of the ilmenite particle. Nor has a segregation of iron taken place.
- When potassium carbonate is the only additive to the system, potassium diffuses into the ilmenite particle but forms a layer of potassium silicates on the sand particle. In this case the iron segregation does take place.

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A

Elemental analysis

Appendix A shows the complete elemental analysis of bed samples and fly ashes done by SP Sveriges Tekniksa Forsknigsinstitut.

Table A.1: Weight percentages of elements in bed samples, representing bottom ashes

Element	**Fresh** wt %	**1 h** wt %	**48 h** wt %	**72 h** wt %
Iron, Fe	36	34	29	21
Titanium, Ti	28	27	25	27
Calcium, Ca	0.22	0.92	4.3	5.7
Potassium, K	<0.05	0.87	3.7	4.0
Silica, Si	0.67	2.3	1.3	3.5
Manganese, Mn	0.21	0.27	0.55	0.64
Magnesium, Mg	2.0	2.0	2.6	2.3
Aluminium, Al	0.17	0.17	0.13	0.25
Barium, Ba	<0.1	<0.1	0.1	<0.1
Sodium, Na	0.1	0.1	0,2	0.1
Phosphorus, P	<0.05	0.06	0.28	0.37

Table A.2: Elements in bed samples, representing bottom ashes

Element	**Fresh** mg/kg	**1 h** mg/kg	**48 h** mg/kg	**72 h** mg/kg
Copper, Cu	42	70	27	30
Vanadium, V	1200	600	960	810
Crome, Cr	590	370	550	560
Cobalt, Co	520	320	420	400
Nickel, Ni	290	490	210	130
Zinc, Zn	<10	200	900	620
Lead, Pb	<5	9	31	95
Cadmium, Cd	<1	<1	3	1
Molybdenum, Mo	<5	<5	<5	<5
Arsenic, As	<20	<20	<20	<20

Table A.3: Weight percentages of elements in fly ashes

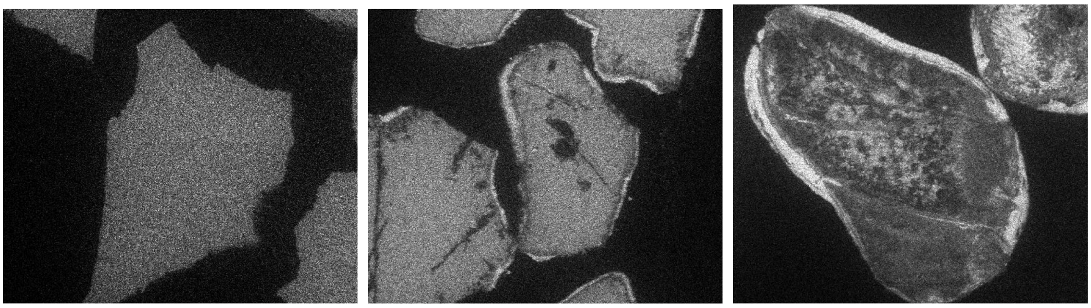
Element	**1 h** wt %	**20 h** wt %	**28 h** wt %	**44 h** wt %
Iron, Fe	5.66	15.6	17.5	13.3
Titanium, Ti	3.09	4.95	10.9	6.65
Potassium, K	4.24	3.10	3.11	4.18
Calcium, Ca	10.8	14.3	7.2	10.9
Silica, Si	24.5	14.0	15.5	17.2
Manganese, Mn	0.66	0.76	0.51	0.69
Magnesium, Mg	1.52	1.98	1.85	1.96
Aluminium, Al	0.95	0.98	1.0	0.89
Barium, Ba	0.11	0.1	0.08	0.11
Sodium, Na	0.4	0.31	0,27	0.39
Phosphorus, P	0.4	0.42	0.27	0.39

B

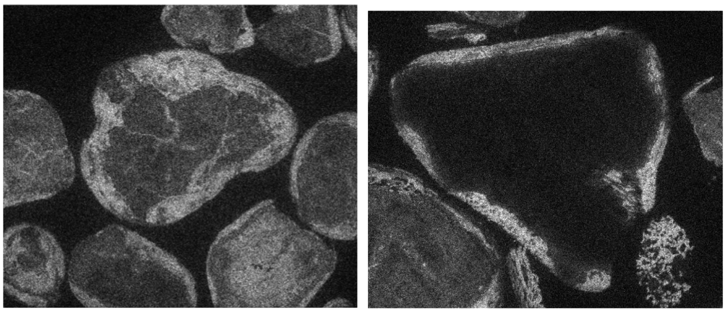
SEM/EDX mapping of Ilmenite

Appendix B shows the mapping of Fe, Ti, Ca and K over ilmenite particles that have been used as bed material for different retention times int the Chalmers 12 MWth CFB boiler combusted with biomass.

B.1 Iron



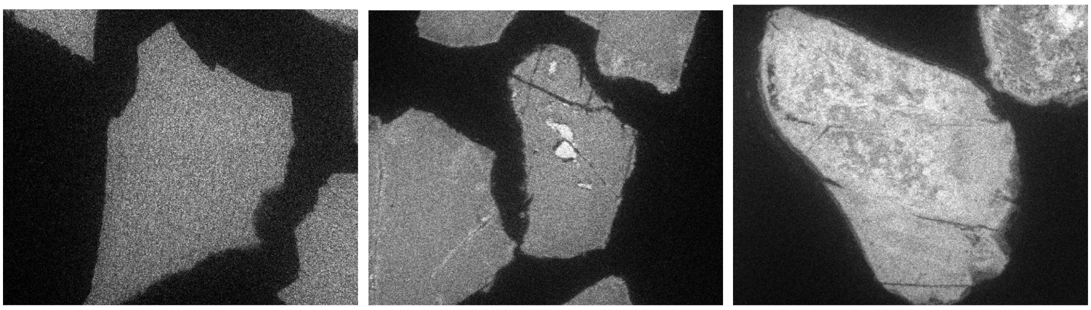
(a) Fresh ilmenite (b) 1 hour (c) 24 hours



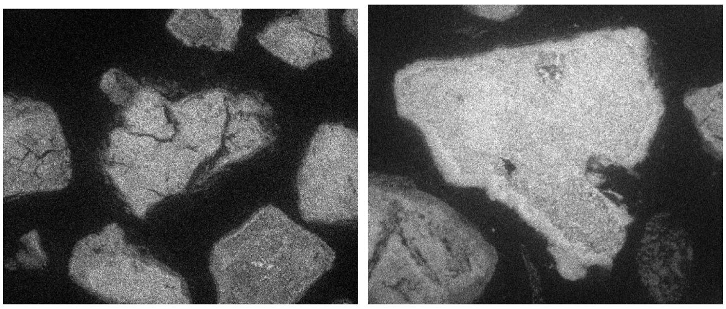
(d) more than 24 hours (e) 72 hours

Figure B.1: SEM with EDX mapping of Iron on an ilmenite particle

B.2 Titanium



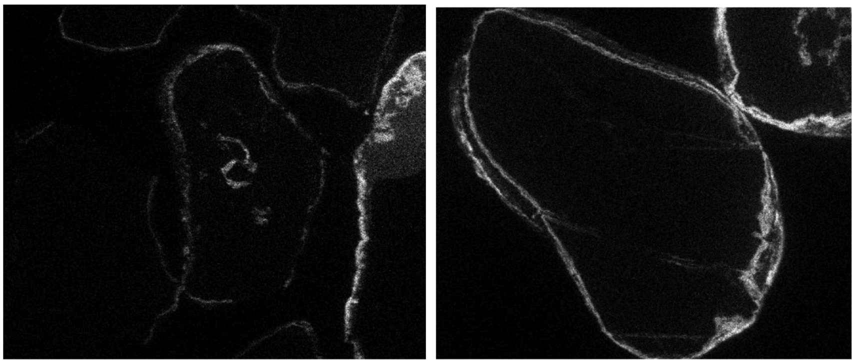
(a) Fresh ilmenite (b) 1 hour (c) 24 hours



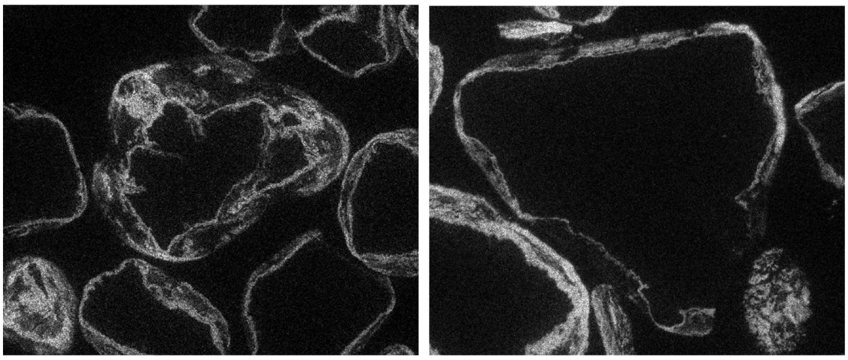
(d) more than 24 hours (e) 72 hours

Figure B.2: SEM with EDX mapping of Titanium on an ilmenite particle

B.3 Calcium



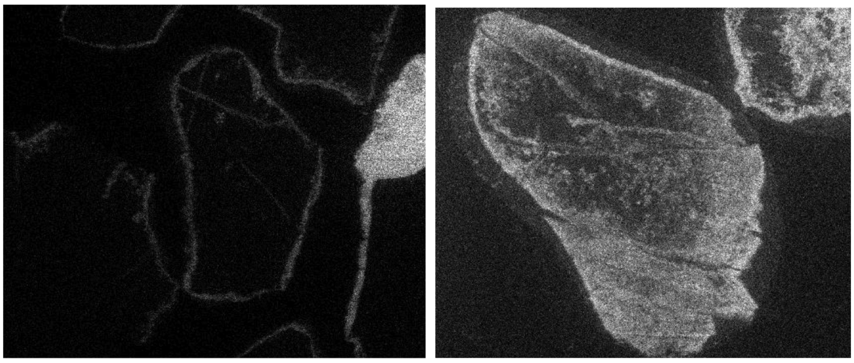
(a) 1 hour (b) 24 hours



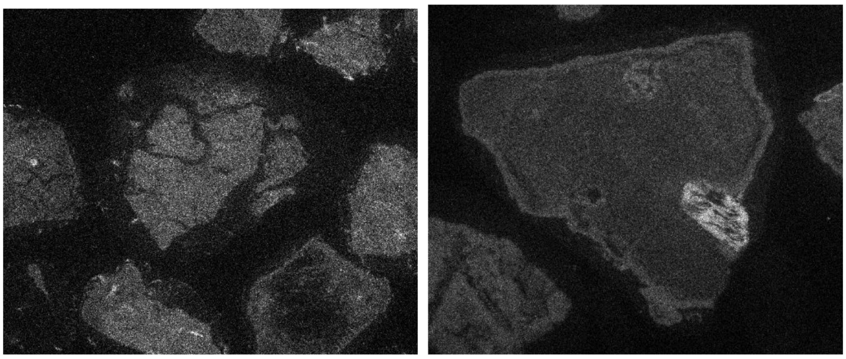
(c) more than 24 hours (d) 72 hours

Figure B.3: SEM with EDX mapping of Calcium on an ilmenite particle

B.4 Potassium



(a) 1 hour (b) 24 hours



(c) more than 24 hours (d) 72 hours

Figure B.4: SEM with EDX mapping of Potassium on an ilmenite particle

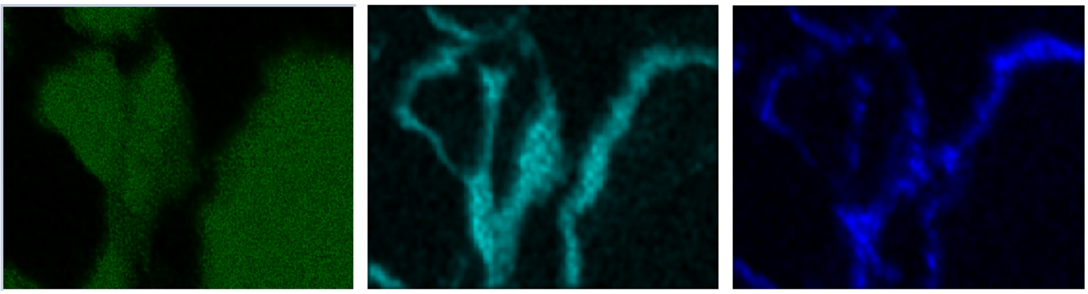
C

SEM/EDX map of Sand

Appendix C show the SEM with EDX mapping of Si, K and Ca on silica sand particles that have been used as bed material at different retention times in the Chalmers 12MWth CFB boiler combusted with biomass.

C.1 1 hour

Map over silica sand which has been used as bed material in the 12 MWth CFB boiler, combusted with wood chip biomass for 1 hour.

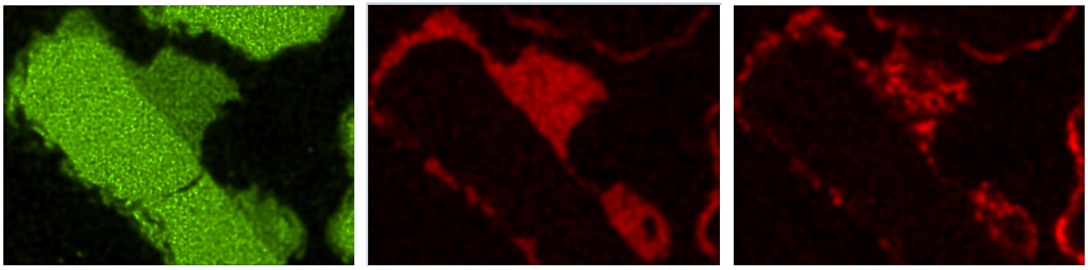


(a) Si mapping (b) K mapping (c) Ca mapping

Figure C.1: SEM with EDX mapping of Si, K and Ca on a sand particle used as bed material for biomass combustion with the retention time 1 hour in the boiler

C.2 24 hours

Map over silica sand which has been used as bed material in the 12 MWth CFB boiler, combusted with wood chip biomass for 24 hours.

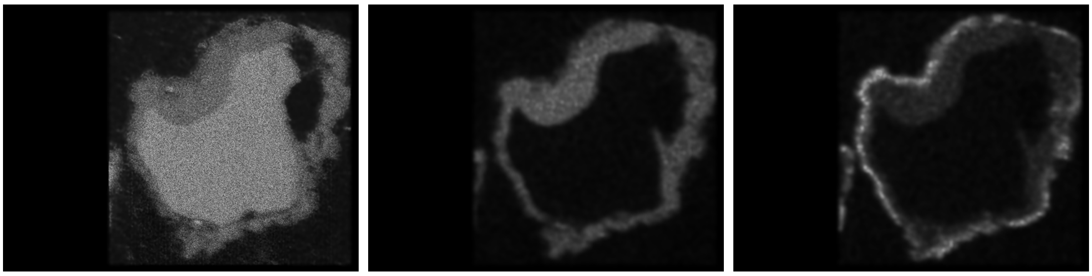


(a) Si mapping (b) K mapping (c) Ca mapping

Figure C.2: SEM with EDX mapping of Si, K and Ca on a sand particle used as bed material for biomass combustion with the retention time 24 hour in the boiler

C.3 72 hours

Map over silica sand which has been used as bed material in the 12 MWth CFB boiler, combusted with wood chip biomass for 72 hours.



(a) Si mapping (b) K mapping (c) Ca mapping

Figure C.3: SEM with EDX mapping of Si, K and Ca on a sand particle used as bed material for biomass combustion with the retention time 72 hour in the boiler

D

Potassium capturer

Appendix D presents calculations that investigate how much potassium is possible to capture in ilmenite and after how long time the ilmenite is saturated with potassium.

D.1 Conditions

The Chalmers 12MW$_{th}$ CFB boiler is fired with biomass. The biomass used is woodchips with the composition presented in tables D.1 and D.2. The amount of fuel, $\dot{m}_{fuel}$, fed to the boiler is 2000kg per hour.

The amount of bed material, m$_{bedmaterial}$ circulating in the boiler is 2000 kg.

Table D.1: Composition of woodchips on dry basis

	wt. % dry basis
C	49.7
O	44
H	5.9
N	0.12
S	<0.02
Cl	<0.01
Ash	0.5

Table D.2: Ash composition of woodchips

	wt. % in ash obtained at 550 °C
Ca	26.0
K	12.3
Mg	3.69
Si	2.05
P	2.01
Na	0.79
Mn	0.78
Al	0.44
Fe	0.34
Ba	0.23
Ti	0.04

	g/mol
$\mathbf{M}_{Fe}$	55.845
$\mathbf{M}_{Ti}$	47.867
$\mathbf{M}_{K}$	39.098
$\mathbf{M}_{O}$	15.999
$\mathbf{M}(FeTiO_3)$	151.710
$\mathbf{M}(KTi_8O_{16})$	678.025

D.2 Theoretical values

Assuming that all Ti in $FeTiO_3$ forms KTi_8O_{16}, it can be calculated how much K can be bound into the bed material and how long time it will take before the bed material is saturated with K.

Amount of Ti in $FeTiO_3$

$$X_{Ti} = \frac{M_{Ti}}{M\ (FeTiO_3)} = \frac{47.867}{151.710} = 0.3155 \tag{D.1}$$

If all bed material consists of ilmenite and the amount of Ti in the bed material would then be

$$m_{Tiinbedmaterial} = X_{Ti} \times m_{bedmaterial} = 0.3155 \times 2000\text{kg} = 631.0329\text{kg} \tag{D.2}$$

The amount of Ti in KTi_8O_{16} is

$$Y_{Ti} = \frac{M_{Ti}}{M\ (KTi_8O_{16}\ )} = \frac{8 \times 47.867}{678.025} = 0.56478 \tag{D.3}$$

The amount of K in KTi_8O_{16} is

$$Y_K = \frac{M_K}{M\ (KTi_8O_{16})} = \frac{39.098}{678.025} = 0.05766 \tag{D.4}$$

The total amount of KTi_8O_{16} formed if all Ti in the bed material is used is

$$m(KTi_8O_{16}) = \frac{m_{Tiinbedmaterial}}{Y_{Ti}} = \frac{631.0329\text{kg}}{0.56478} = 1117.3059\text{kg} \tag{D.5}$$

The total amount of K bound in KTi_8O_{16} is then

$$m_{Kcaptured} = Y_K \times m(KTi_8O_{16}) = 0.05766 \times 1117.3059\text{kg} = 64.4238\text{kg} \tag{D.6}$$

The total amount of potassium that is possible to store in 2000 kg of ilmenite is 64.4 kg. Next step is to calculate how much potassium is supplied to the boiler per hour and how many hours can pass by before the ilmenite is saturated with potassium.

The potassium is intruduced into the boiler through the fuel where it is a composite in the fuel ashes. The fuel ashes supplied to the boiler per hour is

$$\dot{m}_K\ =\ X_{ash} \times\ X_{Kinash} \times \dot{m}_{fuel} = 0.005 \times 0.123 \times 2000\text{kg/h} = 1.23\text{kgK/h} \tag{D.7}$$

The amount of hours the boiler could run with 2000kg of ilmenite as bed material before the material is saturated with potassium would the be:

$$\mathrm{t} = \frac{\mathrm{m}_{Kcaptured}}{\dot{\mathrm{m}}_{fuel}} = \frac{64.4238\mathrm{kg}}{1.23\mathrm{kgK/h}} = 52.37\mathrm{h} \tag{D.8}$$

D.3 Experimental values

The amount of potassium supplied to the boiler is the same as in the theoretical case, namely 1.23 kgK/h.

For the experimental values the amount of potassium that is possible to store in the bed material will be varied based on the measured values obtained from linescans of different samples of ilmenite from the boiler.

Three experimental values are choosen, 1 wt%, 2 wt% and 2.5 % of potassium captured in an ilmenite particle.

$$\mathrm{m}_{Kcap1\%} = 0.01\mathrm{kg}_{Kcaptured}/\mathrm{kg}_{bedmaterial} \times 2000\mathrm{kg}_{bedmaterial} = 20\mathrm{kg}_{Kcaptured} \tag{D.9}$$

$$\mathrm{m}_{Kcap2\%} = 0.02\mathrm{kg}_{Kcaptured}/\mathrm{kg}_{bedmaterial} \times 2000\mathrm{kg}_{bedmaterial} = 40\mathrm{kg}_{Kcaptured} \tag{D.10}$$

$$\mathrm{m}_{Kcap2.5\%} = 0.025\mathrm{kg}_{Kcaptured}/\mathrm{kg}_{bedmaterial} \times 2000\mathrm{kg}_{bedmaterial} = 50\mathrm{kg}_{Kcaptured} \tag{D.11}$$

The time passed before the bed material is saturated will then be

$$\mathrm{t}_{1\%} = \frac{\mathrm{m}_{Kcap1\%}}{\dot{\mathrm{m}}_{fuel}} = \frac{20\mathrm{kg}}{1.23\mathrm{kgK/h}} = 16.26\mathrm{h} \tag{D.12}$$

$$\mathrm{t}_{2\%} = \frac{\mathrm{m}_{Kcap2\%}}{\dot{\mathrm{m}}_{fuel}} = \frac{40\mathrm{kg}}{1.23\mathrm{kgK/h}} = 32.52\mathrm{h} \tag{D.13}$$

$$\mathrm{t}_{2.5\%} = \frac{\mathrm{m}_{Kcap2.5\%}}{\dot{\mathrm{m}}_{fuel}} = \frac{50\mathrm{kg}}{1.23\mathrm{kgK/h}} = 40.65\mathrm{h} \tag{D.14}$$