

Recycling or depositing – a study of ilmenite ore used as oxygen carrier in chemical-looping combustion and fluidized bed boiler

Maria Brorsson

Department of Environmental Inorganic Chemistry, Chalmers University of Technology,
S-412 96 Gothenborg, Sweden

Abstract

The aim of this work is to evaluate ilmenite that has been used as an oxygen carrier and gain more understanding of the deactivation of it. Furthermore, the aim is to look at possible solutions to dispose of the used ilmenite material. This report investigates the state of the material after use as a bed material in two different thermo chemical processes, chemical-looping combustion and circulating fluidized bed combustion. The ilmenite material is a popular candidate due to its low price and sufficient mechanical and chemical stability in fluidized bed reactors. The end goal is to find possible solutions for material handling after depletion -landfill depositing, recycling or usage of the depleted ilmenite as a feedstock for the titanium dioxide industry.

Even though ilmenite shows promising properties as bed material, earlier research indicate deactivation of the oxygen carrier. This report looks at the changes in elemental distribution in the material with Scanning electron microscope equipped with EDX and X-ray diffraction. The crushing strength of the particles was tested. It is found that the crushing strength of the material declined after being used and the iron in ilmenite make iron oxide layers on the edges of the particles. Leaching tests performed in water showed that the ilmenite had no effect. The possibility of landfill can therefore be considered. There might not be a way to dissolve and recycle the used ilmenite as bed material with water only.

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1. Introduction

According to the 2013 IPCC report there is at least a 95 percent certainty that anthropogenic activities are the main cause for the climate changes seen today. (Stocker, o.a., 2013) Anthropogenic emissions of greenhouse gases originate mostly from burning of fossil fuels, such as oil, coal and natural gas for generation of electricity and heat (Stocker, o.a., 2013). In order to decrease the CO₂ emissions in to the atmosphere, alternative solutions for capturing and storing CO₂ and more effective electricity generation (thermal conversion) need to be found were less CO₂ equivalents per kWh are released into the environment.

Carbon capture and storage (CCS) technologies is one possible way to proceed. CCS is a process that aims to utilize for example depleted oil and natural gas reserves, deep down into the earth's crust, for storage of liquid CO₂ (Halmann & Steinberg, 2000). It can also be done by releasing CO₂ on the sea floor, deep enough to keep it in a liquid form where the gas has high enough density to stay on the ocean floor. (de Lasa & Hossain, 2008). The main point of CCS is to store the greenhouse gasses that would otherwise be increasing the greenhouse effect.

Chemical-looping combustion (CLC) represents one of the possible and promising alternatives for CO₂-capture for CCS. CLC equivalent techniques for more efficient burning have been known since the mid-1950 (Lewis & Gilliland, 1954). It is based on the concept of burning fuel with oxygen only provided by a solid oxide rather than with air, which contains almost 80% nitrogen. By doing so one can avoid N₂ from the air to be mixed with the combustion gases. The technology offers a way of getting smaller gas volumes and cleaner CO₂ (Lewis & Gilliland, 1954). This is important for CCS, since smaller gas volumes are much easier to handle. (Adanez, o.a., 2010) (Abad, o.a., 2011).

CLC is a process that uses a fluidized bed particles to acts as oxygen carrier (OC) between a combustion reactor and an air reactor (Lyngfelt, 2013) (Linderholm, Knutsson, Schmitz, Markström, & Lyngfelt, 2013). It has been evaluated many times for solid fuels. (Mattisson, Lyngfelt, & Leion, Chemical-looping with oxygen uncoupling for combustion of solid fuels, 2009) (Leion, Mattisson, & Lyngfelt, Solid fuels in chemical-looping combustion, 2008) (Leion, Mattisson, & Lyngfelt, The use of petroleum coke as fuel in chemical-looping combustion, 2007) (Berguerand & Lyngfelt, 2008)

Oxygen carriers can also be used for combustion in Circulating Fluidized Bed Boilers (CFBB) and can when altered, in a similar fashion, transport oxygen in one reactor. (Jansson & Leckner, 1982) (Corcoran, 2013). The conversion of fuel becomes more efficient and the heat is dispersed more evenly. (Thunman, Lind, Breitholtz, Berguerand, & Seemann, 2013) The report will cover ilmenite tested in CLC and CFBB at Chalmers university of Technology. The purpose is to investigate the used ilmenite and look at possibilities for the material after usage.

2. Background

This chapter aims to explain how chemical-looping combustion and fluidized bed boilers works and what role the oxygen carrier plays in the processes. It will also give a short presentation about ilmenite. Where it comes from, how it is used as an oxygen carrier and some of the possible explanations of the deactivation of the particles found so far.

2.1 Chemical-loop combustion

The most commonly used setup for performing a continuous CLC process is two interconnected fluidized bed reactors, one air reactor (AR) and one fuel reactor (FR) as shown in figure 1 below. Both of them contain a fluidized bed of oxygen carrier which facilitates the circulating between the reactors. A fluidized bed is particles that have a gas flow which lifts or moves the particle. V_{mf} is the critical flow at which the force of the gas exceeds the gravitational force on the particles, and the bed material enters a fluidized state. The oxygen carrier has the notation $Me_xO_{(y-1)}$ when it enters the AR and Me_xO_y when it exits the AR in the figure below. This means that the carrier has gained one oxygen atom per unit. In the FR the oxygen carrier becomes reduced and then the bed particles recirculate with the gas to the AR. At the top of the FR a gas mixture of H_2O and CO_2 exits, under normal operation conditions. CO_2 can then be stored with appropriate CCS technique or utilized in another chemical process. To the FR a stream of Fuel, such as coal, syngas or biofuel is added to the reactor. The notation Air, entering the AR, is normal air with around 20% oxygen that the bed can pick up.

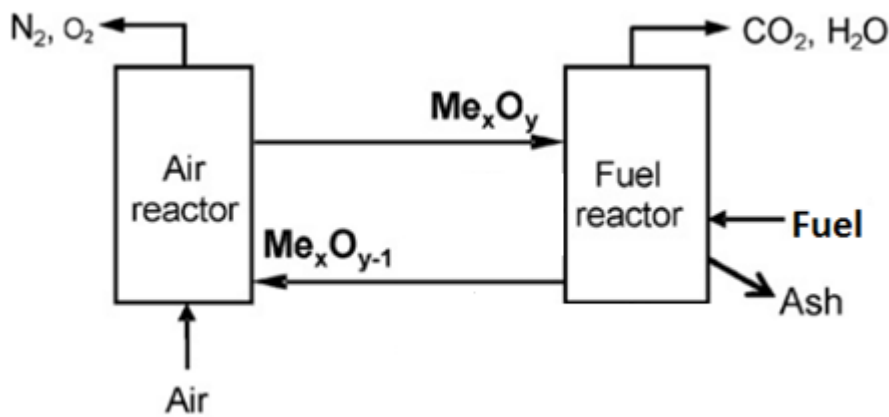
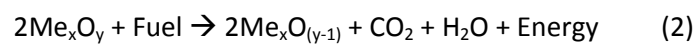


Figure 1. A widely used, general schematic of a CLC setup with a carbon stripper.

In the AR the oxygen carrier oxidizes following equation (1). The oxidized OC is then transported to the FR where it is reduced by the fuel according to equation (2). The OC is then re-circulated back to the air reactors for oxidation.



2.2 Combustion in Fluidized Bed Boilers

The combustion in CFBB is a commonly used technique to burn solid fuels in a single reactor unit. It contains a fluidized bed with materials that can be circulated or replaced continuously as needed. In the figure below, figure 2, we see a principal schematic of a CFBB unit with oxygen carrying material in the bed. At the bottom of the reactor the primary air is added and can be regulated. On the left we see the fuel feed of solid fuel. At the top right the flu gas exits and at the bottom right the oxygen carrier circulates to, in this case, and external gasifier. However the gasifier is specific for the Chalmers boiler (Thunman, Lind, Breitholtz, Berguerand, & Seemann, 2013).

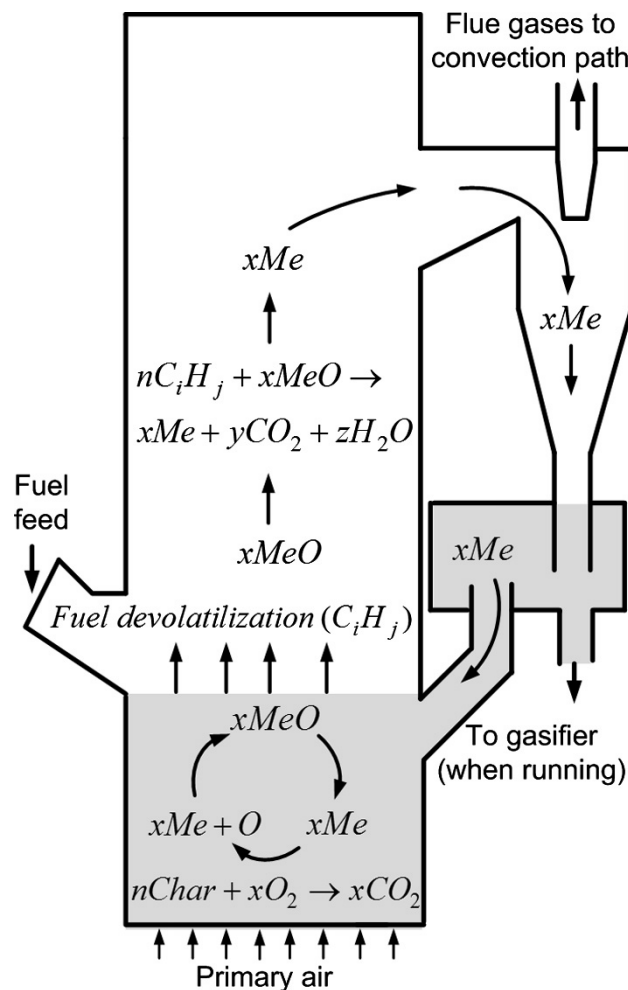


Figure 2 An elaborate schematic of a Combustion fluidized bed boiler with oxygen carrying material as bed (Thunman, Lind, Breitholtz, Berguerand, & Seemann, 2013).

The goal of a combustion unit is to convert as much of the fuel as possible into heat and/or work. The fuel conversion in the CFBB be can be increased by increasing the primary flow of air (gaseous oxygen) into the reactor but this decreases the overall efficiency. (Thunman, Lind, Breitholtz, Berguerand, & Seemann, 2013) The CFBB has a fluidized bed in the main reactor that disperses the fuel, air and heat evenly over the combustion chamber (Thunman, Lind, Breitholtz, Berguerand, & Seemann, 2013). When the particles in the fluidized bed in a CFBB unit is replaced with a suitable oxygen carrier the CFBB becomes more efficient at converting the fuel and produce cleaner off-gases without the need for extra airflow. (Thunman, Lind, Breitholtz, Berguerand, & Seemann, 2013) (Corcoran, 2013).

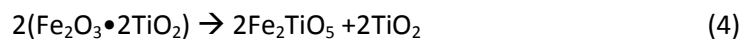
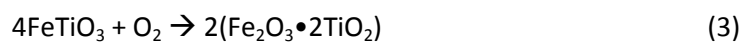
2.3 Ilmenite as oxygen carrier

A lot of research has already been done to find a suitable OC (Abad, o.a., 2011) (Corcoran, 2013) (Hallberg, Leion, & Lyngfelt, 2011) (Leion, Mattisson, & Lyngfelt, 2009) (Mayer, o.a., 2013) (Moldenhauer, Rydén, Mattisson, Younes, & Lyngfelt, 2014) (Schwebel, o.a., 2014) (Schwebel, Leion, & Krumm, 2012) (Leion, Lyngfelt, Johansson, Jerndal, & Mattisson, 2008). The OC of choice must fulfill certain requirements in order to be considered a suitable candidate. It is important that the material has sufficient reactivity towards atmospheric oxygen and fuel. Mechanical strength, high melting point and low manufacturing cost are also favored criteria. The OC needs to withstand the

conditions in the fluidized bed reactor and large quantities are needed due to the possible material degradation. Different Fe-, Cu- and Mn-oxides have been tested to find the most suited OC (Mayer, o.a., 2013) (Leion, Mattisson, & Lyngfelt, 2009) (den Hoed & Luckos) (Leion, Mattisson, & Lyngfelt, 2009). Using chemical-looping with oxygen uncoupling (CLOU) for combustion of six different solid fuels, 2009). Ores and by-products from the metal industry have been tested because of their low cost, available quantities and the oxide content which provides abilities to carry oxygen. (Leion, Mattisson, & Lyngfelt, 2009).

Ilmenite was found in a study to be a good candidate. (Leion, Mattisson, & Lyngfelt, 2009) It's not the most efficient OC but it's cheap and mechanically stable which makes it good for use in a fluidized bed. (Leion, Mattisson, & Lyngfelt, 2009) The main component of the ore is FeTiO_3 but depending on where in the world it comes from, there are ores containing more or less titanium dioxide and other phases of titanium (McNulty). The world's reserves as of now are mainly located in South Africa, Australia, India and North America, and are being mined for the raw titanium (Murty, Upadhyay, & Asokan, 2007). Ilmenite today is mostly used for titanium dioxide production and a small part for pig iron and titanium metal (Findorak, M. Fröhlichová, & Legemza, 2014)(Mehdilo & Irannajad, 2012). Titanium dioxide, which is mostly used for pigment, is abundant from other sources and extracting ilmenite for pigment have not been prioritized until later years (Mehdilo & Irannajad, 2012). This is because ilmenite has lower content of titanium and needs more processing (McNulty) (Murty, Upadhyay, & Asokan, 2007). One of the problems with ilmenite used in the pigment industry is the separation of iron from the ore (Mehdilo & Irannajad, 2012). The already ongoing mining and low price makes it a good candidate as an OC in CLC- and CFBB-processes (Leion, Mattisson, & Lyngfelt, 2009) (Corcoran, 2013) (Abad, o.a., 2011) et al.

A previous done laboratory study with ilmenite as an OC in CLC showed that the ilmenite seems to undergo oxidation/reduction with at least two likely intermediates. Possible phase are Fe_2O_3 , $\text{Fe}_2\text{O}_3 \bullet 2\text{TiO}_2$, pseudobrookite, rutile and ilmenite. (Leion, Lyngfelt, Johansson, Jerndal, & Mattisson, 2008) The most often suggested processes that ilmenite undergoes when used as an OC is summarized in equation (3) and (4) below.



There are multiple theories for the reasons of declining activity of the ilmenite when used as an OC. One reason can be the migration of iron to the surface of the particles. This in turn increases reactivity, but decreases the oxygen carrying capabilities. And the particles show cracks in the same places where the iron is enriched. (Corcoran, 2013) (Adanez, o.a., 2010) Both laboratory and upscale tests show that there is a considerable activation time for ilmenite. (Abad, o.a., 2011) (Adanez, o.a., 2010) And one study suggested pre-calcination of the ilmenite. (Adanez, o.a., 2010)

The aim of this work is to further evaluate ilmenite that has been used as an OC and gain more understanding of the deactivation of it. Furthermore, the aim is to look at possible solutions to dispose of the used ilmenite material. One goal with OC based technologies today is to make it useful for large scale energy plants running on biomass or other renewable fuels. The handling of used material is an issue which has to be investigated. Possible solutions for the handling of used ilmenite are through deposition in landfills or chemical recycling of the material. Material recycling is

regarded as the preferred option at least environmentally. According to the Swedish environmental agency, the possibility of landfill has to be examined and evaluated in every single case. A permit for one combustion plant might not go through for another of the same type. This depends on factors like location and/or fuel.

Several series of samples from earlier studies with different running parameters, both CLC and CFBB, are obtained and compared with fresh ilmenite from Norway, Titania. (Corcoran, 2013) (Linderholm, Knutsson, Schmitz, Markström, & Lyngfelt, 2013) A more detailed list follows later on in the text. In the first phase of the experiments only differences in the materials crushing strength and appearance are noted. Later on, samples that show different properties, both generally and compared to unused ilmenite, are examined closer with Scanning Electron Microscope (SEM) and X-ray diffraction (XRD), where the focus was to look for morphological and chemical changes that can explain the observed deactivation. All taken samples are investigated for the option of being disposed into landfill or as a building material by a series of leaching tests that are later analyzed with Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) to see if used ilmenite potentially pollutes water when exposed to rain and weather. It is also investigated if the possibility of dissolving the material in a clean and non-toxic solvent like water is possible.

2.4 Deactivation of oxygen carriers

The redox, oxygen carrier-loop in CLC and CFBB is repeated continuously and could continue indefinitely if the OC did not deactivate with time (Adanez, o.a., 2010) (Corcoran, 2013) (Abad, o.a., 2011) (Hallberg, Leion, & Lyngfelt, 2011) (Moldenhauer, Rydén, Mattisson, Younes, & Lyngfelt, 2014) (de Lasa & Hossain, 2008). This is the main problem being evaluated in this report. An earlier laboratory scale study showed increase in reactivity, with increasing numbers of cycles, of ilmenite used as an OC with syngas as fuel. There was no decrease in reactivity after 37 cycles. (Leion, Lyngfelt, Johansson, Jerndal, & Mattisson, 2008) When ilmenite were run for longer time and more cycles in another experiment it reaches a peak and then declines as seen in this figure 3. The figure is from a study made on ilmenite during consecutive red-ox cycles in CLC in a laboratory scale reactor with solid fuel (Adanez, o.a., 2010).

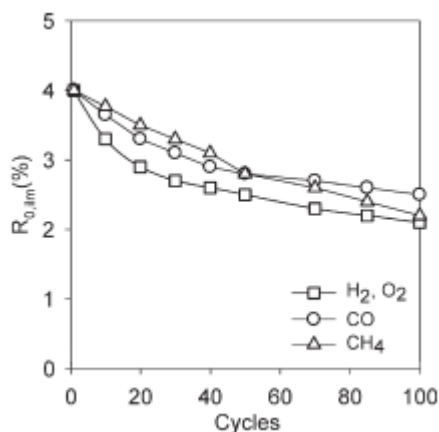


Figure 3 Variation of the oxygen transport capacity plotted against running cycles (Adanez, o.a., 2010)

3. Experimental set-up

This chapter aims to describe the methods used to analyze the different ilmenite sample and what operational conditions the samples were exposed to prior to analysis.

3.1 Sample source

All the described samples are obtained from Chalmers University, department of Energy Technology. Materials from the fluidized bed of a 100kW CLC pilot unit and a 12 MW CFB boiler were taken out at different exposure times on earlier experiments (Linderholm, Knutsson, Schmitz, Markström, & Lyngfelt, 2013) (Corcoran, 2013). Samples of fresh ilmenite, heat-treated ones and calcinated were also analyzed as listed in table 1. The bed materials were exposed to two different types of fuel listed in table 1, bituminous coal in the CLC unit and wood chips in the CFBB. The chosen samples are specified in table 1. The ilmenite this study was originally obtained from Norway Titania. This ore is mined and crushed to a desired grain size between 180 and 250 μm . In the figure 4 below a schematic representation of the 100kW CLC-unit is shown as well as an image of the used setup. (Linderholm, Knutsson, Schmitz, Markström, & Lyngfelt, 2013)

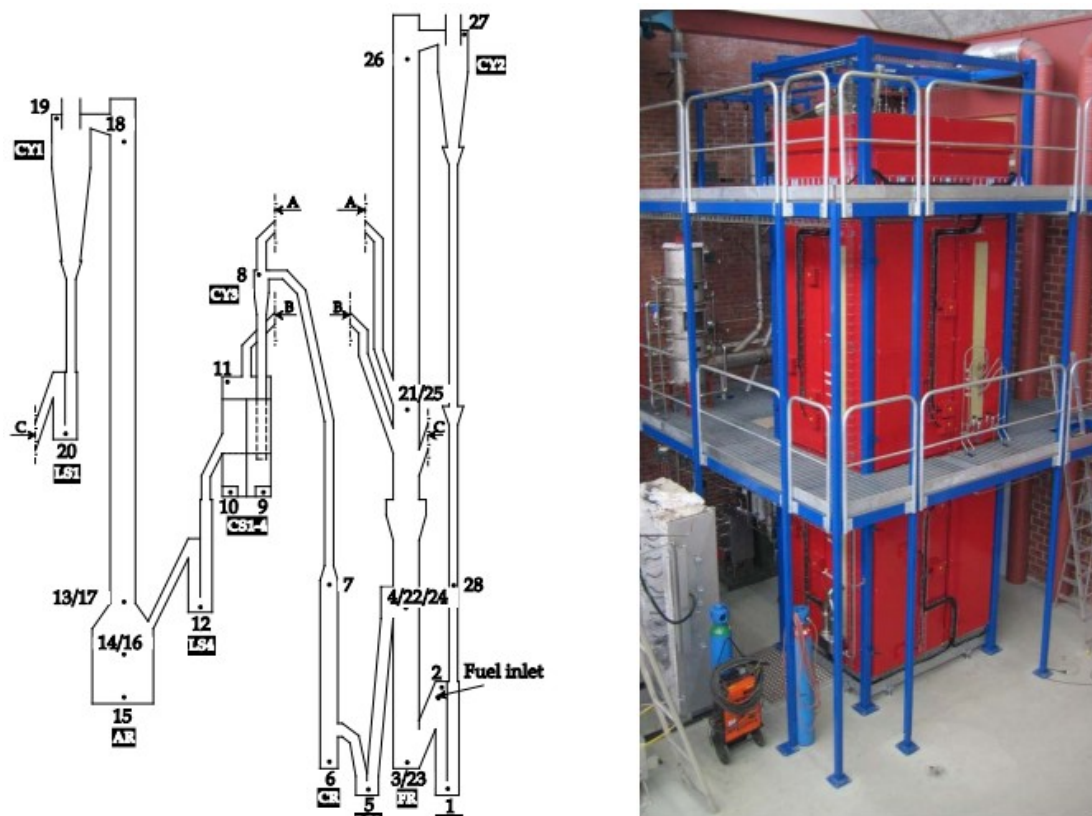


Figure 4 To the left: a schematic map of the CLC pilot unit at Chalmers University, department of Energy Technology, the samples comes from the loop seals (LS2, LS3 and LS4) and reactor filters. All samples were taken after the same runtime. (Linderholm, Knutsson, Schmitz, Markström, & Lyngfelt, 2013) To the right: a photograph of the CLC pilot unit at Chalmers University, Energy engineering department. Picture taken specifically for this report.

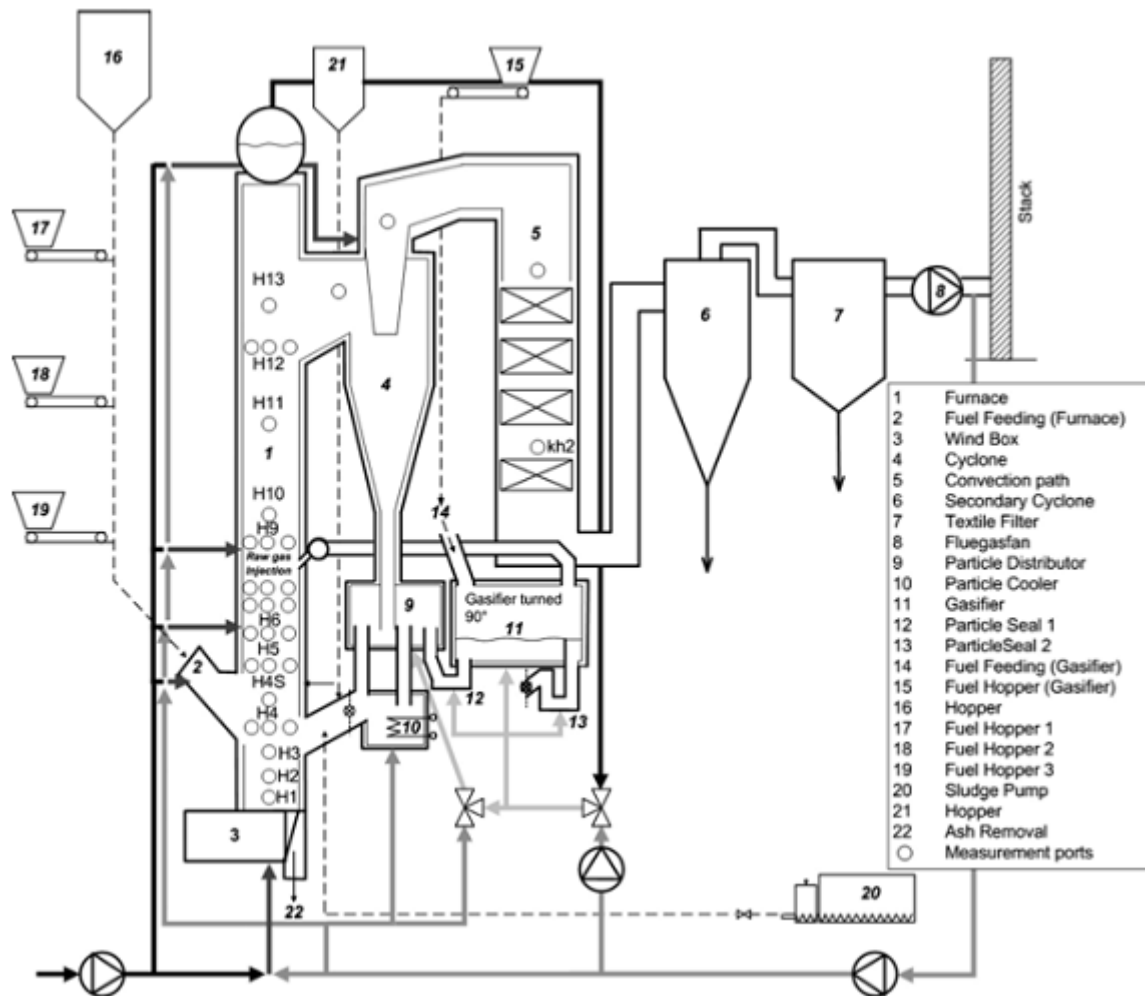


Figure 5 A schematic figure of the 12000kW (12MW) CFB boiler at Chalmers University, department of Energy Technology. The samples come from the cyclone at number 4 at different runtimes. (Corcoran, 2013)

Above is a schematic figure of the 12MW CFB boiler at Chalmers, department of Energy Technology. The samples were taken from the primary cyclone marked as nr 4 in the figure 5 above.

The properties of exposed samples are compared to the ones of fresh materials with consideration to the operation parameters. The location where the samples are extracted (e.g. airlocks, filters or cyclones) on the different reactors are presented in Table 1.

Sample	Runtime (h)	Plant type (kW)	Fuel
Fresh ilmenite CFBB	0		
Ilmenite cyklonleg nr. 4 >24h	24	12000 kW CFBB	Wood chips
Ilmenite cyklonleg nr.4 > 72h	72	12000 kW CFBB	Wood chips
Fresh ilmenite CLC	0		
Ilmenite (reduced) FR, filter	12	100 kW CLC	Bituminous coal
Ilmenite LS2	12	100 kW CLC	Bituminous coal
Agglomerate LS2	12	100 kW CLC	Bituminous coal
Ilmenite LS3	12	100 kW CLC	Bituminous coal

Table 1 Samples chosen for further evaluation, with number, description, runtime (RT), plant magnitude and type of combustion fuel.

Important physical parameters are for example structural integrity and crushing strength. These parameters influence fluidization-properties of the ilmenite (Corcoran, 2013). This is because a weaker particle or a material that loses strength over time will break. The particles in the reactors are subject to agglomeration or particle disintegration due to the force of the airflow in the reactor walls combined with heat. The bed material that breaks down can exit the unit with the ashes and some particles agglomerates on the inside into lumps or incrustation. In worst case scenarios the air/solid balance breaks down and the fluidized bed unit blows away the bed material leaving nothing but gas in the reactor. This happens when the particles become too small for the set airflow and is normally uncommon.

3.2 Crushing strength

A screening of all samples was done by measuring the crushing strength. This was done with a Shimpo FGN-5. The testing was done on 30 particles from each batch of the samples for statistical viability. Crushing strength gives a hint as to how much force the particles can take before breaking. The setup consists of a handheld chisel and an anvil, small enough to have on a table, with a newton meter attached to it. The particles are measured one by one by pressing down with the chisel manually until the first cracking noise is heard. The newton meter then displays at what force the particle broke. This gives a hint to which samples have stronger structural integrity.

3.3 Sample molding and SEM

As a second step samples of interest were prepared for SEM and X-ray diffraction (XRD). The samples chosen were the fresh, unused ilmenite and the ilmenite that showed considerable change in crushing strength and color. For SEM this was done by molding the particles into epoxy in 30 mm molding cups and allowing the epoxy resin to harden for 24h. The produced coupons were fine grinded in order to create a flat cross-section of the ilmenite particles. The grinding was done with a TegraPol-31 and a TegraPol-5 arm for 30 second t with 500, 1000, 2400 and 4000 grit size grinding paper until a smooth, metallic surface was obtained that could be observed in an ordinary optical

Olympus microscope. As a last step the samples were gold plated and had small copper strips wrapped around them to prevent charge buildup in the SEM. This preparation enabled analysis of morphological changes as well as changes in the chemical composition and elemental distribution within the particles by SEM-EDX.

The SEM is an electron microscope that scans an electron beam over the sample in vacuum. The electrons hit the atoms of the samples and emissions are excited from the sample as either secondary electrons or backscattered. Backscattered electrons are high-energy electrons which are emitted when electrons from the beam are elastically scattered by the core of the atoms on the surface of the samples. This collision gives information about the elemental composition of the surface. Secondary electrons are low-energy electrons and give information about the surface structure variation of the particles. A detector transforms the back-scattered and secondary electrons emissions into a signal which is used to create an image of the samples surface. If the sample has a low conductivity there might be a buildup of electrons which can disturb the image. (Goldstein, 2003) This was the reason why gold plating and copper strips were necessary, as epoxy has very low electron conductivity.

3.4 XRD

All samples were also evaluated by XRD for phase compositional changes before and after exposures. XRD is a method for determining the crystalline structure of compounds. By knowing the exact positions of the atoms, their binding length and angle between the bonds, the unit cell parameters are known. Every element has a unique diffraction pattern that is matched to a reference database and the compounds in the sample can be determined with high plausibility.

3.5 Leaching

The leach ability of harmful constituents from a bed material limits the possibility to deposit the bed materials in a landfill. Therefore a bed material that does not leach is cheaper and easier to deposit. A criterion is that good bed materials don't need pretreatment before depositing. Leaching on used ilmenite with water was done on the samples. All the samples collected from the fluidized bed of a 100kW, the 12 MW CFB boiler and the laboratory treated samples including the ones not chosen for SEM and EDX, were then evaluated for potential landfill deposition by their ability to leach in water. This was done by leaching in water according to a modified version of SS-EN 12457-2 for 72h on a shaking table. Modifications to the method were done with respect to the liquid to solid ratio. A liquid to solid ratio of 1:8 were used to create enough sample for both AAS and ICP-OES. The leaching extract was filtered using a 2 µm filter and diluted 1:50 with 1 % HNO₃. The analysis was performed by ICP-OES and AAS for comparison.

3.6 AAS

AAS is used for detection and quantification of elements in solution. In this project an open flame burner were used with acetylene gas as fuel. The AAS were performed on a PE AA800 with a multi element lamp. A manual method was chosen with a wavelength of 306.1 for Fe. The light from just the element lamp is compared to the light absorbed when the lamp beam goes through the flame. A standard curve was constructed with 0.25, 0.5 and 0.75 mg/l Fe dissolved in distilled water, diluted from a 1000ppm stock solution. The method cannot show result below 0.006 mg/l and therefore any lower results are displayed as <0.006 in table 3.

3.7 ICP-OES

ICP-OES, Inductively coupled plasma optical emission spectrometry, is an analytical method that is used to quantify or detect ions and atoms in a solution. This makes it good for finding trace elements but the detection limit varies greatly with the detector used. The ICP uses argon plasma in which electrons are accelerated. The electrons then collide with atoms and energy is transferred to the plasma. Some of the atoms/ions are then excited to a higher state and when they later return to the ground state they emit characteristic wavelengths revealing the type of element. ICP-OES analyses were performed with a calibration curve containing 4 points. A multi standard of Ti, Fe, Al, a natural variation in iron rich ores, and K, known for being present when burning biofuel (Corcoran, 2013) were prepared with concentrations 20 ppm, 10ppm, 5ppm and 2.5ppm to fit the methods detection range. All the leaching samples were diluted ten times with 1 molar nitric acid. The methods detection range for Ti and Fe are 0,005 ppm, for Al 0.02 ppm and for K 0.1 ppm. The choice of elements depended on the theoretical composition of ilmenite (Fe and Ti), the natural variations of other elements in ores and the known elements in the fuels used (Corcoran, 2013) (Mayer, o.a., 2013).

4. Results and discussion

4.1 Elemental changes – possible reasons for deactivation

The initial ocular screening and integrity testing showed changes in color and in crushing strength (CS) when compared to the fresh ilmenite. As mentioned earlier the ore is untreated before use. This might lead to natural variations in composition depending on the origin of the ore. Some deposits might have other metal oxides present as alumina oxide or manganese oxide. Due to the uncertainty of the method with Shimpo FGN-5 when measuring crushing strength and ocular evaluation these values should not be considered as definitive. The hand strength and eyesight of the analyst affects the value. The values obtained are listed in table 2 below.

Sample	Runtime (h)	CS (N)	Ocular description
Frech ilmenite CFBB	0	4,7	Black, metal shine.
Ilmenite cyklonleg >24h nr.4	24	2,7	Black, matt.
Ilmenite cyklonleg >72h nr4.	72	2,2	Dark brown, matt, white particles present.
Fresh ilmenite CLC	0	5,8	Black, metal shine.
Ilmenite (reduced) FR, filter	12	1,1	Dark brown grey, matt, coal and white particles.
Ilmenite LS2	12	3,8	Black, matt. A lot of agglomeration.
Agglomerate LS2	12	1,2	Brown, matt, white particles present.
Ilmenite LS3	12	2,7	Dark brown, matt, white particles present.

Table 2 Table of fresh ilmenite from Norway Titania A/S, samples from the CFB boiler and the fluidized bed reactor.

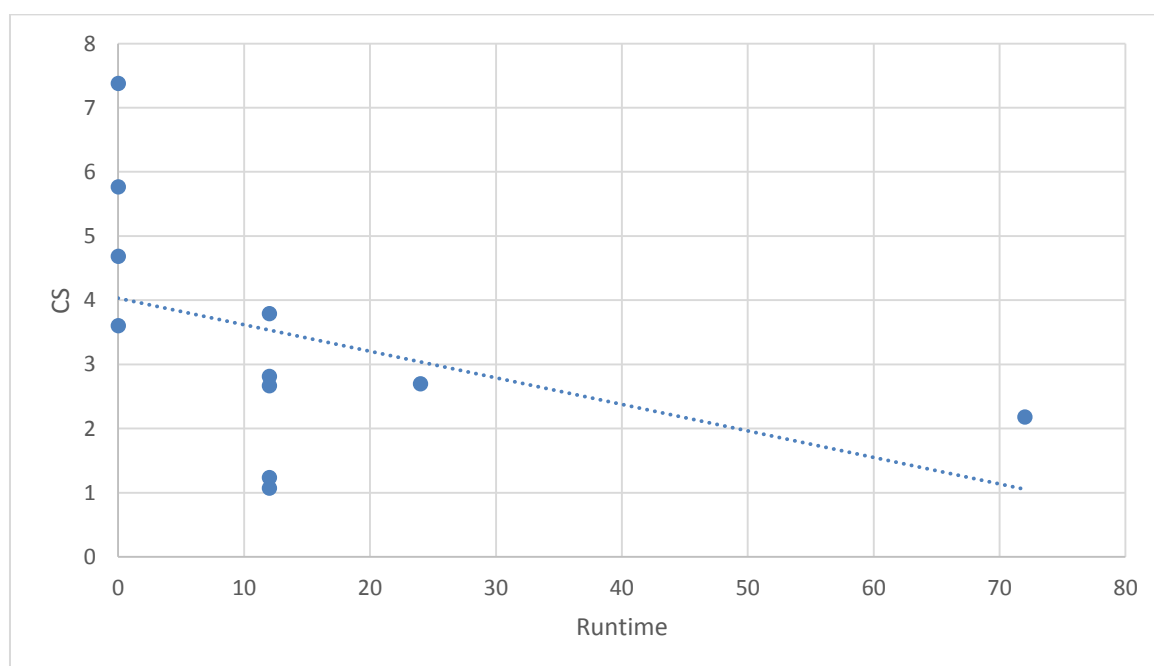


Figure 6 This plot of the CS versus the runtime shows a falling trend line.

The trend in figure 6 show a decrease and therefore a possible loss of structural integrity, but the data are scattered and the trend is therefore uncertain. This phenomenon is supported in earlier research where the incomplete oxidation and reduction of ilmenite is speculated to cause decrease in hardness (den Hoed & Luckos). The particles from the loop seal of the 100 kW CLC unit, described as LS2 in table 2 and figure 3, contained heavy agglomerates. Low crushing strength might cause the material to disintegrate and break down into smaller particles. These particles can then melt and create agglomerates that get transported to the loop seal. The difference in appearance, from black to red, of the ilmenite for samples from the CLC air locks and the boiler bed material suggests oxidation of the material. Fresh ilmenite, from crushed ore, has a black metal glow and the particles have sharp edges as seen in the SEM-image, figure 7 below. However, despite all precautions taken to prevent charge buildup in the sample used in SEM there is still charging artifacts seen in figure 7. When working with ilmenite in the future acquiring a conducting epoxy resin is therefore recommended.

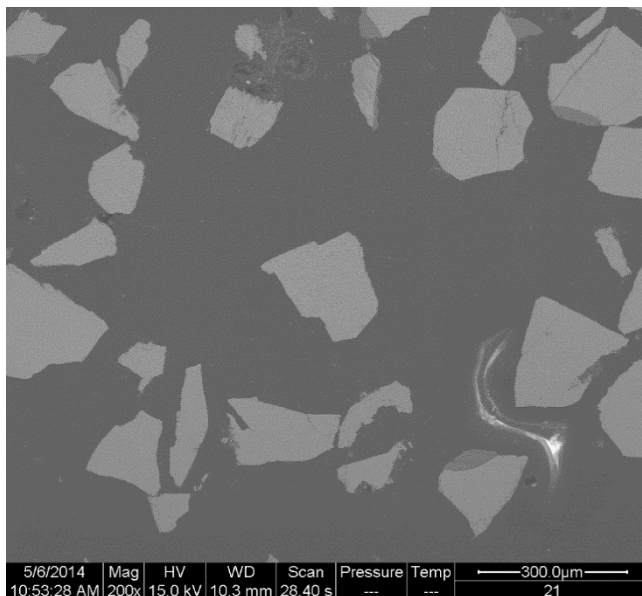


Figure 7 Unused ilmenite from Norway Titania A/S, the white smoky structures in the picture are due to charge buildup.

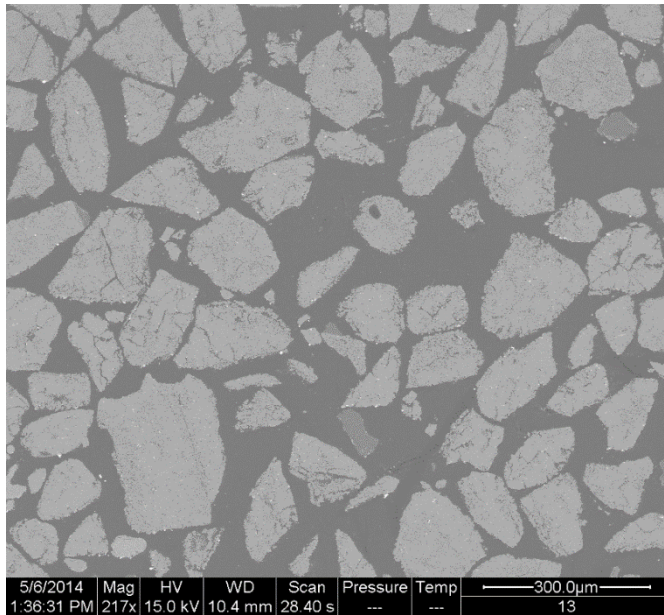


Figure 8 Ilmenite particles after 12 h runtime in the 100kW CLC unit.

In figure 8, a picture of used ilmenite can be seen from one of the particles locks in the 100kW CLC unit. The sample has been in operation for after 12 hours. Comparing with figure 7 there is clearly a difference after usage. The edges are slightly rounder and cracks within the particles have started to form. On particles that have been used as OC in the 12MW boiler for 72 h morphological changes is even more apparent, figure 9. The edges are rounder and there are a lot of bubble-like formations and cracks. The changes in morphological appearance support the decrease in crushing strength as shown previously.

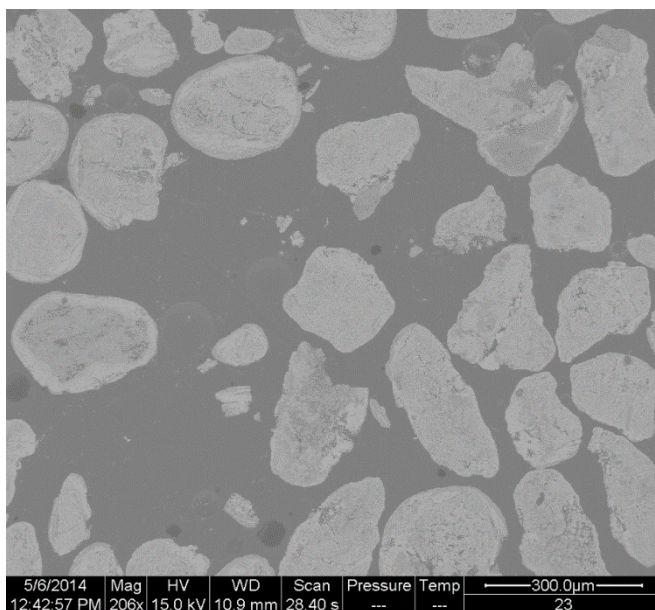


Figure 9 Ilmenite particles after 72h in a CFB boiler.

A closer look at the elemental composition with EDX shows an interesting migration of iron outward to the surface of the particles when the ilmenite is used. This can be a possible explanation for the change of color and deactivation. The particles form iron oxide layers on the surface. The first picture, to the left in figure 10, shows one particle of fresh ilmenite material. The second image is of a particle from the boiler after 72h of running in the CFBB. There is clearly a change in the distribution of the elements across the particle. The Fe, that is the most active element carrying oxygen in ilmenite, is migrating to the edges and forms iron oxides. When the materials then continuously are exposed to heat and mechanical forces the iron oxide layer might become thinner. To conclusively see if this is the case, samples needs to be studied from longer runs than 72h. If this is the case the ilmenite particles might permanently loses its ability to carry oxygen and the lost iron needs to be located for recycling.

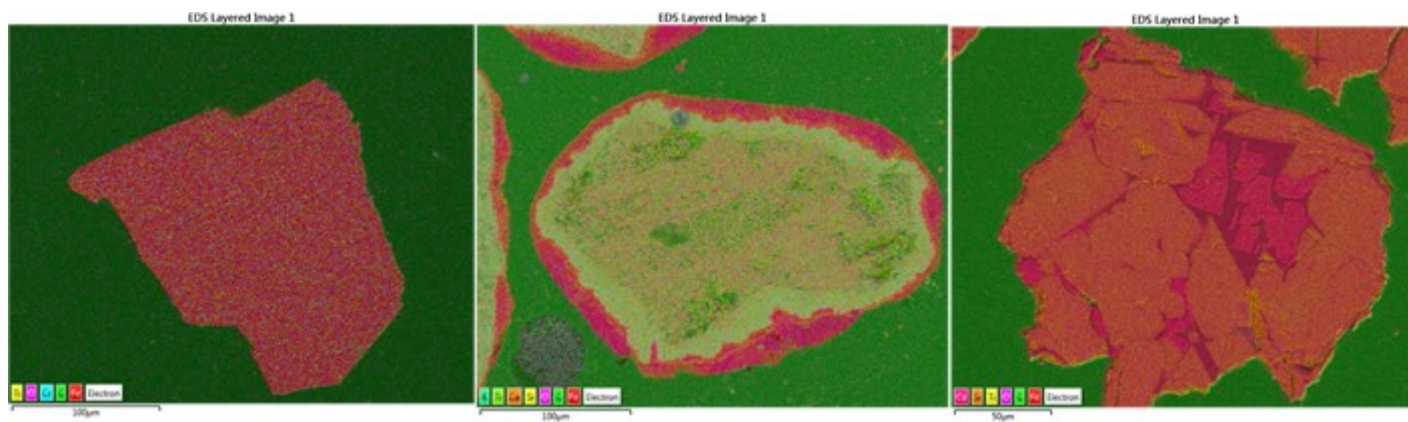


Figure 10 Left: An element mapping of unused ilmenite. Middle: Element mapping of ilmenite from 72h in a CFB boiler. Right: Element mapping of a particle run 12h in a bi-reactor CLC setup. In the figures to the left and right, the red color represents iron, yellow titanium and dark green carbon. In the figure in the middle, the light green color is representing titanium, red is iron and dark green is carbon.

In order to further observe whether the Fe migration can be connected to change in the crystal structure the same sample as were run in the SEM were evaluated with XRD. The fresh ilmenite shows the phases expected and samples used have phases of magnetite. Figure 11 shows an XRD diffractogram from the 12MW boiler sample series. The figure shows the fresh, unused ilmenite from the same batch as the ilmenite feed into the 12MW CLC. As expected the material contains Ti, Na, K, and Ca-containing phases with oxygen and Fe_2O_3 .

Fresh_ilmenite_boiler (TwoTheta)

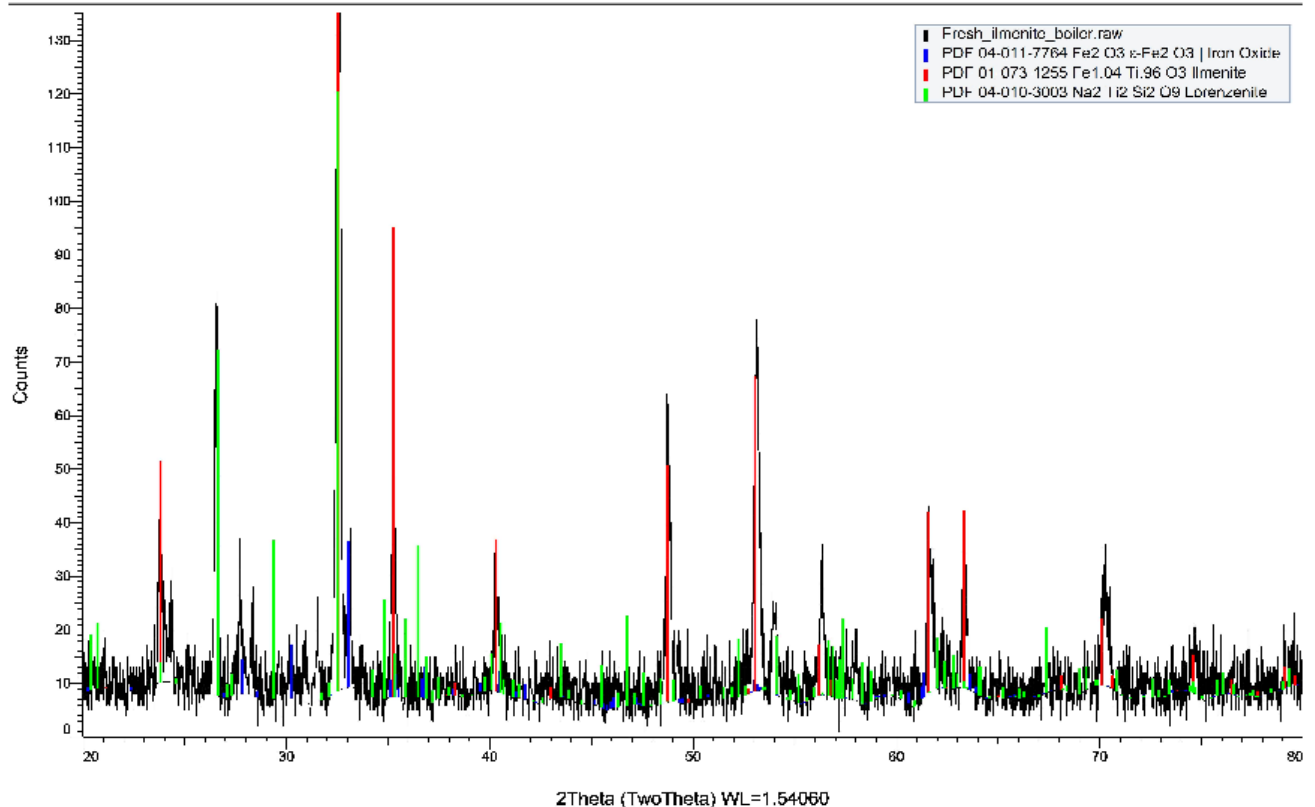


Figure 11 Diffraction with identified phases of ilmenite on fresh ilmenite particles.

Figure 12 from 24 h runtime, shows that some of the phases in the crystal structure have changed in terms of ratio of iron and titanium, with decreased titanium to iron ratio. Other phases are also identified where the titanium has bonded with elements, originating from the fuel. This can suggest that the migrating iron that separates from the ilmenite becomes more available to form other crystal phases. A possible explanation of deactivation can then be that these other crystal phases have a slower expansion rate than the original ilmenite, and therefore chips off when heated. But further investigation is needed. Figure 13 is also from the CFB boiler and just as before shows magnetite.

Ilmenit cyklonleg 24h (TwoTheta)

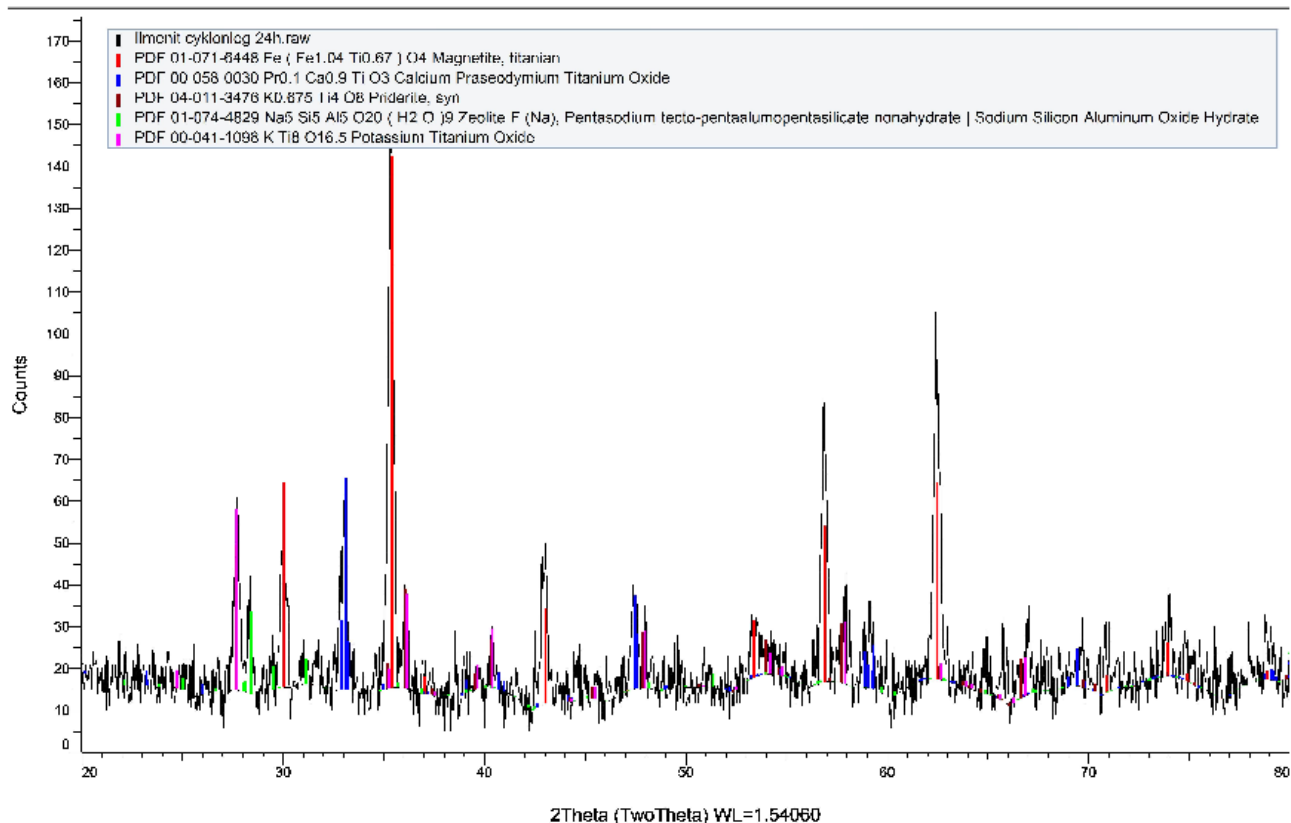


Figure 12 Diffractogram from 24 h runtime.

Ilmenite cyklonleg >72h (TwoTheta)

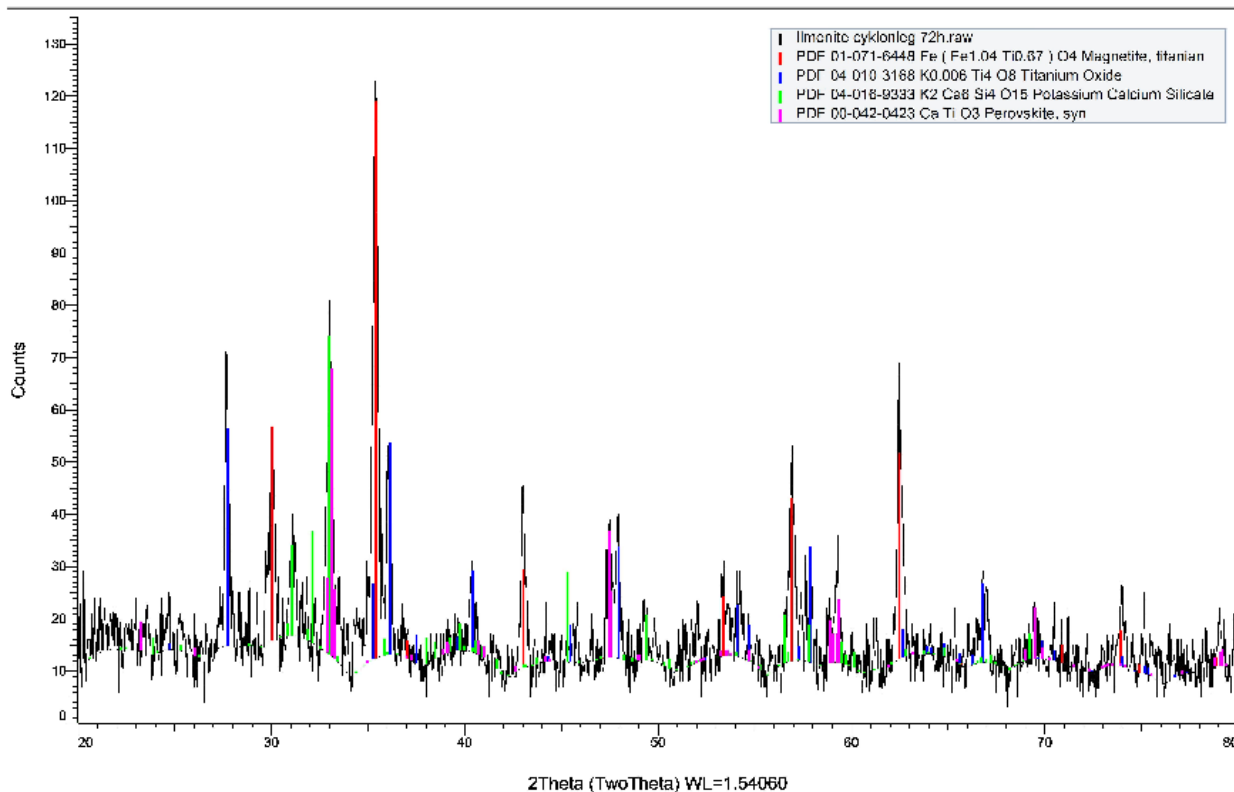


Figure 13 Diffractogram of ilmenite after 72h in the CFB boiler.

Figure 14 a XRD diffractogram is presented for particles used for 12 H in the CLC unit. The sample is taken in the particle lock marked LS4 in figure 4. Pseudobrookite was found in the sample. It is a phase of ilmenite that is more oxidized. This was also seen in an earlier study (Leion, Mattisson, & Lyngfelt, 2009). Generally the material first becomes more oxidized, increases its capacity as an OC, then the iron becomes a separate phase on the surface and may escape as dust. Magnetite seems to be formed after the ilmenite oxidizes and reduces many times, but is hardly present after a few cycles.

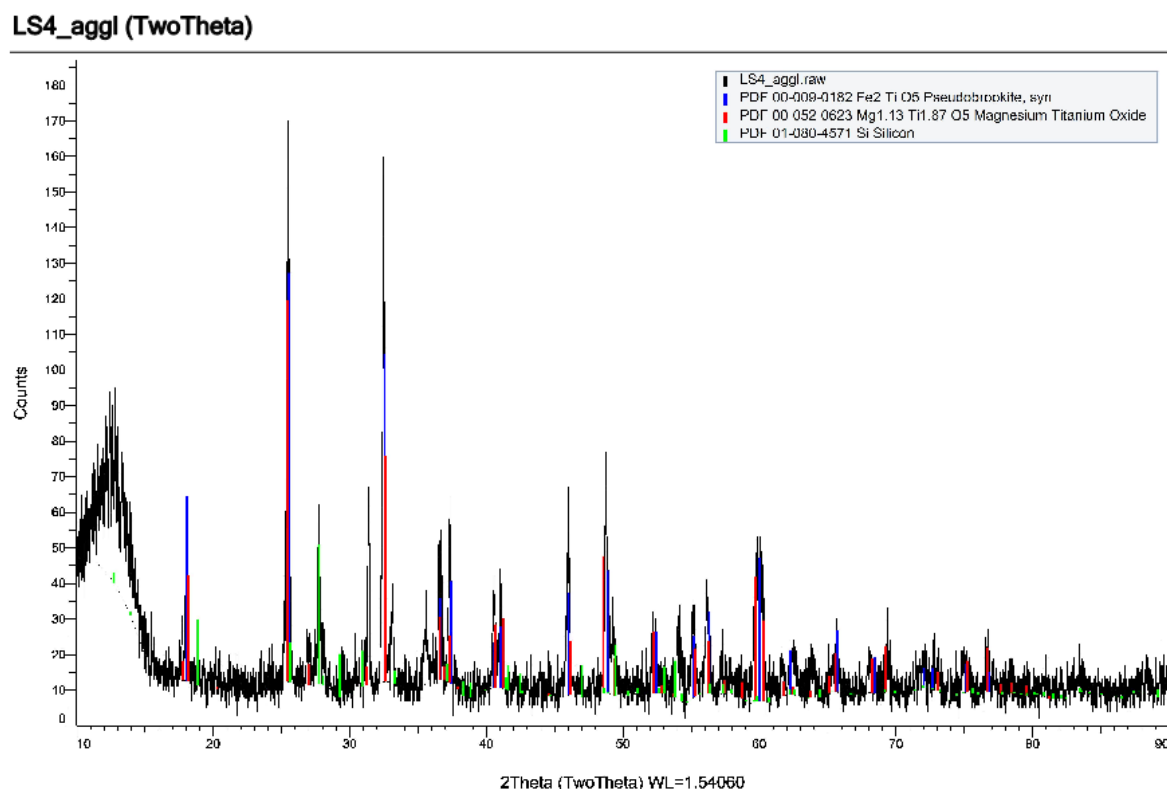


Figure 14 Ilmenite bed material from the 100kW CLC after 12h present are pseudobrookite instead of ilmenite.

4.2 Toxic leakage – possibility of landfill depositing

Table 3 shows the results of the leaching tests. Two different spectrometric methods were used for comparison. The results show little to no migration of iron or titanium from the used ilmenite into water after being used as an OC in the 12MW boiler. The ilmenite used in the boiler was used with biomass as fuel. The effect of the used wood pellets/chips can be seen clearly by the presence of K and is also confirmed by earlier research on the samples from the CFBB (Corcoran, 2013). The dual CLC reactor system of 100kW seems to lose some iron but this is not confirmed by both methods since none of the studied elements were leached in high amounts. A conclusion of this is that the material left cannot be dissolved and recycled with water only. On the other, since hardly anything leaches, it can be deposited safely as filling in constructions and roads and possibly also be investigated for pigment production, all depending on the fuel that has been used. The ilmenite itself does not seem to leach titanium or iron, but further research is needed with emphasis on other elements present in natural ilmenite ore deposits and other fuels such as oil or natural gas. As seen in table 3 there were iron found by the AAS method. Possible sources of error is that the wavelength used in the AAS were not optimal and the calibration curve therefore were not entirely satisfactory, this due to an error with the iron lamp. The results from the ICP-OES are to be trusted more because the instrument had better and stable routines at the time of the experiments.

Sample	AAS Fe (mg/l)	ICP-OES Fe ppm	ICP-OES Ti ppm	ICP-OES K ppm
Ilmenite fresh boiler	<0,006	<0,005	<0,005	<0,1
Ilmenite cyklonleg >24h	<0,006	<0,005	<0,005	43,7
Ilmenite cyklonleg > 72h	<0,006	<0,005	<0,005	16,2
Fresh ilmenite	<0,006	<0,005	<0,005	<0,1
Ilmenite red/filter	<0,006	<0,005	<0,005	0,1
Ilmenite LS2	0,055	<0,005	0,02	<0,1
Agglomerate LS2	0,012	<0,005	0,01	0,5
Ilmenite LS3	0,066	<0,005	0,06	0,2

Table 3 Results of the AAS and ICP-OES tests of the leached materials. Results lower than the methods detection limits or negative, are displayed as < minimum detection limit for the method.

5. Conclusion

The deactivation of the OC when used as a fluidized bed material are more likely to occur because of loss of iron oxide rather than blockage of the particles. Iron migration outwards can also be an explanation for the increase in reactivity seen in the beginning. The iron oxide builds up on the surface when used and due to the oxide layer being weaker than the underlying ilmenite it falls off.

Two solutions for recycling are recommended:

The leaching tests show that the leakage of potentially harmful contaminants, such as K, depends on what fuel is used in the process. More tests, with emphasis on other elements present in ilmenite ores and other fuels rather than bituminous coal and wood chips, need to be done to say this with certainty. But the preliminary results suggest that used ilmenite doesn't leak into the environment if exposed to rain or flood.

Both the elemental analysis of the particles and the leaching tests open up the thought of the titanium being used for the pigment industry as described in chapter 2 of this report. If a cheap and reliable recycling solution for use in CLC or combustion cannot be found, the bed material can possibly be used in the pigment industry, as long as the fuel used in the reactor does not carry harmful elements. This of course, needs to be evaluated individually in each different case of ilmenite use in different plants. As briefly mentioned in chapter 2, one of the problems with using ilmenite as a raw material for titanium dioxide is the need for pretreatment to remove the iron, as opposed to titanium oxide rich silica particles that basically can be fed directly into a cheaper and shorter process. Since the results show that using ilmenite as an OC drains the material of iron, there might be an advantage when trying to find a suitable usage of the deactivated material. Instead of depositing it in landfills it can be a cheaper and more competitive raw material for the pigment industry than ilmenite coming directly from mines.

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