

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Investigation of Ilmenite from Oxygen Carrier Aided Combustion: Sulfur
Interactions and Recovery of Elements

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Cover: SEM micrograph of calcined ilmenite after several cycles of sulfur release and uptake.

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Abstract

Oxygen- Carrier- Aided Combustion (OCAC) is a promising technology for the combustion of solid heterogeneous fuels such as biomass and waste in fluidized-bed (FB) units. In OCAC the conventional bed material silica sand is replaced by an oxygen carrier (OC). Replacing the bed material with an OC has many advantages. It allows the use of heterogeneous fuels, provides a better oxygen distribution inside the combustion chamber and thereby a more even temperature distribution. In this thesis, ilmenite is used as OC bed material.

Even though ilmenite has shown to be a promising OC, the higher price per kg of material compared to the traditionally silica sand is a drawback. In fluidized bed units, the attrition of the bed particles and therewith the loss of bed particles as fines in fly ashes leads to the need of a continuous addition of new bed material. At the same time, because of the ash interactions, parts of the bed material are also removed as a waste stream. Combined these two effects result in a large consumption of bed material. For the case of ilmenite, the loss of bed material by both mechanisms can result in significantly higher cost, if compared with the scenario where sand is used as bed material. Thus, ways to prolong the residence time of the bed material in the boiler and its value should be investigated.

Biomass which can be used as a renewable source of energy is a fuel which is hard to handle. Notably, its alkali content can cause corrosion of the equipment and increase of maintenance costs. One way to counteract corrosion is through addition of sulfur. The effect of sulfur on ilmenite performance has not been investigated earlier which is one of the main questions of the present work.

Furthermore, to increase the value of the ilmenite after its use in boilers, a modified process for the recovery of elements from the ilmenite waste flows has been examined and adapted to already existing process.

The work presented in this thesis is based on a two-week campaign which was carried out in the 12 MW_{th} Circulating Fluidized Bed (CFB) semi-industrial unit. During the campaign, sulfur addition was tested. A range of methods were utilized to study the sulfur effect on the bed particles, including use of SEM-EDX and ICP to characterize the obtained samples. Further use of a laboratory scale quartz reactor to mimic oxidizing and reducing conditions was also performed.

For waste ilmenite generated during the campaign, digestion of ilmenite samples with sulfuric acid has been carried with the aim of recovering Ti. This work shows that sulfur is captured by the ilmenite particles and is mainly bind to the ash elements and that sulfur can also be released, depending on the redox conditions. This allows for a better management of the composition of used bed material. Furthermore, it was found that the used ilmenite from OCAC can represent an advantage for Ti extraction and recovery due to development of pore and cracks, and due to the natural separation of the Ti and Fe phase occurring under FB combustion conditions.

Keywords: Circulating-Fluidized Bed, Oxygen Carrier Aided Combustion, Ilmenite, Sulfur, Biomass, Ash, Leaching, Sulfate process, Recycling

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List of publications

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- I. Mariane Vigoureux, Pavleta Knutsson and Fredrik Lind
Sulfur Uptake during Oxygen-Carrier -Aided Combustion with Ilmenite
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<https://dx.doi.org/10.1021/acs.energyfuels.0c00420>
- II. Mariane Vigoureux, Tomas Leffler, Pavleta Knutsson and Fredrik Lind
Sulfur Capture and Release by Ilmenite Used as Oxygen Carrier in Biomass
Combustor
Fuel, 2022
<https://doi.org/10.1016/j.fuel.2021.121978>
- III. Mariane Vigoureux, Fredrik Lind, Magnus Rydén and Pavleta Knutsson
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Contribution report:

Paper I: Principal author, responsible for experimental work, data evaluation and writing.

Paper II: Principal author, responsible for parts of experimental work, data evaluation and writing.

Paper III: Principal author, responsible for experimental work, data evaluation and writing.

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CHAPTER 1 – INTRODUCTION

As a result of anthropogenic activities, greenhouses gas emissions have reached an alarmingly high level in the atmosphere [1,2], with consequences of a potentially catastrophic global warming of the planet [3,4]. According to the latest international agreement concerning greenhouse gases (The Paris agreement) a maximum increase in temperature of 2°C is suggested. As, one third of the emissions of CO₂ originate from the heat and power sector [5], improvements must be made in this sector to reach the goal for CO₂ emission.

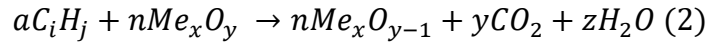
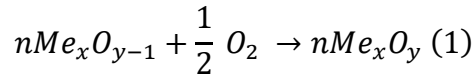
Biomass can be considered as a CO₂ neutral alternative to fossil fuels [6,7]. Biomass fuels are derived mostly from carbon-based materials such as agricultural crop residues and forest products and residues. As a result of the photosynthesis, CO₂ from the atmosphere is captured and transformed into O₂ and carbon-based compounds. Thus, the CO₂ uptake by biomass has the potential to lower the CO₂ levels in the atmosphere [6]. Coupled with Carbon Capture and Storage (CCS), biomass has the potential to target net negative CO₂ emission [8].

At the same time as biomass presents the advantage of being a CO₂ neutral alternative to fossil fuels, it is a complex fuel, difficult to combust and that may present heterogenous composition, irregular size, moisture and ash content, changing in function of the source type and growing conditions [9]. When used in combustion, biomass releases high levels of water vapor and volatiles that contribute to an uneven distribution of heat in the combustion chamber. Moreover, biomass contains alkali metals, which are well known for their corrosive properties. Finally, compared to fossil fuel such as coal, biomass does not contain as much energy per unit. Indeed, 1kg of dry wood release 18 to 21 MJ while the equivalent for coal will release 25 to 32 MJ [10–12].

One of the existing technologies that allows handling biomass is the fluidized bed (FB) conversion. In FB boilers the fuel is combusted in a furnace in presence of a bed material (usually sand) that is fluidized by an air flow. The solid fuels such as biomass are mixed with the sand, which enhances the contact between the fuel and the oxygen and improves the combustion process.

1.1 Oxygen Carrier Aided Combustion (OCAC)

In 2013, Thunman *et al.* proposed a new concept for fluidized bed boilers that has the potential to further improve the oxygen distribution in fluidized bed units [13]: Oxygen Carrier Aided Combustion (OCAC) [14]. During OCAC process, the sand, usually used as bed material, is replaced by an oxygen carrier (OC). An OC is usually a material which contains a metal oxide capable of transporting oxygen from an oxygen rich zone to an oxygen depleted location. The reduced form of the metal oxide ($\text{Me}_x\text{O}_{y-1}$) is oxidized by the air into Me_xO_y (reaction 1). When the Me_xO_y reaches a reducing environment e.g., when it is in contact and reacts with volatiles, the bound oxygen is then converted to CO₂ and H₂O (reaction 2).



As a result of the improved oxygen distribution via new mechanisms, the fuel conversion reaction is enhanced.

In order to be suitable for the process, the OC should be resistant to mechanical stress and have a sufficient lifetime. Further, it should be non-harmful and environmentally benign. It is also important that the price of the OC should make it economically viable.

1.1.1. Ilmenite as oxygen carrier

Ilmenite [FeTiO₃] that is a naturally occurring material, has been extensively studied in Chemical-Looping Combustion (CLC), due to its good oxygen carrying ability provided by its high iron (Fe) content, and excellent mechanical stability. Apart is higher price compared to quartz sand, ilmenite fulfills all the previous listed criteria [15–19] and is relatively abundant. The most important reserves are located in Australia, China, Vietnam [20] and Norway, which further makes it a good candidate as OC for the OCAC process. The behavior of ilmenite under OCAC and CLC conditions has been studied in several studies [12,14–17,19–23].

In ilmenite, the Ti in the TiO₂ form acts largely as support material, while Fe (as Fe (II, III) oxide) plays the role of an oxygen carrier. For the oxygen carrying, Fe goes from its reduced form (Fe²⁺) to its oxidized form (Fe³⁺) in oxidizing conditions thereby changing from a reduced state (ilmenite, FeTiO₃) to an oxidized state (pseudobrookite, Fe₂TiO₅). An intermediate state between ilmenite and pseudobrookite has also been observed and is mainly composed of Fe₃Ti₃O₁₀ [19]. It has been observed, that under cycling reducing and oxidizing conditions, Fe migrates outward the particles due to the oxidizing conditions neighboring the particle [24,26,27].

Throughout the combustion, a loss of particles material as fines occurs due to the attrition inside the combustion chamber. Due to attrition, the particles also eventually obtain a rounder shape [24,28].

Finally, because of the oxidizing and reducing environment, the particle develops cracks and pores [24,27] which can facilitate the oxygen interaction with Fe inside the particle, but also lead to a weaker resistance to mechanical stress and splitting of the particles into smaller pieces. However, it has been observed that rock ilmenite became more resistant to mechanical attrition with time [21].

1.1.2 Ashes

Biomass is a complex fuel that contains a mixture of organic and inorganic compounds. In this study, the focus was on woody biomass. Usually, wood contains the following elements in decreasing order: C, O, H, N, Ca, K, Si, Mg, Al, S, Fe, P, Cl, Na, Mn, Ti and other minor trace elements [9]. Depending on the type of biomass, the ash composition can vary. When biomass is used as fuel, one of the main constraints is the material interaction of the formed ash with heat exchange surfaces causing corrosion and the bed material causing agglomeration.

Concerning corrosion, alkali chlorides are considered as the main cause for deposit formations and further corrosion attacks [29–32].

Concerning agglomeration, the alkali metal containing ash compounds are the ones characterized with low melting point. and causing binding and sintering of the bed particles leading to defluidization of the bed [33,34].

Both corrosion and defluidization of the bed would decrease the efficiency of the fuel conversion and lead to unwanted shutdown of the power plant, maintenance operation, and additional expenses [35].

1.1.3 Ilmenite and ash interactions

In woody biomass, which is the main fuel used in this study, calcium (Ca) and potassium (K) are the major ash compounds. Those two main ash elements have been the subject of different studies and their interaction with ilmenite used as bed material has been followed [26,27].

When it comes to Ca, it has been seen that Ca from the fuel accumulates around the bed particles to form Ca-titanate (CaTiO_3) [27] and can form two calcium layers of $\text{Ca}(\text{Ti}_{0.7}\text{Fe}_{0.3})$ on each side of Fe layer [26].

Concerning K, it has been observed that it diffuses inward the particle and forms a K-titanate phase, $\text{KTi}_8\text{O}_{16}$. K is scarcely present in the heterogeneous outer layer of the particle. Its migration inwards the particle is, however, faster than that of Ca [26,27].

Similar interaction between Ca, K and the ilmenite particle has also been observed in **Paper I**. The effect of the formed ash layer and ash migration on the bed material activity has been previously studied [36–38]. The formation of the ash layer may improve the mechanical stability of the particles [21,38] and the catalytic performance of the bed material could be increased thanks to the addition of inorganic compound containing Ca and K. K_2O -rich ashes with relatively low SiO_2 content can improve the fuel conversion [36].

1.2 Challenges associated with OCAC

1.2.1 Corrosion treatment and sulfur interaction

Corrosion is an important issue to take into consideration when managing combustion plant. Due to its composition, biomass ashes are known to be difficult to handle because of their corrosivity [39]. Indeed, their low sulfur content, high alkali metal content and chloride gives favorable conditions for the formation of potassium chloride (KCl) which is highly corrosive for the heat transfer surfaces equipment. In conventional coal-fired CFB combustors, corrosion of the equipment is minimized by the S content in the fuel and the alkali capture by the fuel ashes themselves. Indeed, it has been observed that, through sulfation of the released alkali salts, less-corrosive alkali sulfates are formed that can prevent the development of corrosive species such as KCl [40,41]. However, sulfation and its effects on biomass-fired OCAC conditions have not been elucidated.

1.2.2 Waste Management of OCAC

The bed material has a limited lifetime in the boiler. After the bed material has been long enough in the boiler and interacted with the fuel ash, its oxygen transferring activity decreases due to Fe depletion, as a result of Fe migration and attrition inside the boiler.

The smaller particles from the bed can be carried away from the cyclone and finish in the fly ash part. The fly ashes fraction is composed of fine particles which end up in the flue gas and are trapped in flue gas cleaning. The other particles end-up in the bottom ashes part which consist of a mix of bed material and ashes. The bottom ash is usually further analyzed before being transported to landfill, where it could serve as a buffer to mitigate acidification [42].

Because of the loss of bed particles in the fly ash and to maintain the bed height in the furnace, bed material is constantly added in the boiler. This constant cycle of bed material exchange creates a waste stream. In summary, the main waste produced is usually landfilled and mainly consists of spent bed material and ashes: fly ashes and bottom ashes and their management is one of the constraints, which must be improved with OCAC.

In the waste management hierarchy (Figure 1), landfilling is considered as the worst-case scenario after energy recovery, recycling, reuse, minimalization and prevention.

This type of management of the produced waste is costly and subject to taxes. The ashes sometime also contain hazardous compounds, and these products are important to handle properly to fulfil the environmental legislation and avoid environmental pollution.

In the present case, prevention is impossible as the ilmenite is the heart of the process. The reuse of the bed material is currently investigated and thanks to the use of magnetic separator which can sort the used but still-usable particles, which can be reimplemented into the process for a longer use [16]. The produced ashes are sometime used in other fields such as concrete production or as filler for road construction. They can also be used as fertilizer for forestry biomass production [42].

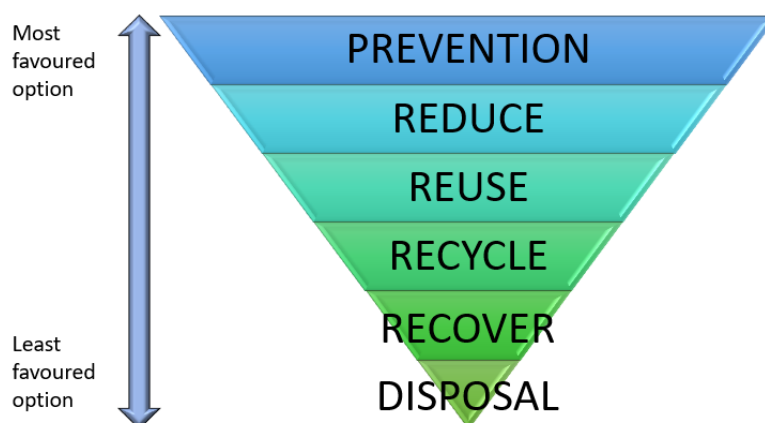


Figure 1. Waste management hierarchy.

1.2.3 Ilmenite processing

To achieve better waste management and lower the amount of waste produced, the bed material waste could be reused to produce valuable by-products. The most common product of ilmenite ore is the white pigment TiO_2 . Indeed, 95% of the ilmenite production is used to manufacture TiO_2 [43].

To extract TiO_2 from raw material such as rutile (~ 95% TiO_2 content), anatase (> 95% TiO_2 content) or pre-treated and concentrated ilmenite (40-80% TiO_2 content), two main pigment processes are generally used: sulfate process or chloride process.

The sulfate process uses hot concentrated sulfuric acid (H_2SO_4) to digest the ilmenite. The obtained leachate is then filtrated, and water is added to hydrolyze the solution, which gives rise to precipitation of hydrated TiO_2 . The hydrated TiO_2 is then calcined between 500 and 1000°C to obtain anatase or rutile.

The chloride method mainly consists of calcination at 900 to 1000°C of the ilmenite with coke and gaseous chlorine to form titanium tetrachloride (TiCl_4). Gaseous TiCl_4 is then condensate to liquid phase and most impurities can be separated as solids. The TiO_2 is then obtained by oxidation of TiCl_4 at high temperature (1200 - 1700°C), which forms TiO_2 and Cl_2 that can be reused for a new batch. Even if the chloride method provides high-quality product and generates less waste products than sulfate process, it requires a raw material with a higher Ti concentration (rutile or synthetic rutile) [44].

Before its introduction in the pigment processes, ilmenite often undergoes pre-treatment. It is often milled to reduce the particles to optimal size [45–50], reduced to facilitate the transition of Fe^{3+} in Fe^{2+} to increase its solubility [51], or placed in an arc furnace to separate the Ti from Fe to later form pig iron and obtain Ti-slag to thus facilitate the further sulfate process [52].

An advantage of using used ilmenite from OCAC into the pigment production process could be: (1) the presence of cracks and pores which could facilitate the digestion; (2) the fact that Fe is already concentrated in specific areas, closer to the surface and thereby easier to separate from Ti-slag; (3) the new composition of used ilmenite, which can present more soluble form of Ti; (4) the cheaper price of the used ilmenite compared to the raw ilmenite. If those new properties are well used, they can represent an advantage compared to the fresh ilmenite, a reason why it can be interesting to develop a new process with the used ilmenite from FB boiler.

One of the constraints for a new process may be the presence of ash elements which can contaminate the Ti extraction process [53]. Indeed, the composition of the feedstock material and interference of the impurities during the different steps are crucial parameters for pigment extraction process. It is for this reason that investigation of the impact of ashes element is of importance for the development of a new recycling process. Moreover, the quality of the obtained product is important to study for further commercialization of the process.

1.3 Aim and scope

The aim of this research has been to investigate the possibility of reusing the used bed material from OCAC and understand the interaction of added sulfur with the bed material particles during different conditions. A two-week campaign has been conducted in 12 MW_{th} semi-industrial CFB boiler to obtain representative samples, with and without additional sulfur exposure. **Paper I** showed that sulfur was accumulated in the particles, and preferentially within the ash layer. In **Paper II**, the samples from the 12 MW_{th} CFB boiler have also been tested in a laboratory fluidized bed batch reactor system to understand better the S interaction with the particles and the surrounding atmosphere. The used ilmenite from the sulfur campaign has been leached in laboratory with sulfuric acid in **Paper III** to test its suitability as material for pigment production.

1.3.1 Recovering of elements

As it currently exists a knowledge gap concerning the valorization of used ilmenite, the **Paper III** presents a new approach for recovery of the used ilmenite from OCAC into a valuable product. The goal of this paper is to understand and determine in both unused and used ilmenite from OCAC the fate of the elements Ti and Fe and the main ash elements Ca and K during the first step of the extraction of TiO₂ in sulfate process. This could allow for the development of an adapted process for this type of ilmenite and then reduce the cost of the source for pigment production and the amount of waste from FB boilers and their handling cost.

1.3.2 Reduction of the used amount of sulfur

Paper I and **Paper II** investigate the interaction of sulfur with ilmenite particles from the bed. These papers give a comprehensive picture of the mechanism of uptake and release of the sulfur during OCAC conditions. The influences that ashes have on sulfur capture and release have also been studied. Understanding the mechanism of sulfur uptake and release, and the conditions that influence these processes, can facilitate the optimization of sulfur additions under OCAC conditions to mitigate corrosive attacks on heat transfer surfaces. The acquired knowledge is also important for optimizing the amount of sulfur additive, while keeping the level of waste material handling as low as possible. Moreover, the release of the accumulated S from the bed can be an advantage concerning the fate of the used material as a sulfur depleted material represents a less hazardous product when it goes to landfill.

CHAPTER 2 – EXPERIMENTAL

The experimental work covered by this thesis was conducted in 12 MW_{th} semi-industrial CFB boiler and in a laboratory scale batch fluidized bed reactor. The 12 MW_{th} CFB boiler was used to obtain representative bed samples, generated during close to industrial scale conditions. The laboratory scale fluidized batch reactor was used to investigate the bed material behavior during OCAC conditions with sulfur addition. Investigation of suitability of applying used ilmenite as feedstock for pigment production was carried out in laboratory environment.

2.1 Chalmers 12 MW_{th} CFB-boiler

The boiler used during the experimental campaign is located in the campus of Chalmers University Technology in Gothenburg, Sweden. The furnace is 13.6 m high and has a cross section area of 2.25 m². The boiler is used to produce heat for the campus area and district heating to the city grid during the cold season. The boiler is specifically adapted for research purposes. A schematic description of the boiler is shown in Figure 2. More details about the boiler and how it is operated have been provided by Thunman *et al* [14]. During the experiments, the average temperature was maintained between 860 and 880°C. The pressure was kept constant by the addition of fresh bed material, to compensate for elutriated fines. The fuel used during the campaign was wood chips (spruce and pine wood) and was fed at a rate of 2 tones/h. The elemental composition of the fuel is provided in Table 1.

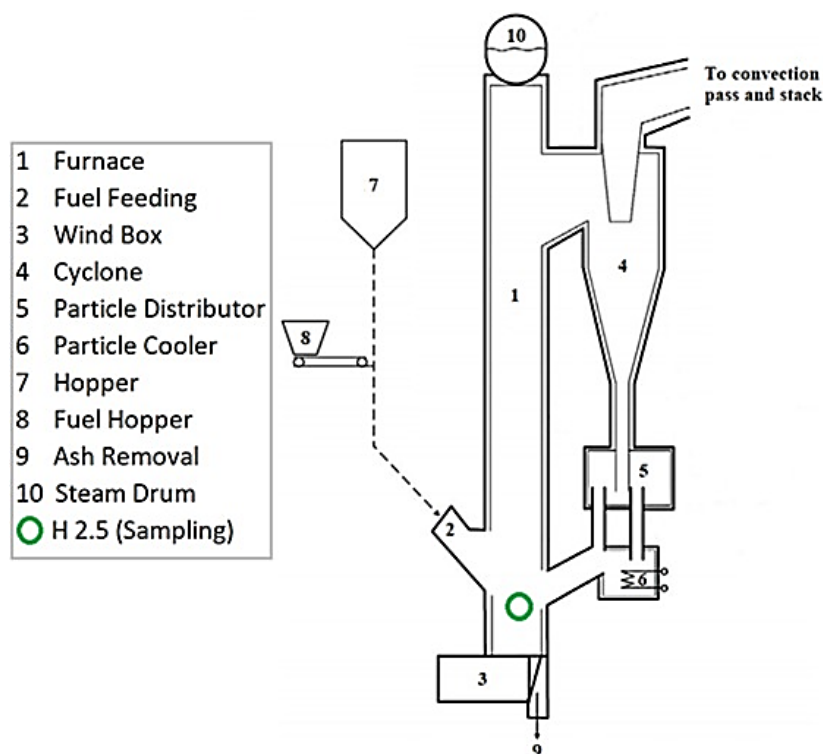


Figure 2. Schematic description of the Chalmers 12 MW_{th} CFB boiler.

The CFB boiler is equipped with sampling holes that allow access to the inside of the combustion chamber, e.g., to collect samples. To collect the bed material, a cooled suction probe was used. Around 1 kg of bed material was collected on each sampling occasion. The obtained samples were then analyzed and used for further laboratory scale experiments.

Table 1. Composition of the wood chips (based on fuel as received) used as fuel in the present work.

Characteristic	Wood chips
Moisture wt. %	38.50–45.30
Volatiles wt. %	43.80–50.10
Ca wt. %	0.11
K wt. %	0.06
S wt. %	<0.02
Ash wt. %	0.40–0.60
Lower Heating Value	
Dry ash-free MJ/kg	18.60

The bed material used in the experiments is rock ilmenite concentrate. It came from Norway and was supplied by Titania AS. The size of the particle was in the range of 100 – 300 μm . The ilmenite was received in its reduced form, FeTiO_3 , with an element composition as shown in Table 2. The composition of used ilmenite that contains more ash elements is later detailed in Table 4.

Table 2. Elemental composition of ilmenite in its non-oxidized form (in wt. %), as provided by Titania AS. The balance is oxygen.

Element	wt. %
Fe	34.20
Ti	27.90
Mn	0.48
Mg	0.44
Al	0.19
Si	0.15
K	0.07
Ca	0.06
Na	0.04
P	0.01
S	<0.02

2.1.1 Campaign

A two-week campaign was organized to obtain used ilmenite, which has interacted with wood ash, and to investigate the impact of sulfur addition on these interactions (**Paper I** and **Paper II**).

Detailed schematic illustration of the two-week campaign is shown in Figure 3. During the campaign, sulfur was added in the combustion chamber. During the first week (Experiment I), sulfur was fed from the start of the experiment for three entire days, with a fresh batch of ilmenite as bed material.

During the second week of the campaign (Experiment II) the material was exposed to OCAC conditions and sulfur was added only after the fourth day of operation. In the second case, the difference was the development of an ash layer around the particle prior to the sulfur feeding. This difference allowed improved understanding of the impact of the ash layer components with the sulfur interaction.

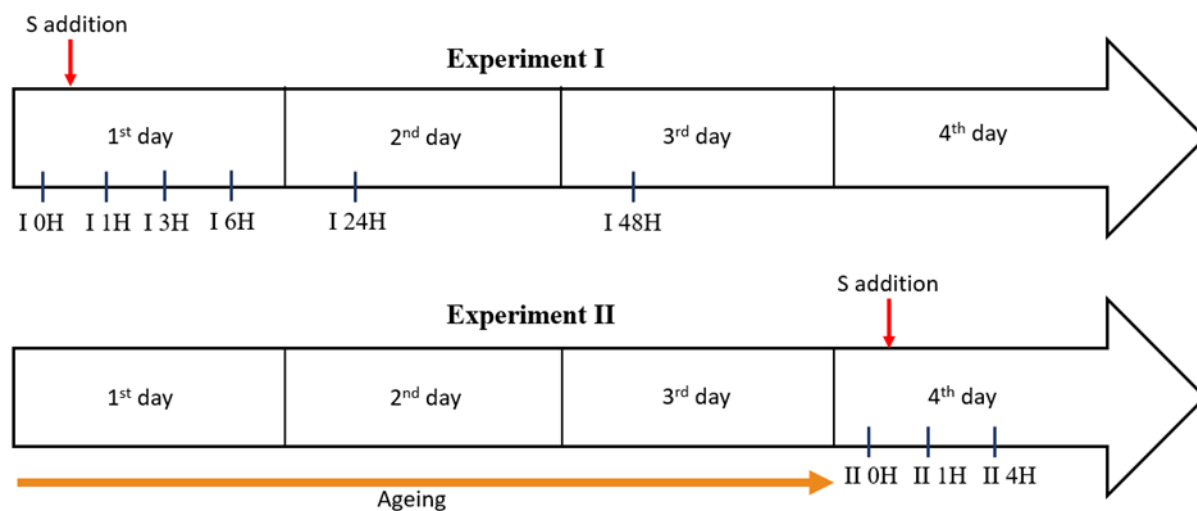


Figure 3. Summary of the experimental campaigns I and II, where the axes represent the residence time in the boiler. Sampling times are represented along with the sample's notation.

2.1.2 Sulfur addition

The addition of elementary sulfur is sometimes used in combustion processes to mitigate corrosion. Various types of sulfur additives have been used in industry, including elemental sulfur and sulfates such as ammonium sulfate, aluminum sulfate, and ferric sulfate [41]. The severity of corrosion on heat transfer surfaces is reduced due to the sulfation of KCl into K_2SO_4 which is less-corrosive [40]. Previously, sulfur-rich peat was mixed with the fuel to supply the necessary sulfur amount into the boiler [54]. However, peat is now considered as a fossil fuel and is subject to a fossil fuel tax, so its use has been phased out.

In the present work, sulfur addition was realized by feeding sulfur through a separated feeding system connected to the combustion chamber of the 12 MW_{th} boiler. This allowed for top feeding of 1.5 kg/h of elementary sulfur in granular form to the fluidized bed. During the first

week, the S was added for 48 hours. In the second week of the campaign, the boiler was first operating with ilmenite as bed material and without sulfur additive for three days. Then, after 78 hours in normal combustion condition, elementary sulfur was added (Figure 3).

2.2 Batch reactor test

To investigate the behavior of the collected ilmenite samples with sulfur, a laboratory scale quartz batch reactor (referred to as “reactor”) was used. The reactor system has been used in different research areas, particularly for chemical looping combustion (CLC) research, and is described in details elsewhere [23]. A schematic representation of the reactor is shown in Figure 4. The reactor is 82 cm high and 2.2 cm in diameter. 15g of bed material are used in the reactor. The bed is located 37 cm from the bottom of the reactor, resting on a porous quartz plate that allows gas to penetrate through and fluidize the bed. Two thermocouples measure the temperature under and inside the fluidized bed, 2 cm above the porous quartz plate. A pressure probe measures the pressure difference between the top and bottom of the reactor during the experiment. A pipe at the bottom of the reactor distributes the different inlet gas: CO/H₂, N₂, O₂ and SO₂.

A pipe at the exit of the reactor collects the outlet gas to a condenser. The remaining dry flue gas is analyzed in a Rosemount NGA 2000 instrument and was thereafter released to the ventilation.

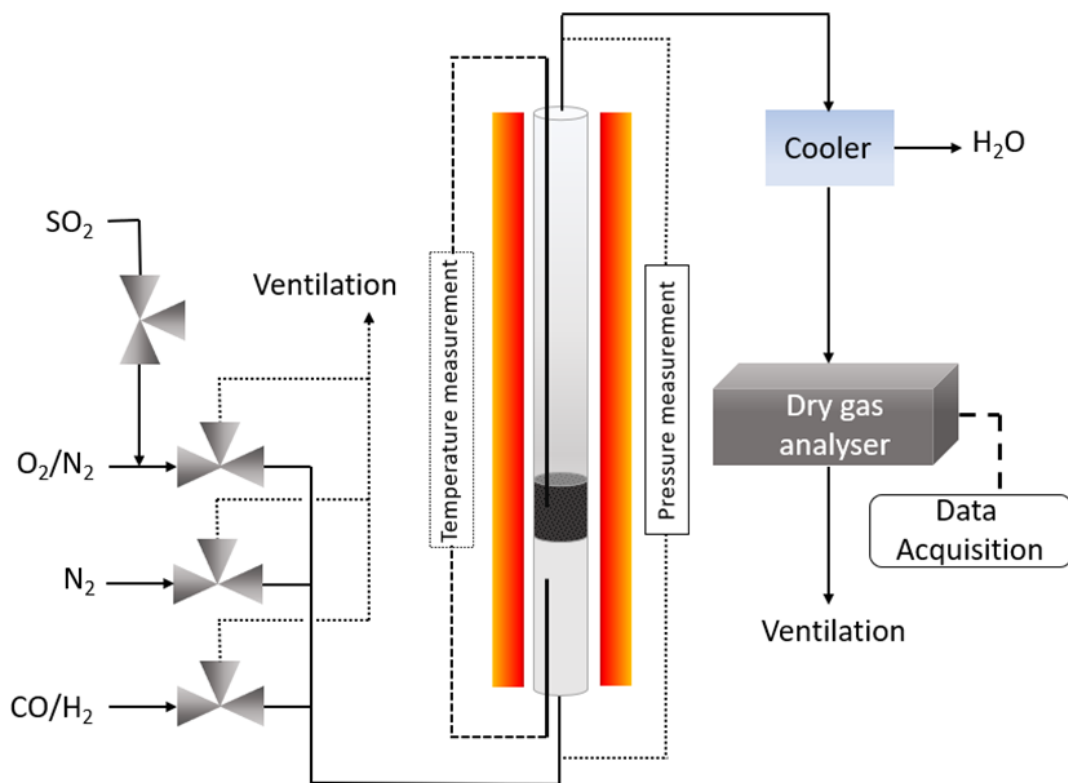


Figure 4. Layout of the setup for laboratory-scale fluidized bed batch reactor.

Cycles of oxidizing and reducing conditions were tested. Oxidizing phases correspond to a gas mixture of 5% O₂ in 95% N₂. Between each oxidizing and reducing phase, inert gas (N₂) was run for 20 seconds to flush the potential resting gas in the reactor and pipes. Thereafter, syngas consisting of 50% CO and 50% H₂ was used to simulate reducing conditions. The tested bed material undergoes several redox cycles, and more details are given in Table 3.

Table 3. Operation parameters used for testing of bed materials during batch experiments in laboratory fluidized bed reactor.

Phase	Gas Mixture (mole%)	Gas flow (ml_N/Tmin)	Temperature (°C)	Time (s)
Oxidizing	O ₂ /N ₂ (5/95)	1000	950	600
Inert	100 % N ₂	1000	950	180
Reducing	CO/H ₂ (50/50)	900	950	20
Inert	100% N ₂	1000	950	180
Oxidizing with SO ₂	SO ₂ /O ₂ /N ₂ (1/5/94)	1000	950	1,200

To test the sulfur capture and release conditions, the tested bed material was exposed 20 to 50 minutes to SO₂ during oxidizing conditions. A mixture of 1% SO₂, 5% O₂ in 94% N₂ was used to simulate those conditions. More details about the system are given in **Paper II**. The results of these experiments will be detailed in Chapter 3, section 3.1.

2.3 Leaching of ilmenite with sulfuric acid

2.3.1 Fresh and used ilmenite

In this thesis, the focus was on the first step of the sulfate process. The goal of the study was to investigate the possibility to extract TiO_2 from ilmenite that has been used in the OCAC process. A secondary goal was to investigate the possibility of recovering other elements present in used ilmenite.

Laboratory scale experiment was developed for elemental recovery. The process was first tested with fresh ilmenite, before it was used to digest ilmenite samples from the campaign in the 12 MW_{th} CFB boiler.

A composition comparison between the two types of ilmenite used in the extraction process is given in Table 4.

Table 4. Ilmenite composition before and after 3 days in the 12 MW_{th} CFB boiler fueled with wood (in wt.%). The balance is oxygen.

Element	Ilmenite as received (wt%)	Ilmenite after 72 h in OCAC (wt%)
Fe	36.0	21.0
Ti	28.0	27.0
Mn	0.2	0.6
Mg	2.0	2.3
Al	0.2	0.3
Si	0.7	3.5
K	<0.05	4.0
Ca	0.2	5.7
Na	0.1	0.1
P	<0.05	0.4

2.3.2 Sulfuric acid leaching conditions

The first step of the sulfate process consists of the digestion of ilmenite with concentrated sulfuric acid (H_2SO_4 , 96-98%) at a temperature of 110°C for up to four hours. Two grams of crushed ilmenite with a particle size of less than $45\ \mu\text{m}$ were placed in a 250 ml round-bottom flask and heated in a silicon oil bath (Figure 5). Constant stirring was applied to allow for a better interaction between the ilmenite and the acid and even temperature. More details about the procedure are given in **Paper III**.

Once the ilmenite was digested, it was poured in a beaker, and left overnight at room temperature for decantation. The supernatant was then collected and diluted with diluted H_2SO_4 before analysis. The solid fraction was mounted in epoxy to be analyzed with a Scanning Electron Microscope (SEM). The results will be explained in Chapter 3, section 3.1.

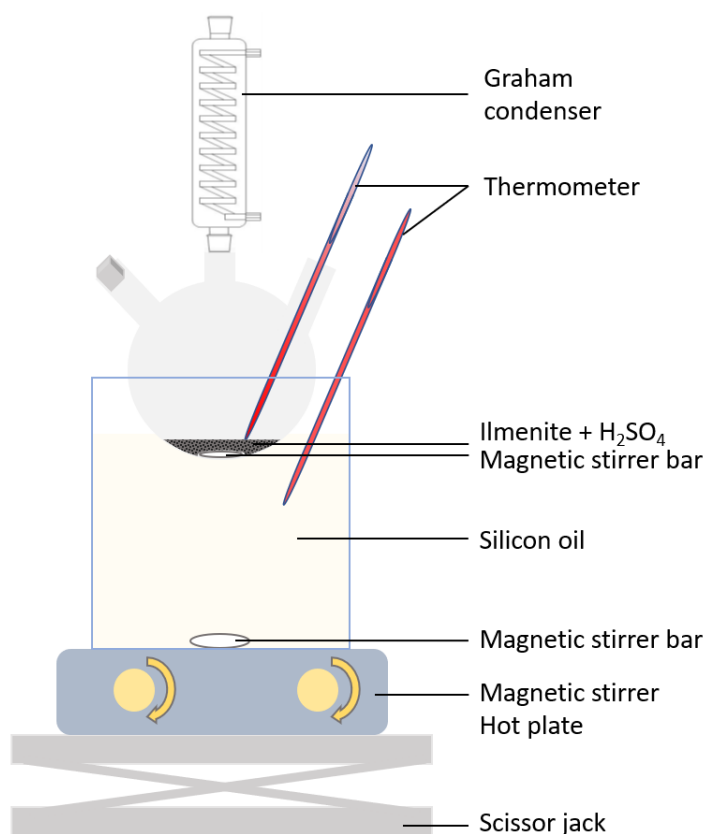


Figure 5. Schematic representation of the set-up used for the leaching of ilmenite with sulfuric acid for up to 4 hours at 110°C .

2.4 Characterization techniques

2.4.1 *Characterization of bed material*

Different characterization techniques were used to analyze the collected samples. Qualitative and quantitative techniques were carried on.

The total elemental analysis of the extracted samples from the 12 MW_{th} CFB unit and laboratory reactor was carried on with Inductively Coupled Plasma-Sector Field Mass Spectroscopy (ICP-SFMS). The analysis was performed by the external company ALS Scandinavia AB according to the standard ISO/IEC 17025, after digestion of the sample by fusion/HNO₃, HCl and HF in a quartz melt.

To evaluate the morphological changes between samples and to appreciate the elemental distribution within the particles, electron microscopy was used. Scanning Electron Microscopy coupled with Energy Dispersive X-ray (SEM-EDX) was performed with a Quanta 200FEG system equipped with Oxford 177 EDX detector. For imaging, back-scattered electron signal was used. The imaging was performed in low-vacuum mode and with charge reduction. Copper tape was used on the sample holder to avoid charging. The samples were mounted in epoxy and polished to carry on cross section analysis. Representative particles were selected based on their shape, porosity, ash layer, thickness and composition. It is important to notice that, due to the continuous feeding of new bed material into the system, the obtained samples can contain particles with different residence time. It is for this reason that representative particles were selected for the microscopy analysis. Line scan analysis was performed on particles to have an overview of the composition of the different layers of the particles. Surface analysis of the samples was also performed by SEM-EDX with a tabletop microscope Phenom Pro X where particles were mounted on carbon tape.

BET (Brunauer-Emmett-Teller) surface area analysis were performed with N₂ to evaluate the evolution of the porosity of the particles. A Micromeritics TriStar 3000 was used for these investigations.

2.4.2 *Characterization of leachate after ilmenite digestion with sulfuric acid*

The obtained liquid fraction was analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The ICP spectrometer used for the analysis was the iCAP PRO XP ICP-OES. The focus was made on the two main elemental constituents of ilmenite, Fe and Ti, as well as the main ash elemental constituents Ca and K. The results are shown in **Paper III**.

CHAPTER 3 – RESULTS AND DISCUSSION

In this chapter, results from the papers included in the thesis are presented. The results are divided into two main topics: outcomes about sulfur interaction with ilmenite during OCAC conditions (**Paper I** and **Paper II**) and outcomes from the leaching with sulfuric acid (**Paper III**)

3.1 Sulfur interaction with bed material

This section refers to **Paper I** and **Paper II**. It highlights the main findings about sulfur interaction with ilmenite particles during OCAC conditions.

Observations from **Paper I** showed that sulfur was captured by the bed material. Further investigations about the sulfur capture and release mechanisms are described in **Paper II**. To better understand the interactions between sulfur and bed material, analysis of different samples from the 12 MW_{th} CFB boiler and from lab scale reactor exposures was carried out. Subsections 3.1.1 and 3.1.2 present the observations of samples exposed to two different conditions, oxidative and reductive.

3.1.1 Sulfur release by ilmenite

Sulfur release as SO₂ was observed during the campaign in the 12 MW_{th} CFB boiler. This observation is presented in detail in the included **Paper I**. The outlet gas showed an increase in the SO₂ concentration when the fresh ilmenite bed material was added to the combustion chamber. These observations are visible in Figure 6. As the bed material was not previously exposed to elementary sulfur, it can be concluded that this is the release of sulfur which is naturally present in ilmenite.

To verify this hypothesis, fresh sample of ilmenite was compared with sample which has spent 1 hour in the boiler during combustion of biomass. The samples have been analyzed by ICP-SFMS method and the total elemental analysis was determined. It was observed that the sample which spent 1 hour in the boiler contained less sulfur than the fresh ilmenite, thus confirming the observation described above.

The release of sulfur after its capture has also been investigated in a laboratory scale reactor in **Paper II** (more details about the sulfur capture by the bed material particles are given in subsection 3.1.2). It was observed that the sulfur from the ilmenite was released in form of SO₂ during oxidizing conditions. SO₂ was then expected to be released by ilmenite particle during reducing conditions. The ilmenite samples exposed to biomass combustion condition and elementary S addition were tested in a laboratory scale reactor. The release of SO₂ was observed during exposure to reducing syngas (CO/H₂). The total sulfur present in the ilmenite particles was released after 5 to 9 redox cycles.

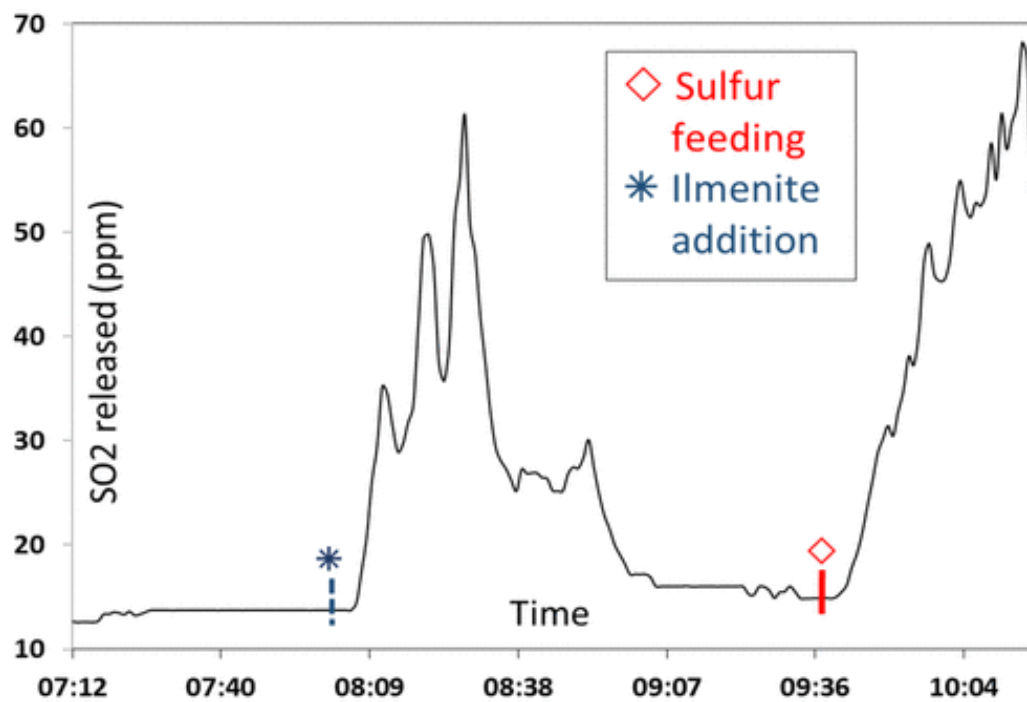


Figure 6. SO₂ release from bed material in the 12 MW_{th} CFB boiler during the first day of ilmenite campaign.

3.1.2 Sulfur capture by ilmenite

Sulfur capture in the bed material was observed during the campaign in the 12 MW_{th} CFB boiler. The total elemental analysis of the bed material after the campaign reveals the presence of sulfur and its accumulation over time, during operation of the boiler. The sulfur capture can also be followed on the SEM-EDS images. The particles reveal an accumulation of sulfur in the ash layer of the particle or in their core, depending on the preliminary conditions when it was fed into the combustion chamber (Figure 7 and 8). Those results are presented in more details in **Paper I**.

	Un	I 0H	I 6H	I 48H	II 0H	II 4H
Cross-section						
Ti						
Fe						
Ca	*	*				
K	*	*				
S	*	*	*		*	

Figure 7. EDX map of cross section of bed particles from 12 MW_{th} CFB boiler showing ash elements and sulfur accumulation inside and on the surface of the bed particles. The asterix indicates no detection of the corresponding elements.

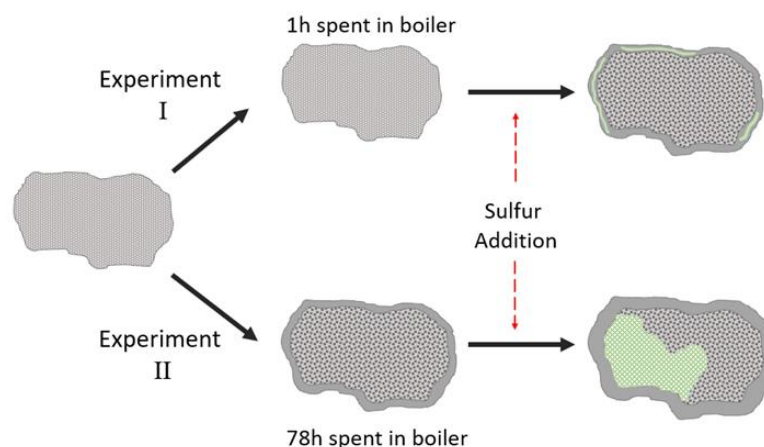


Figure 8. Schematic summary of the main findings of Paper I. Sulfur accumulates in the particles over time and is located in different location depending on the presence or non-presence of ash layer during sulfur addition.

It was observed that sulfur was accumulated in the ash layer when it was fed with fresh ilmenite. Thus, the sulfur was caught during the formation of the ash layer around the particle and was bound mainly with Ca and K (Figure 8, Experiment I). In comparison, sulfur was found in the core of the particle when it was fed with particles which already had an ash layer, supposing that it is able of passing through the ash layer (Figure 8, experiment II).

The accumulation of sulfur was also confirmed by EDX line-scan (Figure), in which it was seen that it was more present in the ash layer in case of addition with fresh ilmenite, (Experiment I) and more present in the core in case of addition with ilmenite bed particles which already have an ash layer (Experiment II).

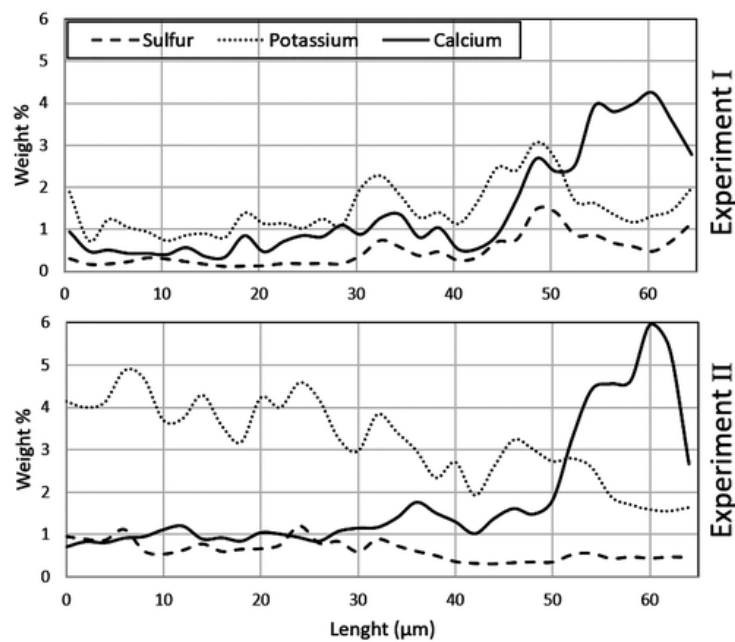


Figure 9. EDX line-scan results of the cross section of representative particles from the two experiments in the campaign. The left part corresponds to the core of the particles while the right part corresponds to the edge.

Mechanisms for sulfur capture were evaluated in a laboratory scale reactor (**Paper II**), where the uptake and released was followed and recorded.

Figure 10 shows redox cycles with SO_2 addition and release. Once no SO_2 was detected after a reducing cycle (0), sulfur was added in form of SO_2 in oxidizing conditions (1% SO_2 and 5% O_2 in N_2) for 50 min to the ilmenite bed particles (1). As SO_2 was initially not detected, it is confirmed that sulfur was captured in the bed. However, ilmenite reached saturation after 20 min of SO_2 exposure. After the uptake, sulfur was released again in form of SO_2 during reducing phase where a peak of SO_2 was observed (1). Three additional redox cycles (with only 5% O_2 in N_2 for oxidizing conditions) showed that SO_2 is released progressively during reduction (cycles 2 to 4). It has been observed that sulfur uptake and release was a reversible phenomenon as the bed material was able to capture sulfur from SO_2 once it has been released from the particle.

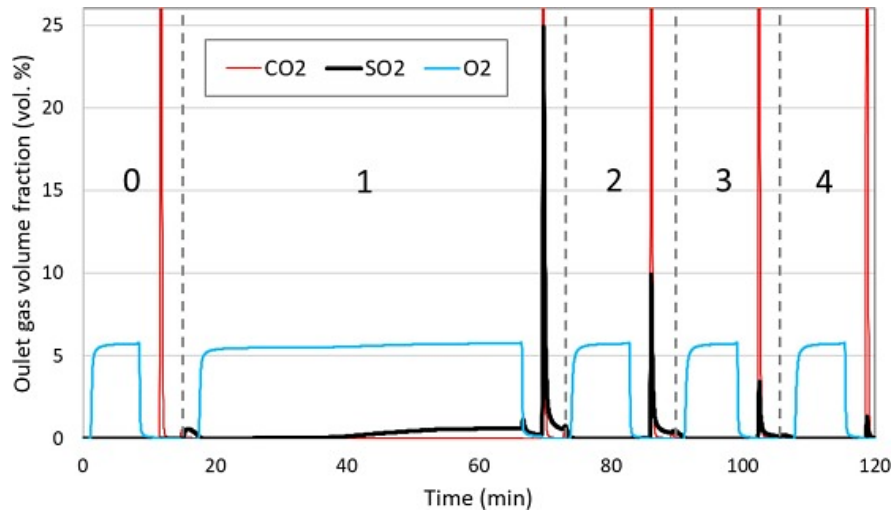


Figure 10. S uptake and release in form of SO_2 at oxidizing and reducing conditions. Reducing phases are visible thanks to the CO_2 peaks while oxidizing phases are visible thanks to O_2 plateau.

Finally, thermodynamic equilibrium with FactSage 7.2® [55] Predom software was made. Different compositions were found in ilmenite, in function of the presence of ash elements Ca and K or not. When exposed to sulfur, Ca and K from the ash layer interact with SO_2 and form K_2SO_4 , $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ and CaSO_4 . Sulfur is released in form of SO_2 during reducing conditions. After reduction, K is found in form of K_2O and Ca under the form CaO . More details of the mechanism are given in **Paper III**. The main sulfur uptake and release mechanisms found in this research are summarized in Figure .

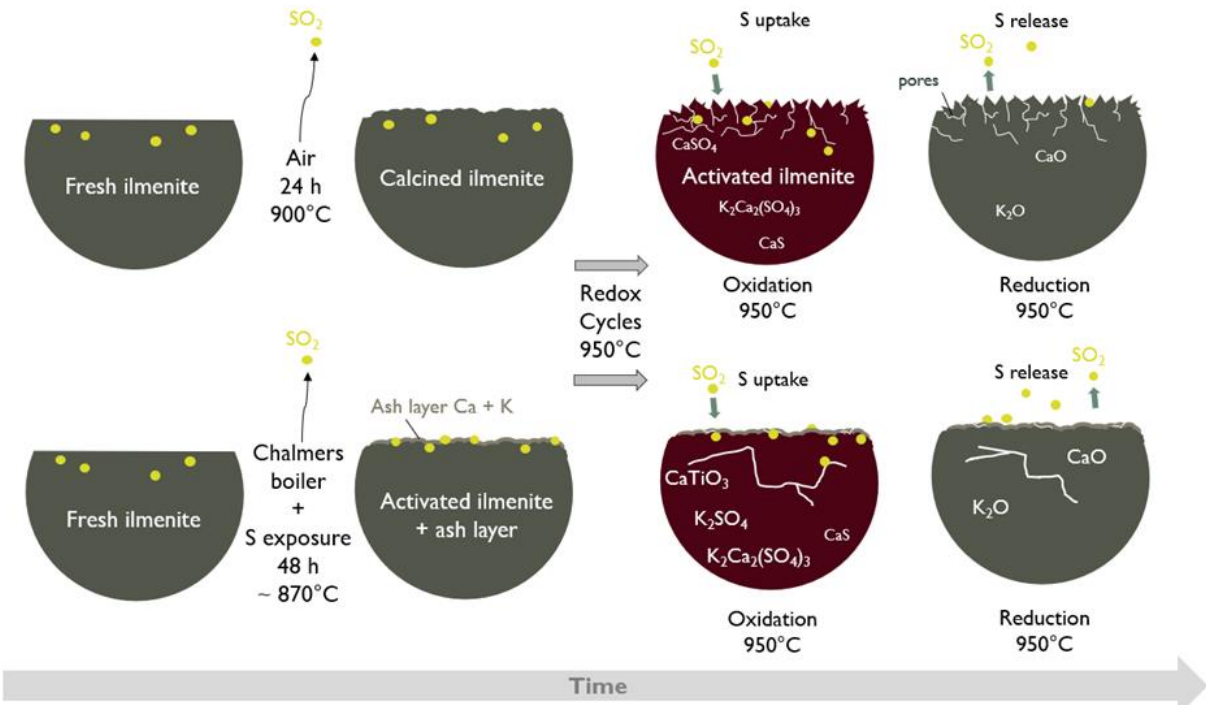


Figure 11. Schematic summary of findings from Paper II. The S is accumulated and released in form of SO_2 . Its uptake take place during oxidative conditions while it is released during reductive conditions. Thermodynamic calculations revealed that the S can be coupled to K and Ca in different forms.

Paper I and **Paper II** showed that:

- Ca and K were accumulated in the ilmenite particles during combustion
- Sulfur can be captured by ilmenite with SO₂ under oxidizing condition
- Sulfur is released as SO₂ during reducing condition
- The capture and release of sulfur is a reversible phenomenon
- Ilmenite which contains ash element capture more SO₂ than fresh ilmenite, which does not have an ash layer
- Sulfur was often found together with Ca and K, likely as sulphates.
- EDX line-scan reveals that sulfur and K followed each other closely throughout the particle cross section. The affinity was also confirmed in the **Paper II**, where SEM-EDX after the sulfur capture reveal that sulfur was found in the same location with Ca and K. FactSage calculations also showed that it is possible to find K sulfate and other sulfate in the ilmenite, following the capture of sulfur. It also suggests that a mix phase of Ca, K and S forming K₂Ca₂(SO₂)₃ is created.

3.2 Leaching extraction - Leachate and solid composition

This section refers to **Paper III**. It summarizes the main findings observed after digestion of fresh and used ilmenite from OCAC with sulfuric acid.

In the case of used bed material, a morphological change was observed in SEM-EDX. Indeed, compared to fresh particles, used particles from OCAC present an increased prevalence of pores and cracks. This observation confirms previous research about OCAC and CLC showing that repeated exposure to oxidizing and reducing conditions, high temperature and mechanical attrition results in particle swelling, increase in active surface area and appearance of pores and cracks. These observations are supported by BET measurement, which show an increase of the surface area in used ilmenite. The surface area is of 1.05 m²/g for fresh ilmenite while it reaches 2.07 m²/g in used ilmenite. The density was also affected by the morphological change and apparent increase of porosity. Lower density was found in the used ilmenite (1 830 kg/m³) compared to fresh ilmenite (2 360 kg/m³).

It was also observed that the used particles present an accumulation of fuel ash elements. Ca and K are found on the surface and within the particles, which was expected (Figure 12). Indeed, literature revealed that K and Ca from the wood fuel migrate inward the ilmenite particles and bind to Ti to form potassium-titanate KTi₈O₁₆ in the core of the particle and calcium-titanate CaTiO₃ on the surface of the particles [27].

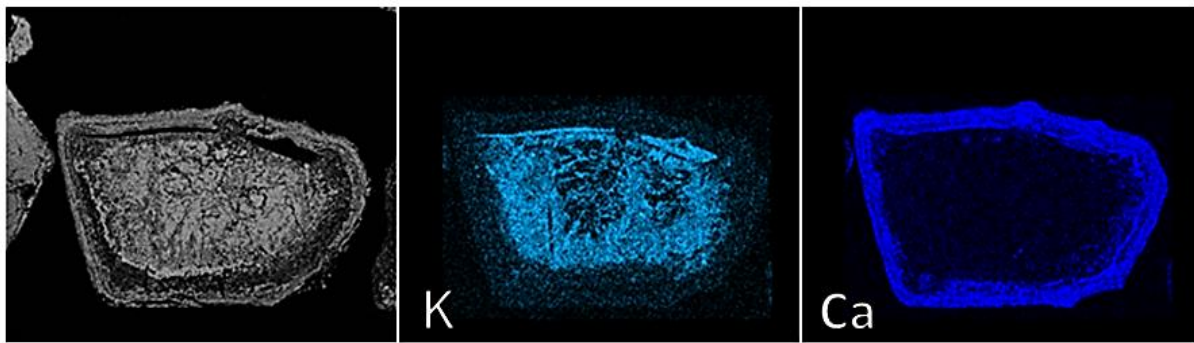


Figure 12. SEM micrograph and EDX intensity map of the cross section of used ilmenite particles from 12 MWth CFB boiler. K is more prevalent in the core of the particles while Ca is concentrated to an ash layer on the particle surface.

The leachate fraction obtained after 30 min, 1-, 2-, and 4-hours digestion has been analyzed with ICP-OES. It has been observed that most of the leachable compounds were released after two hours. The concentration of Ti, Fe, Ca and K in the leachate after two hours of digestion is shown in Table 3. It is clear that the used ilmenite releases more Ti in the leachate than the fresh ilmenite. Indeed, 6 times more Ti has been detected in the leachate from the used ilmenite, compared to the fresh ilmenite.

Elevated concentrations of Fe, Ca and K have also been detected in the leachate of the used ilmenite. Almost 8 times more Fe was detected in the solution from the used ilmenite, compared to the one from the fresh ilmenite.

Table 3. ICP-OES results from the leachate obtained after 2 hours of digestion with sulfuric acid at 110°C. Concentrations are presented in mg/l. Focus has been put on Ti, Fe, Ca and K.

	Ti	Fe	Ca	K
Fresh ilmenite (mg/l)	1751	114	53	22
Used ilmenite (mg/l)	10569	893	1271	1614
Increased (%)	6	8	24	73

K and Ca are also found in higher concentration in the leachate from used ilmenite, compared to the fresh ilmenite leachate. Indeed, Ca concentration is 24 times higher and K, 73 times higher in the leachate of used ilmenite. This is explained by the fact that these elements are more prevalent in the used ilmenite, after having been subject to wood fuel ash in the boiler. In the case of fresh ilmenite, K and Ca are present only in low concentration (0.75 g/kg for K and 2 g/kg for Ca). The results reported in Table 3 show that it is possible to extract Ti, Fe, Ca and K from used ilmenite with this method.

The improved leaching behavior of used ilmenite with respect to Ti, Fe, Ca and K can be explained by the fact mentioned above, i.e., that pores and cracks increase access to the core of the particles for sulfuric acid. This observation is in accordance with observations found in the

literature that “microcracks and micro holes enhance the leaching rate of Fe by providing a path for acid to penetrate” [56]. Consequently, the new morphological properties acquired during the combustions conditions could represent an advantage for industry. Indeed, by increasing the porosity, there is less need for energy for crushing before digestion and easier access of the acid to the core of the particle.

Industries use different pre-treatment methods before the digestion of ilmenite with sulfuric acid, to facilitate the enrichment in Ti of the feedstock and the leaching. Pre-reduction is sometime used to convert ferric iron (Fe^{3+}) into ferrous iron (Fe^{2+}), which is more soluble in acid solution [51].

However, there are also contradictory observations which show that oxidation of the ilmenite can be applied as a pre-treatment [57,58]. This is because transformation of Fe into hematite (Fe_2O_3) allows for a better leaching of Fe. Thereby, by using OCAC as a pre-treatment for ilmenite, the oxidation state of the ilmenite (ilmenite or pseudobrookite) could be changed and adapted.

Previous studies show that solubility of Ti in H_2SO_4 can be enhanced by alkaline roasting of ilmenite [46]. Kramer *et al.* [59] compared the solubility of $\text{FeO} \cdot \text{TiO}_2$ and $\text{K}_2\text{O} \cdot \text{TiO}_2$ and found that the Gibbs energy of formation of Ti (IV) hydrolysis form for $\text{K}_2\text{O} \cdot \text{TiO}_2$ is lower than the one of $\text{FeO} \cdot \text{TiO}_2$, meaning that the titanate of alkali is more soluble than the titanium form.

By exposing the ilmenite to K at high temperature, OCAC could reproduce favorable conditions for the alkaline roasting of ilmenite, thus reducing the energy used in this type of pre-treatment. Indeed, previous observations showed that potassium titanate ($\text{KTi}_8\text{O}_{16}$) is formed in the core of the particle during OCAC [26,27]. This could increase the solubility of Ti by reducing the activation energy, which could decrease in temperature and H_2SO_4 concentration required to digest the particles, in comparison with fresh ilmenite particles.

The migration of Fe observed during the OCAC and CLC conditions could represent an advantage for the pigment industry. Fe tends to segregate into islands in form of hematite (Fe_2O_3) at the edge of the particles, during repeating oxidizing and reducing cycles [24]. This could make the Fe more accessible and easier to digest, making the isolation of Ti easier.

Despite the advantages that the recycling of ilmenite from boilers could represent for the extraction of TiO_2 , there are also potential pitfalls. One possible drawback could be the presence of contaminants from the ash. This could hinder the pigment extraction and give a final product of poorer quality. Even if that is the case, a market for less pure products exists and it has been reported that some customers could accept a pigment of 85% purity [60]. However, the interaction between ash elements, used ilmenite and sulfuric acid during the extraction steps is important to understand, in order to develop a controllable and standardized process. Literature shows that Fe can alter the color quality of the TiO_2 pigment [61,62]. Thus, Fe present in the leachate should be removed during the process to avoid impact on the final product. For this, a separation method should be developed.

It could also be of interest to develop a method that will allow the handling of elements such as Ca and K, to further improve the pigment production process. Possibly, a process could be developed so that Ca and K can be extracted and used in different applications.

Figure 13 summarizes the main findings of the **Paper III**. The paper showed that:

- The use of ilmenite in fluidized bed boilers can act as a pre-treatment for the ilmenite ore and could allow the reduction of the energy consumption of the overall process.
- The applied method allows for extraction of Ti, Fe, Ca and K from fresh and used ilmenite.
- The used ilmenite develops pores and cracks during the OCAC process, which facilitates leaching by enhancing the exchange surface area and particle permeability.
- The crushed used ilmenite from OCAC CFB boiler releases more Ti and Fe in the leachate than crushed fresh ilmenite.
- The crushed used ilmenite from OCAC CFB boiler releases the main wood fuel ash elements Ca and K in the leachate as a result of to their accumulation in and around the used ilmenite particles.
- The difference in leaching yield between used and fresh ilmenite could also be due to the solubility enhancement of the Ti in used ilmenite, due to its titanate-sulfate form which is more soluble than titanium coupled with iron (FeTiO_3).
- Most of the leaching takes place already after two hours of digestion at 110°C .

Improvement of the method is still needed to reach an industrial yield. Subsequent steps of the sulfate process also need to be investigated, with focus on the purity and composition of the obtained products. Extraction and separation methods could be developed to further improve the quality of the product and recover useful elements which can fulfill new purposes. Finally, industrial scale experiments should be tested.

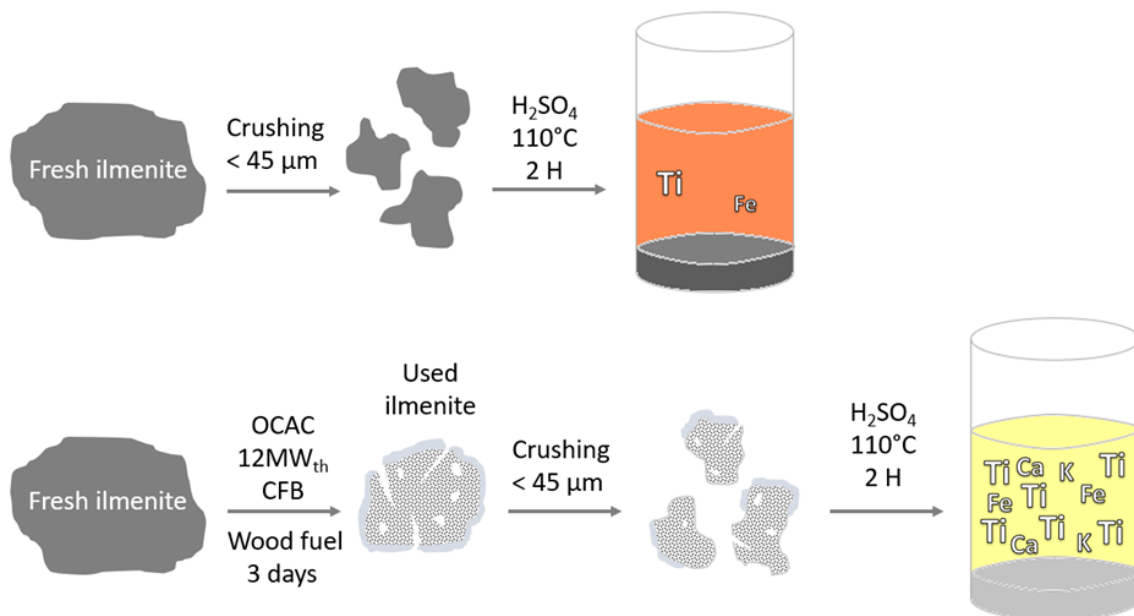


Figure 13. Schematic representation of the experimental steps and the results obtained from the leaching of fresh ilmenite (first line) and used ilmenite extracted from a 12 MW_{th} CFB boiler (bottom line). Used ilmenite which has pores and cracks due to OCAC conditions release higher amounts Ti, Fe, Ca and K in the leachate.

CHAPTER 4 - CONCLUSIONS

This aim of this thesis has been to investigate the interactions between sulfur and ilmenite during OCAC and consider a novel method for management of waste ilmenite generated in OCAC process.

The impact of sulfur additions on the performance of the ilmenite particles as OC in OCAC has also been investigated. Usually, sulfur is added in combustion to counteract corrosion due to the release of alkali chlorides from the wood and waste-derived fuel. It has been shown that sulfur interacts with the bed material and with ash elements from the biomass fuel. It has been observed that sulfur is captured by the ilmenite particles during OCAC. The sulfur is then coupled with the main ash elements Ca and K found in the ash layer around the bed material as well, as in the core of the particles. The release of sulfur in the form of SO_2 has also been observed in 12 MW_{th} CFB boiler and under reducing conditions in a laboratory quartz batch reactor. Ilmenite bed particles can capture sulfur again in the form of SO_2 under oxidizing conditions. The capture and release of sulfur in ilmenite particles is a reversible phenomenon that could be handled by changing the redox conditions in the boiler.

The possibility of the recovery of elements such as Ti has been investigated for ilmenite which has been used as bed material during OCAC with wood fuel. Concentrated sulfuric acid at 110°C was used to mimic the first step of the sulfate process and digest the particles of ilmenite. Used ilmenite showed a better performance in terms of leaching, compared to fresh ilmenite. The used bed material released up to six times more Ti in the leachate compared to fresh ilmenite. The explanation for the observed phenomenon is the presence of pores and cracks formed during OCAC operation. This facilitates for the sulfuric acid to reach the core of particles and allows the particles to be digested, thus giving a higher elements concentration in the obtained leachate. The higher concentration of Ti obtained with used ilmenite could also be due to the presence of potassium titanate, which is formed during interaction with alkali originating from the ash during OCAC. Potassium titanates have a higher solubility in acids compared to titanium coupled with iron (FeTiO_3) found in fresh ilmenite. This could contribute to explaining the higher solubility of the used bed material. It has also been observed that most of the leaching occurred in the first two hours of the experiments. One drawback of having used ilmenite from OCAC as a feedstock for the pigment industry could be the presence of ash compounds Ca and K in the leachate. This would need to be handled downstream and possibly be recovered as well.

CHAPTER 5 - OUTLOOK

Further research is needed, both about sulfur interactions with the bed material and about the recovery of elements of interest from the used ilmenite. Further research can be oriented to:

- Develop the understanding about the mechanism of sulfur capture and release. Work can be carried out on other element interaction with sulfur and on the impact of sulfur on the activity of the bed material.
- Investigate the possibility of reusing ilmenite. The process parameters of the method used in this study could be explored and improved to obtain increased yield. Parameters that could be examined include ilmenite/sulfuric acid ratio, temperature, sulfuric acid concentration. The subsequent steps of the sulfate process also need to be studied and evaluated with used ilmenite. The obtained leachate should be hydrolyzed, and the obtained precipitate should be analyzed. Further understanding is needed to recover elements such as Fe, Ca and K.
- Investigate the possibility of using used ilmenite from other processes, such as CLC with gaseous fuel which is known to result in particle swelling but for which no ash elements are added.
- Investigate the interference with further process steps of the sulfate process of ash elements such as Ca and K, to determine their impact on the quality of the final obtained product.

NOMENCLATURE

BET	Brunauer – Emmett – Teller
CCS	Carbon Capture and Storage
CFB	Circulating Fluidized Bed
CLC	Chemical Looping Combustion
FB	Fluidized Bed
OCAC	Oxygen Carrier Aided Combustion
OC	Oxygen Carrier
SEM-EDS	Scanning Electron Microscopy coupled with Energy Dispersive X-ray
ICP-SFMS	Inductively Coupled Plasma - Sector Field Mass Spectrometry
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectrometry

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