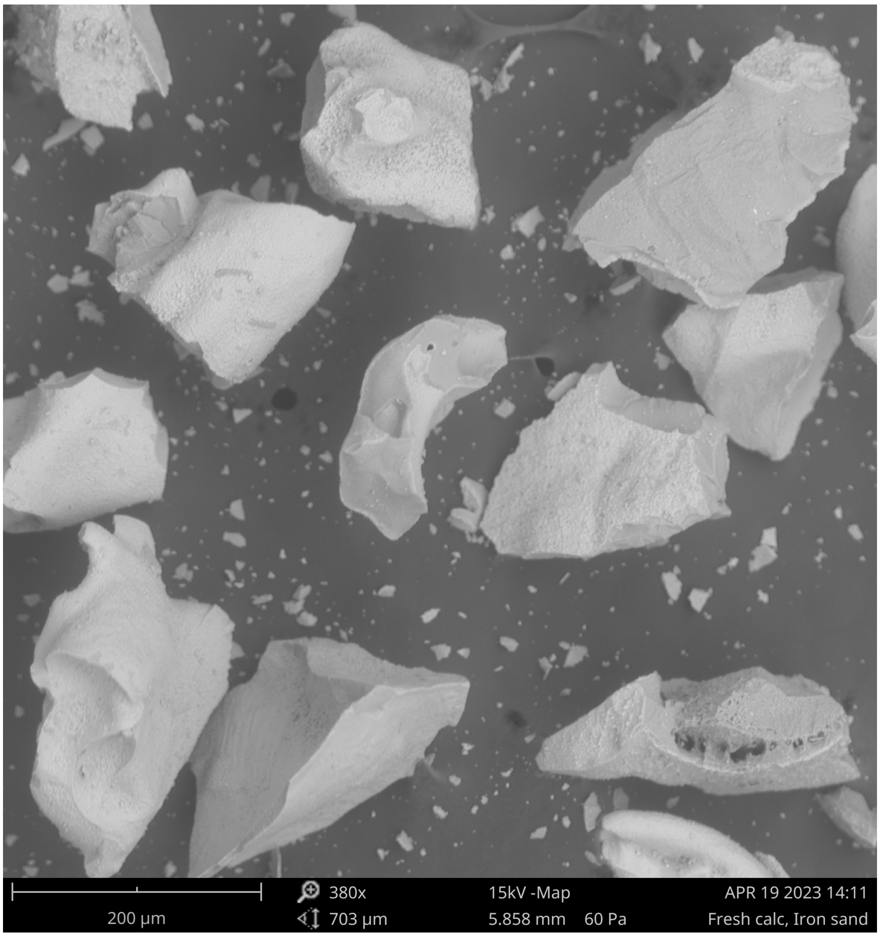

Attrition analysis of oxygen carriers in combustion appliances

- Mechanical stress on particles in fluidized beds

Bachelor's thesis in chemical engineering

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Department of Chemistry and Chemical Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg 2023
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Cover art: SEM image of iron sand particles, Erik Sandell

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Abstract

Carbon capture and storage (CCS) is a technology which can help reduce emissions of CO_2 into the atmosphere and thereby reduce environmental impacts. Ideally, this is implemented by storing pure CO_2 gas in stable geological structures. However, this can be challenging to achieve due to emissions often being a mixture of CO_2, nitrogen and other byproducts. Chemical looping technology (CLT) can simplify this process by implementing an oxygen-carrying material instead of air to supply oxygen for the reaction. This removes nitrogen from the combustion process and resulting exhausts which consists of CO_2 and water. The oxygen-carrying material used in CLT is often metal oxide particles circulated between two fluidized bed reactors. The harsh conditions in the systems lead to attrition of the particles and future implementation of this technology requires a material that is inexpensive, well suited for the reactions, and with a long lifespan in the process.

Therefore, this study aims to analyze the attrition rate of different oxygen carrier materials, namely, ilmenite, iron sand, mill scale, LD slag, and synthetic ilmenite. Each material was also examined at different reduction degrees.

The most attrition-resistant materials were ilmenite and iron sand and the least resistant were LD-slag and synthetic ilmenite. Most materials were not considerably affected by reduction. Mill scale showed increased attrition in partially oxidised and highly reduced states with cracks forming in the particles visible in SEM imagery.

Keywords: attrition, fluidized bed, mechanical strength, chemical looping gasification, CLC, OCAC, combustion, oxygen carrier

0.1 Foreword

This study was conducted by two students at Chalmers University of Technology at the Institution for Chemistry. Our initial idea was to write about material properties such as steel and concrete strength or metal recycling. After some consideration and a communication problem and misunderstanding which almost caused us to miss the deadline for registration, we got a material science project just in time to not miss the window for registration. Therefore we would like to thank our examiner, Henrik Leion and our supervisors, Victor Purnomo and Robin Faust for their time, help and flexibility.

Erik Sandell, Mattias Hertzberg, Gothenburg, Juni 2023

Acronyms

Below is the list of acronyms that have been used throughout this thesis listed in alphabetical order:

AR	Air Reactor
CCS	Carbon capture and storage
CLC	Chemical Looping Combustion
CLG	Chemical Looping Gasification
CLT	Chemical looping technology
FBC	Fluidized bed combustion
FR	Fuel Reactor
ID	Inner diameter
LD	Linz-Donawitz
OC	Oxygen carrier(s)
OCAC	Oxygen carrier aided combustion
SEM	Scanning electron microscope

Contents

1

Introduction

1.1 Background

Combustion of fuel to generate heat and electricity is commonly used worldwide. This can be done in many ways and one of the more modern applications of this is in fluidized bed combustion (FBC). FBC reactors uses a sand like material which is fluidized by a gas stream. This technology has several advantages over conventional methods, such as being flexible in fuel composition, adsorbing volatile compounds from the combustion, and having a good distribution of heat in the reactor[1]. FBC reactors in Sweden mostly use silica sand as bed material even though oxygen carriers have been tested and used commercially [2]. A suitable replacement for the sand is metal oxide particles, often called oxygen carriers (OC) because they fill the same role as sand while also improving the distribution of oxygen in the reactor by releasing and absorbing oxygen. The use of OC in FBC reactors is called oxygen carrier-aided combustion (OCAC), which reduces emissions of CO and NO and increases efficiency [1]. Another use of OC in combustion is Chemical looping combustion (CLC) in which OC is used in a combustion chamber much as in OCAC. However in CLC, there is no air intake to the combustion chamber, the oxygen needed for the combustion is instead released from the OC through reduction. The reduced OC is then transported from the combustion chamber to an aerated chamber. In this chamber, the OC oxidizes to replenish its oxygen content and is then transported back to the combustion chamber to restart the cycle. This type of OC loop can also be used in other processes where less oxygen is needed, such as syngas production through a process called chemical looping gasification (CLG). A collective term for these types of processes is called chemical looping technology (CLT)

A notable effect of CLT implementation is the lack of nitrogen present in the reaction chamber. As the intake of air takes place in a separate chamber, only oxygen is further transported to the reaction chamber. In CLC this means the exhaust gas of the combustion chamber contains mostly CO_2 and water. This makes the process of carbon capture and storage (CCS) more efficient as it reduces the Energy intensive separation needed to purify the CO_2 for storage.
In CLT the particles are subjected to harsh environments with high temperatures, chemical reactions and mechanical attrition, so it is important that the material used can withstand these factors for the process to be viable. The focus of this thesis is to evaluate the properties of several different OC to find suitable materials

for upscaling. This will be done by measuring attrition rate, crushing strength and analysis in a scanning electron microscope (SEM).
The oxygen carriers studied in this thesis are compounds where iron oxide is the main oxygen-carrying component [3]. Some are by-products from industries while others are mined or synthetically made. The main characteristics of a viable OC are: high attrition resistance, high reactivity, environmentally sound, relatively abundant and low cost [3][4]. The OC studied will also be examined in varying reduction degrees to evaluate how this might affect the attrition resistance. This is of certain interest for CLG where the OC operate at reduced states for efficient syngas production.

1.2 Aim

The aim of this study is to examine the viability of different oxygen carriers by measuring attrition rates. This is to determine what material is the most suitable when upscaling the process to an industrial scale. This will be done by evaluating the different materials attrition resistance.

1.3 Goal

The goal of the study is to yield credible results in attrition rates of the different materials that can be used in further studies of materials suitable for CLC.

1.4 Limitations

This study will only consider the mechanical properties as mentioned previously. There are many types of OC avaliable with different compositions and this thesis will be limited to a few in which iron oxides is the main oxygen carrying component. The study will also only consider OC materials for CLC and CLG (gasification). There are other looping technologies as well, such as CLR (reforming), however, in this report, chemical looping technologies (CLT) will only refer to CLC and CLG.

2

Method

2.1 Jet cup method

The jet cup is a customised device built by a student project for simulating and evaluating the high-speed attrition on particles often used in fluidized beds [5] [6]. It is an apparatus consisting of a conical cup with a diameter spanning from 13 to 25 mm and an air inlet at the bottom with 1.5 mm ID. The inlet is placed in a way so that the air creates a vortex resembling the current inside of a cyclone. This cup is attached to a 634 mm high gravitational separator (also conical in shape). A filter module (Parker P31FA12CGMN) with a pore size of 0.01 µm (Parker P31KAOOESC) was mounted on the top of the separator to collect fine particulates produced by attrition of the OC particles. A humidifier was also attached before the air inlet to reduce static charges which could lead to particles agglomerating and adhering to the inner walls of the jet cup. This humidifier lets air pass through a water column inside a plastic container filled with room-temperature water at atmospheric pressure.

The experiment was started by disconnecting and weighing the filter. The cup was removed from the separator and a sample of approximately 5 g was placed into it. After attaching both the filter and cup again, the airflow was regulated (Bosch-Rexroth AS1-RGS-G014-GAI-040) to approximately 10 litres per minute (which equals a superficial velocity of 94 meters per second with the given nozzle diameter). A rotameter (Kobold KFR-4244-NO) was used to check the value because the saturation of the filter could, in some cases, cause a back pressure, affecting the airflow. Every 10 minutes the filter was removed and weighed. After one hour the test was finished and the remaining sample in the cup was collected and weighed.

$$Index(I) = \frac{\text{Attrition rate (g/min)}}{\text{Total mass of sample from the start (g)}}$$

2.2 Crushing strength test method

The crushing strength test was performed to measure the strength of the individual particles of a certain OC. First, a single particle of the sample material was placed on a flat plate. This plate is located on top of a scale which when pressed on will assert a force measured by the scale. So pressure was then applied with the help of a press (similar to a pen or screwdriver but with a flat bottom). The force required to crush the particle was measured and noted and in that way, it could be determined how hard the OC were.

Because of the small particle size, each particle had to be crushed very carefully, and the force's mean value was calculated for each sample material of 100 particles. As some particles are softer or harder than the bulk, the top and bottom 10% of the measured values were discarded as outliers to lower the standard deviation.

2.3 Scanning electron microscope

When finished with the jet cup testing, each sample material was divided into three subsamples:
New - untouched particles used as a reference,
Cup - particles collected from the cup after the testing,
Fines - particle dust collected in the filter.

To further evaluate and analyze the effects the jet cup could have had on the different sample particles, a scanning electron microscope (SEM) was used to investigate the shape and chemical composition of the particles before and after the attrition experiments. The SEM used in this project was a Phenom ProX. This SEM can identify the particle elements while examining the samples by taking a picture and choosing a point from which to analyse the elements. The SEM uses an electron beam directed towards a sample which results in electrons scattering off the sample. These electrons are then detected and the data is used to create an image or to analyse the atomic composition of the sample.[7]

Particles of each subsample were placed on a piece of carbon tape, on a metal platter which was then placed in the SEM using a platter holder for electrically non-conductive materials. Of each subsample, five pictures were taken and in each picture, five or six examining points were chosen totalling a number of at least 25 points per subsample.

3

Materials

In the following section, information about the samples will be presented so as to provide a better understanding of the materials used.

Ilmenite , $FeTiO_3$, is a black mineral used for mining titanium. It is a low-cost mineral and therefore promising as an OC on an industrial scale. The initial oxygen transport capacity was measured to be 4% [8]. Ilmenite can be enriched in TiO_2 concentration (synthetic rutile) and TiO_2 has been proven to work as the best support for nickel- and copper-based OC. However, for Fe, the best inert was Al_2O_3 and ZrO_2, though not necessarily proving that TiO_2 was unsatisfactory [9] [10].

Synthetic ilmenite is, as the name implies, very similar to ilmenite though it generally had, when used in CLC in one study, better conversion of CO and H_2. The synthetic ilmenite used in that study was made by mixing pure Fe_2O_3 and TiO_2 powders [11]. The synthetic ilmenite used in this thesis consists of 50% Fe_2O_3 and 50% TiO_2.

Ironsand is a powder and a by-product from the copper industry, consisting of mostly magnetite, Fe_3O_4, and hematite, Fe_2O_3 which are types of iron oxides [12] [13] [14]. Hematite can also be found in corroded iron or steel more known as rust. In many cases, rust has a red/orange type of colour.

Millscale is a byproduct from the steel industry. It is created by when hot steel comes in contact with the oxygen in the air and is broken apart from the steel. Millscale is composed of oxides, mainly iron [15]. Millscale can be pulverized, enabling its use as an OC.

LD-slag is a material composed of mainly lime and iron oxide but also silica, magnesium oxide, and manganese oxide. Other uses for LD-slag are the manufacturing of cement or as raw material in mineral wool[16].

3.1 Sample states

Calcination means that the different samples have been heated to a very high temperature though without melting the material. The materials used in this thesis were calcined at 950 degrees celcius. The goal of this process is to strengthen and oxidize the particles, simulating the conditions in the air reactor. [17]

Oxidation is somewhat similar to calcination but instead of heating up the material , oxidation refers to the donation of electrons which in this study often means it attracts oxygen atoms.
Reduction is the opposite of oxidation whereas instead of giving away electrons, it receives electrons causing it to release its oxygen atoms.

3.2 Mass conversion degree

The mass conversion degree is a fraction that represents the oxidation state of a material. "1" (or 100%) means that the material is fully oxidised and, for example, 0.99 (99%) means that the material has lost 1% of its weight from a fully oxidised state (which is not equal to 99% oxidised). All materials except fresh calcined were prepared in a fluidized bed batch reactor [18] and oxidised or reduced according to the table below. The oxidizing and reducing agents were 5% O_2 in N_2 and syngas (50% CO + 50% N_2), respectively.

Table 1

Omega values				
Sample material	Fresh calcined	Fully Oxidised	Partially Oxidised	Highly Reduced
Ilmenite	1	1	0.9908	0.9801
Ironsand	1	1	0.9915	0.983
LD-slag	1	1	0.9933	0.9876
Synthetic ilmenite	1	1	0.99	0.979
Mill scale	1	1	0.9576	0.9138

4

Results

This chapter will present the initial outcomes of the conducted research such as crush and jet cup tests and SEM analyses needed for the study's objectives. Some of the findings in this section will be accompanied by a few minor comments to shed light on some specific aspects whereas a comprehensive discussion will be presented in the following chapter.

4.1 Crush test

Because of high standard deviations the highest and lowest 10% of measurements were excluded from the results. The particles tend to be strongest when fresh calcined, softer with lower oxidation and the highly reduced particles tend to be the softest. This, however, does not necessarily mean they will experience the most attrition.

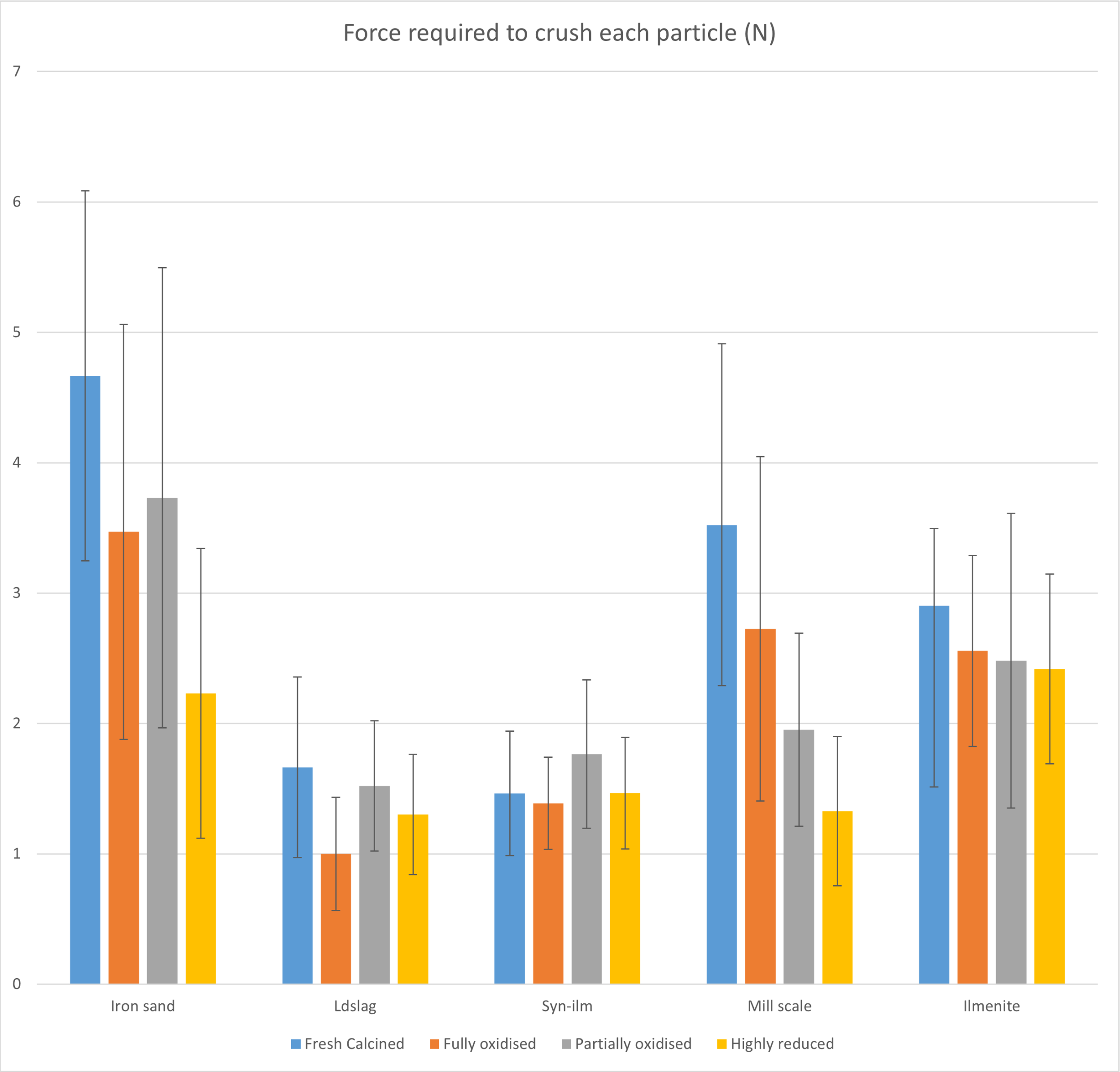

Figure 4.1: Graph depicting the required force to crush each sample particle

4.2 Jet cup

The results from the jet cup attrition tests were compiled into diagrams listed below. The values used in the diagrams are weight% of fines produced in the y-axis and the time as the x-axis. Due to the high amount of fines produced by LD-slag and synthetic ilmenite, two versions were made of each diagram. One of which LD-slag and synthetic ilmenite were excluded to make the diagram more clear, as it would otherwise be hard to compare the other OC. The diagrams are labelled depending on the oxidation/reduction degree of the materials and the attrition rate of sand has been added as a baseline to compare with (coloured green). Trend lines and corresponding equations have been added using Excel to give an approximation of the attrition rate for each material. This trend line has only been added once for sand as this equation is unchanging and its omission makes the diagram easier to read.

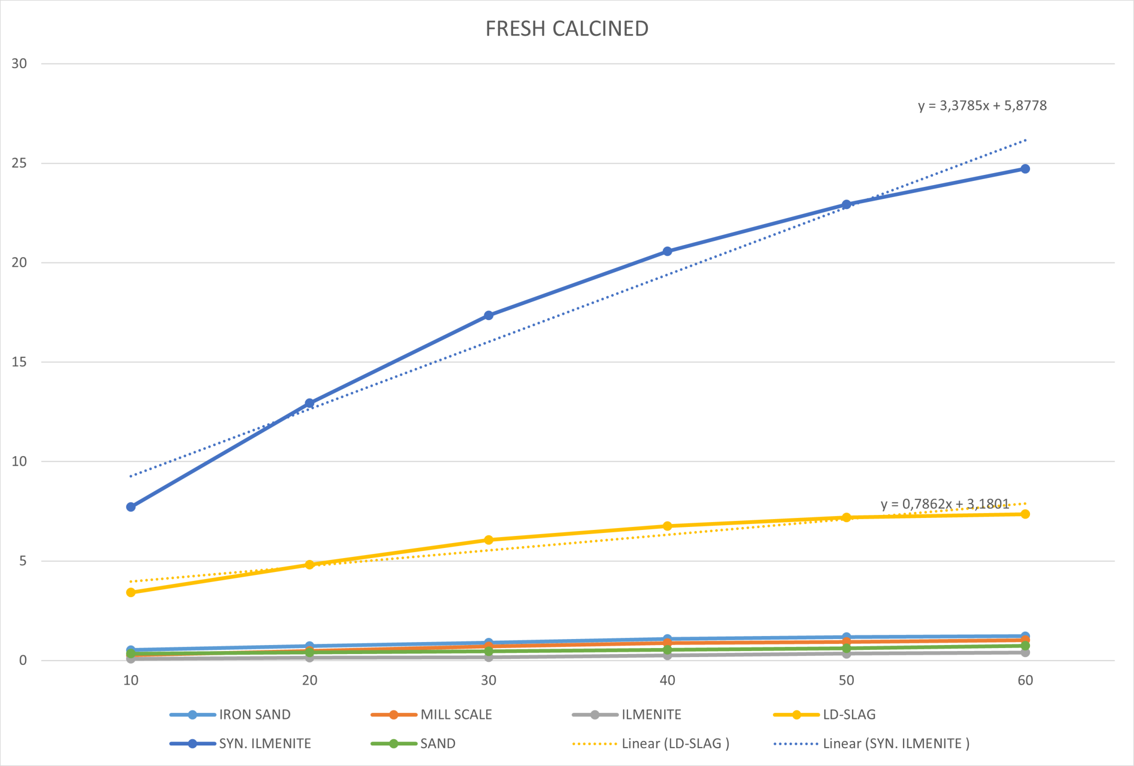

Figure 4.2: Graph depicting percentage change in weight loss relative to initial weight with trendlines

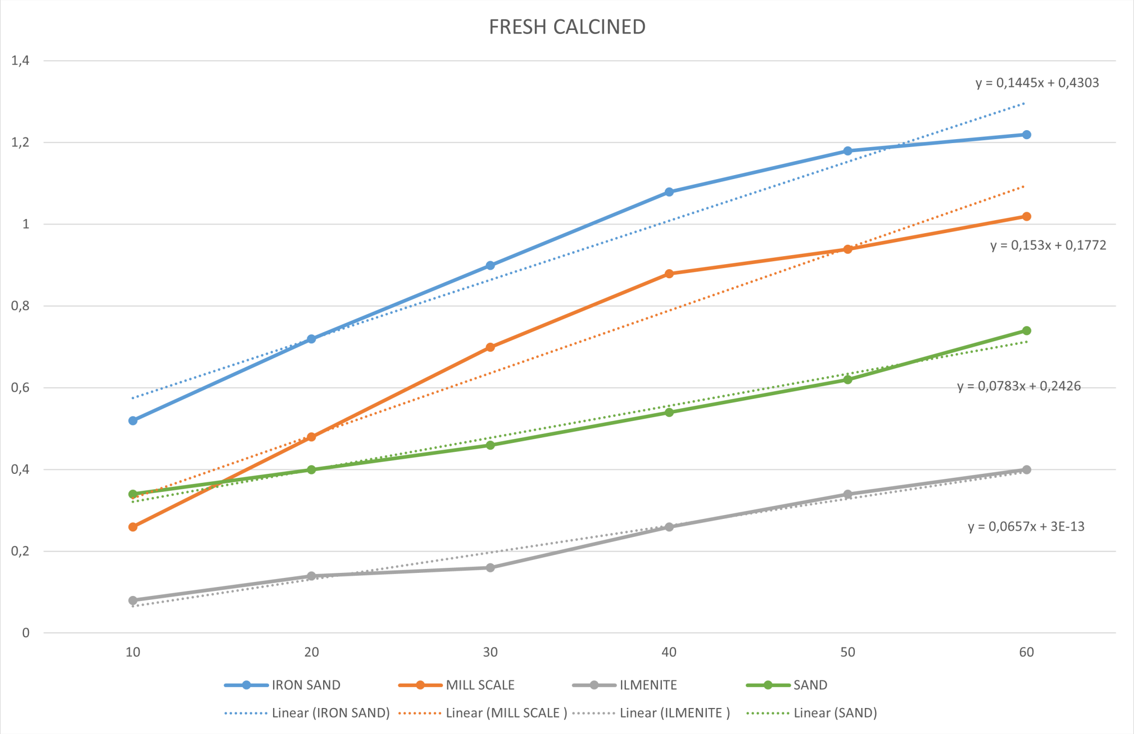

Figure 4.3: Same graph as previously but focused on the lowest four samples due to smaller weight change

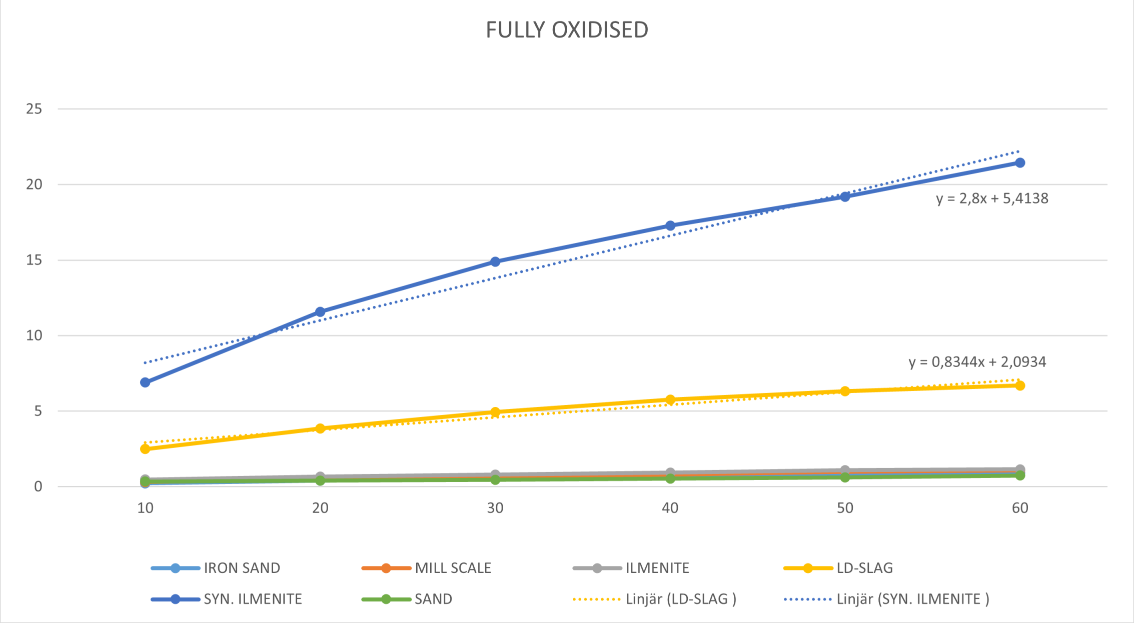

Figure 4.4: Graph depicting percentage change in weight loss relative to initial weight with trendlines

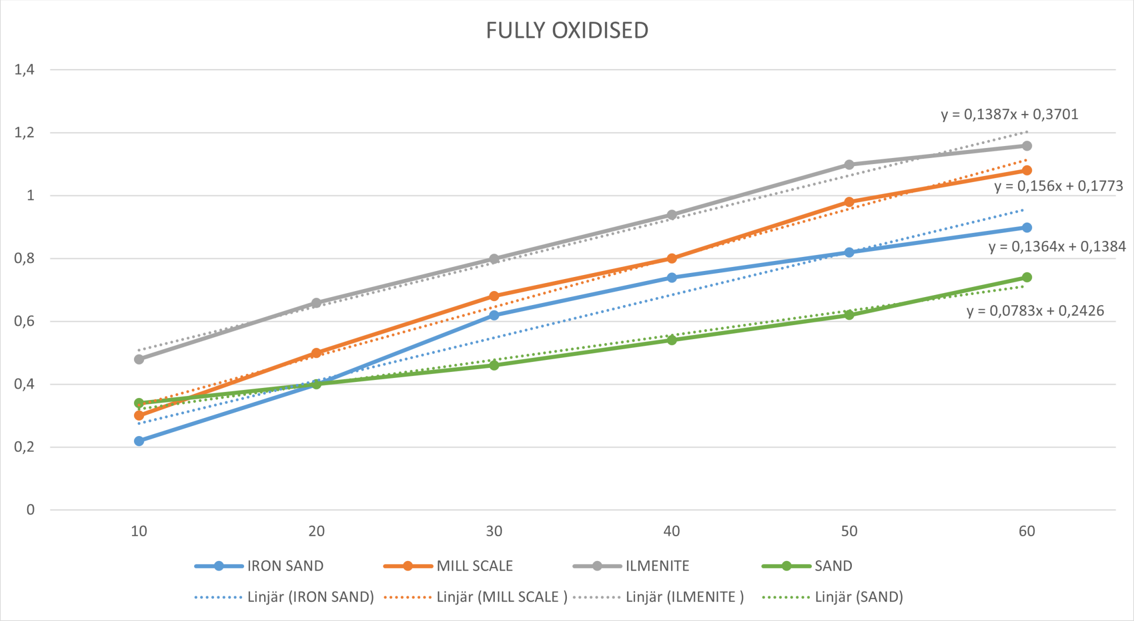

Figure 4.5: Same graph as previously but focused on the lowest four samples due to smaller weight change

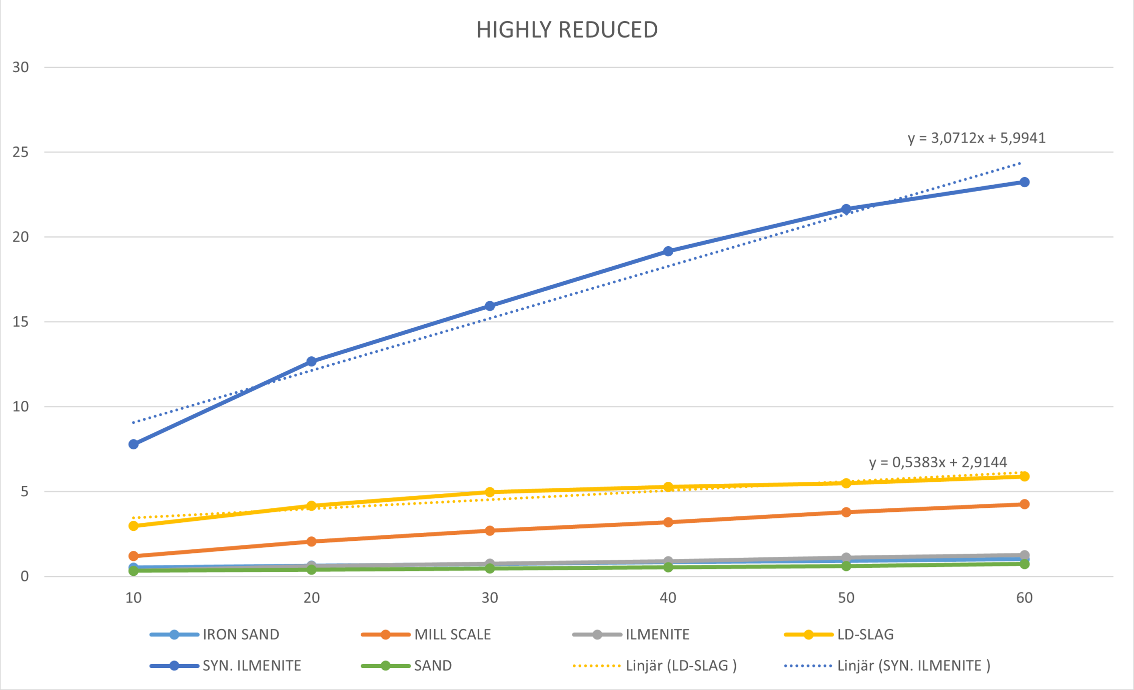

Figure 4.6: Graph depicting percentage change in weight loss relative to initial weight with trendlines

Figure 4.7: Same graph as previously but focused on the lowest four samples due to smaller weight change

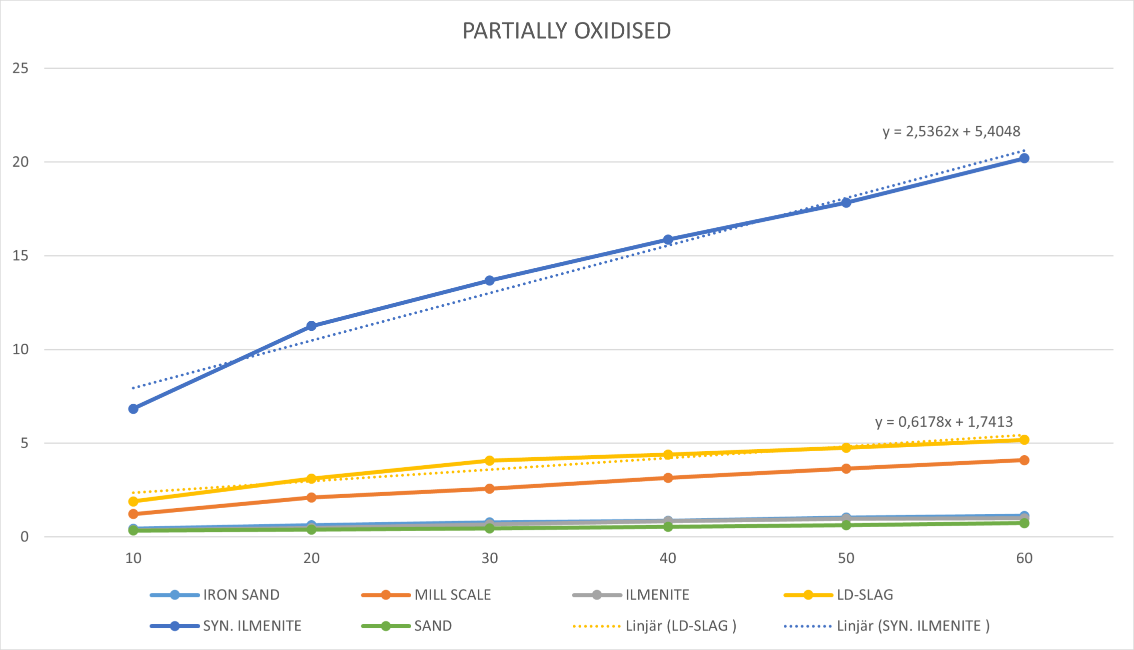

Figure 4.8: Graph depicting percentage change in weight loss relative to initial weight with trendlines

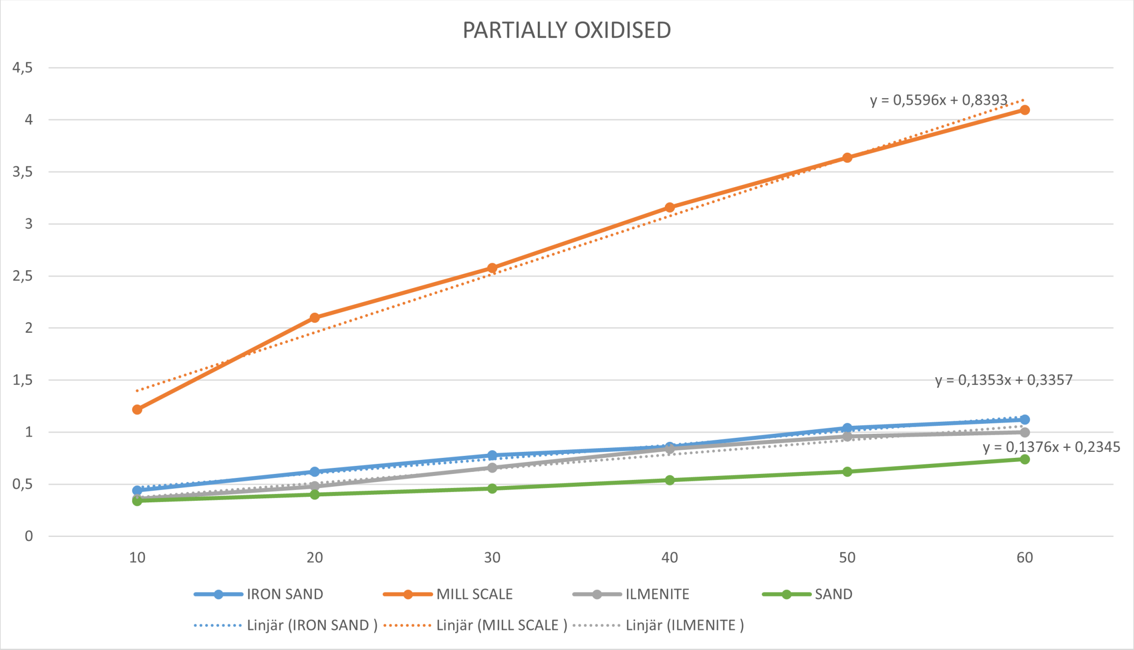

Figure 4.9: Same graph as previously but focused on the lowest four samples due to smaller weight change

4.2.1 SEM images and element analyses

Fresh Calcined Ilmenite consists of mainly oxygen, iron and titanium with some trace elements like magnesium, silicon, aluminium, sodium and calcium. The composition did not change after the jet cup tests.

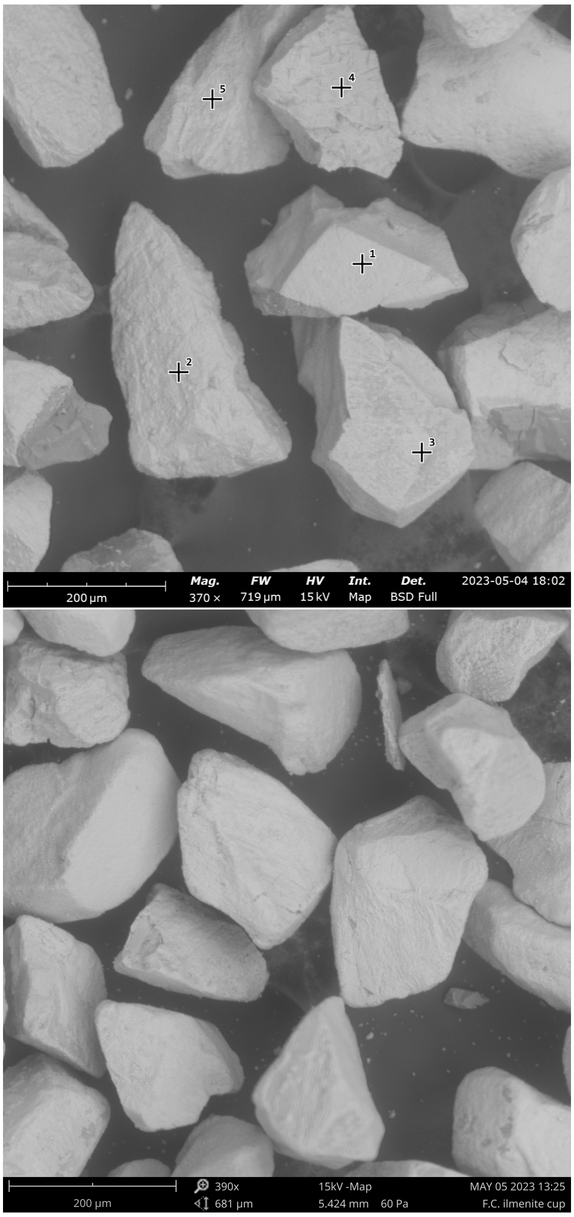

Figure 4.10: Picture of ilmenite before (above) and after tested in the jet cup

Fresh Calcined Synthetic Ilmenite was slightly richer in titanium and had a consistent amount of silicon compared to regular ilmenite. Otherwise, it consisted of oxygen, iron and titanium.

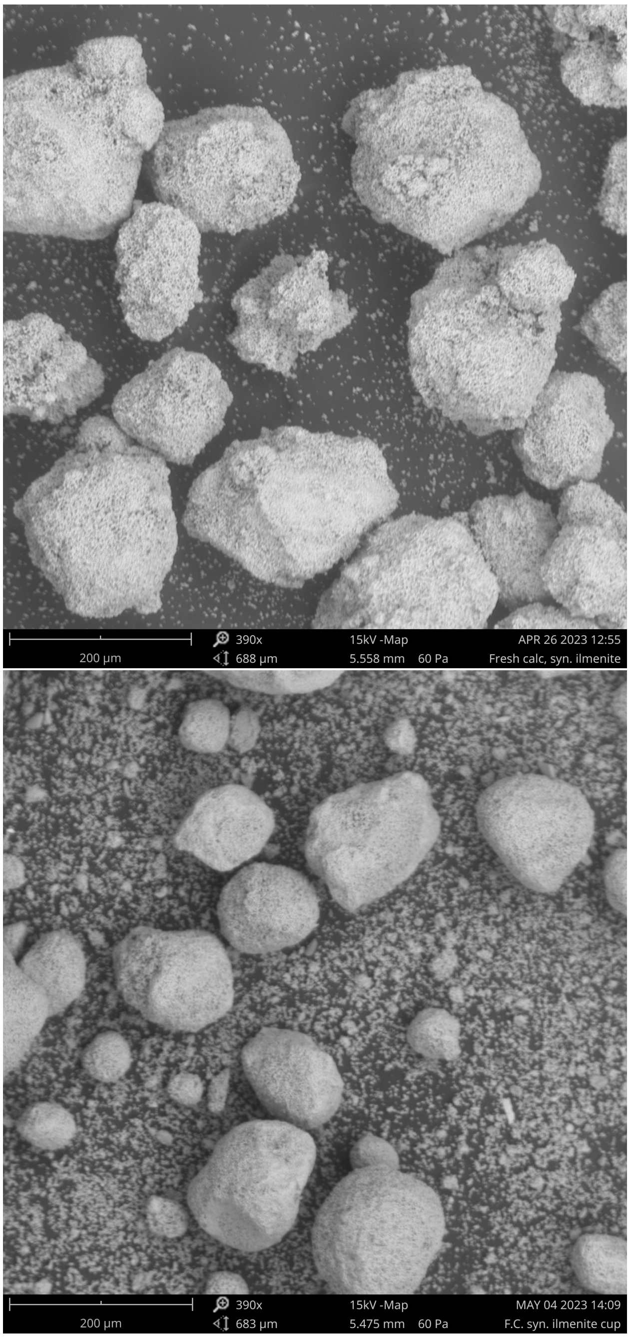

Figure 4.11: Synthetic ilmenite already contained a lot of dust before being run through the jet cup test and the particles had become notably rounder from abrasion.

Fresh Calcined Mill scale consisted of exclusively oxygen and iron with one case having a trace of manganese. After the jet cup tests, there was a slightly higher concentration of iron in the cup residue and consequently a higher concentration of oxygen in the fines but no larger change in composition other than that.

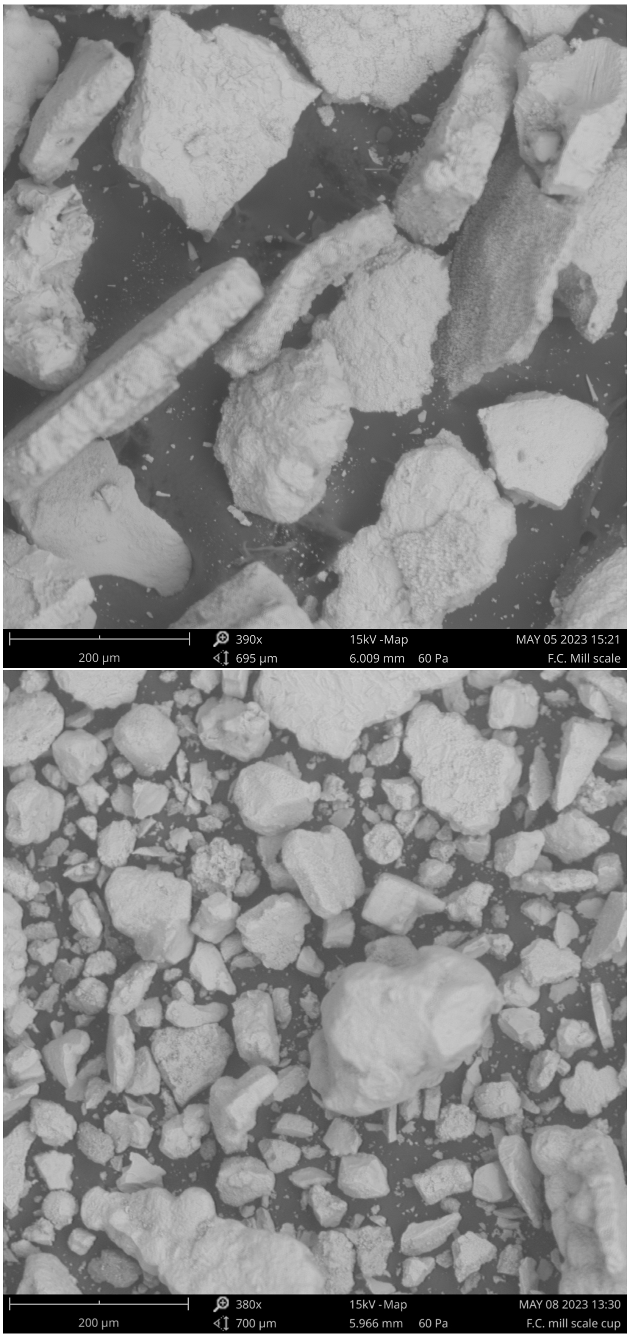

Figure 4.12: Mill scale differs from the other sample particles because of its scale-like shape which was quite unique.

Fresh Calcined LD-slag consists of iron, oxygen, silicon and calcium with trace amounts of magnesium, chromium, vanadium, aluminium, titanium and manganese. This elemental composition was consistent in fines and particles left in the jet cup after testing.

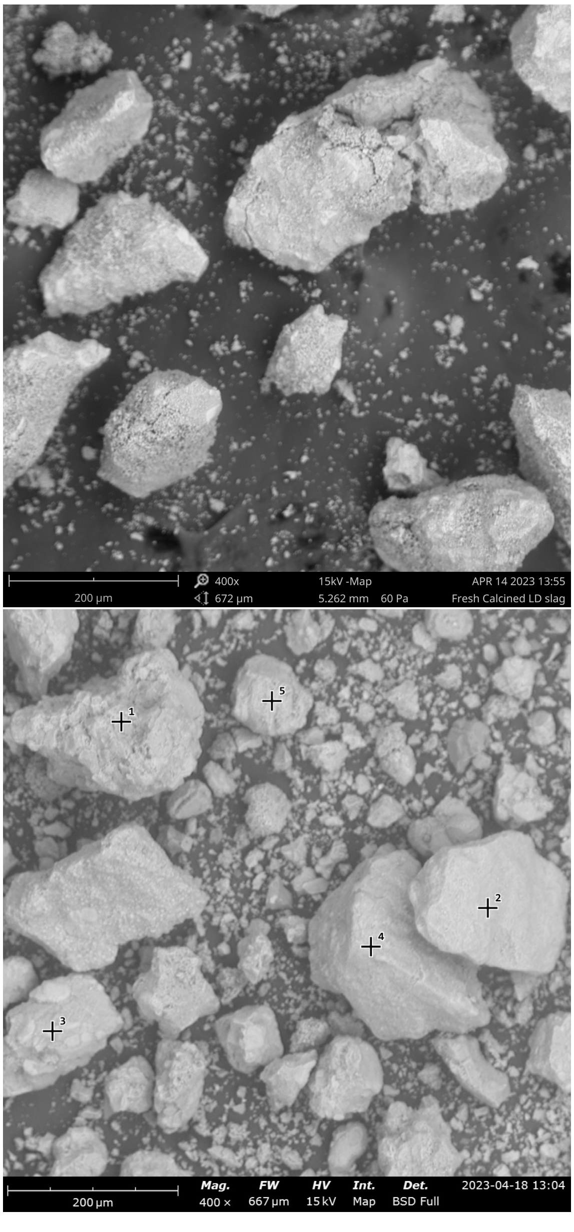

Figure 4.13: Similar to synthetic ilmenite, new LD-slag also contained a lot of fines

Fresh Calcined Iron sand sand consisted mainly of oxygen, iron and copper with some traces of calcium, zinc, manganese, silicon, chromium, magnesium and aluminium.

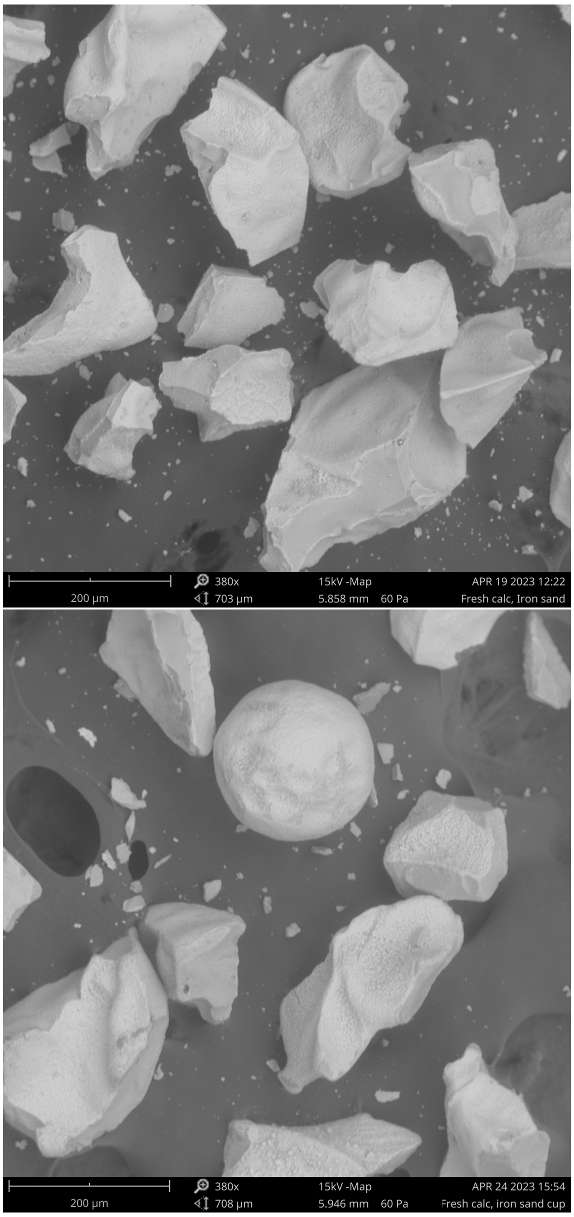

Figure 4.14: Iron sand has a very irregular shape but is somewhat rounded after being run in the jet cup

Highly Reduced Ilmenite consists of mostly oxygen, iron and titanium with some traces of manganese, silicon, magnesium, aluminium, sodium, and calcium. Highly Reduced ilmenite has some cracks in the particles.

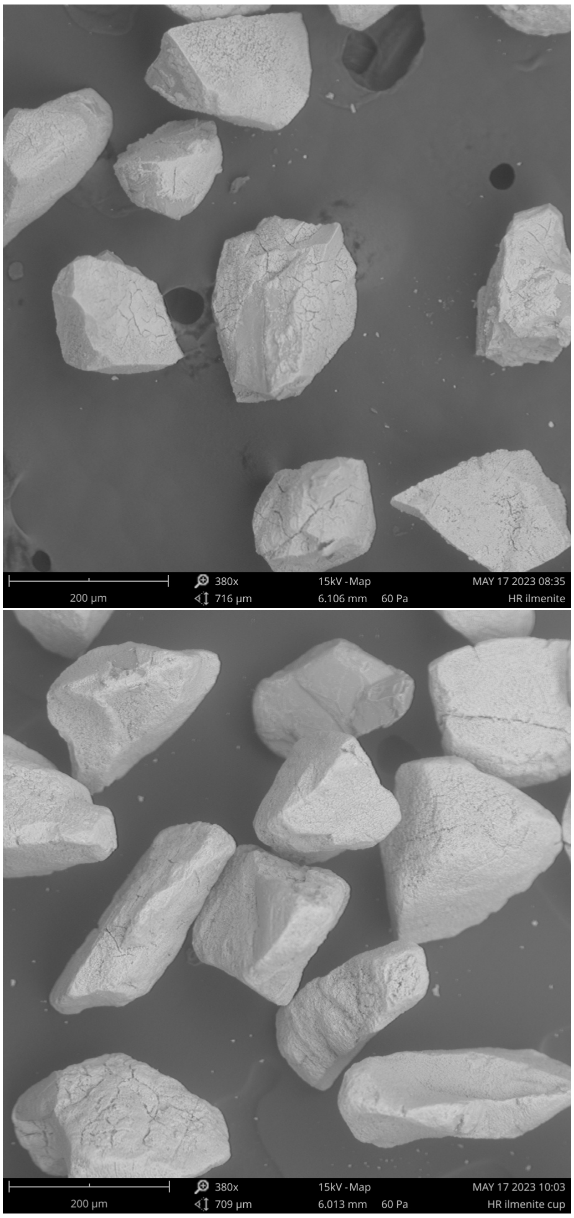

Figure 4.15: Some cracks have started to form in the particles

Highly Reduced Synthetic Ilmenite was not scanned in SEM due to the inferior results in the jet cup tests and time constraints.

Highly Reduced Mill scale much like its fresh counterpart, consisted almost exclusively of iron (40-90%) and oxygen. These numbers were consistent in both fines and in the cup after testing. However, in the fines, several larger particles with high amounts of calcium (16-26%) and traces of titanium, chromium, vanadium, silicon, magnesium and manganese could be found.

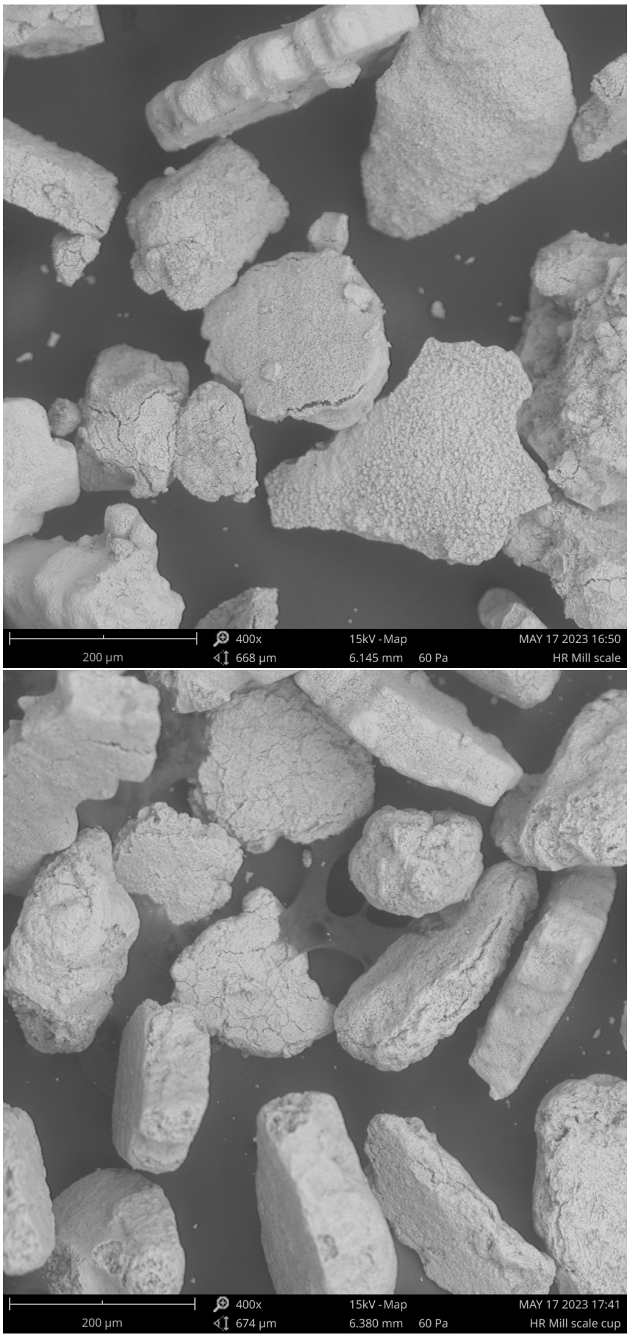

Figure 4.16: Much like the H.R. ilmenite, cracks can be seen in some particles.

Highly Reduced Iron sand was very similar to fresh calcined iron sand which was oxygen and iron though there was less traces of copper and more traces of calcium, manganese, silicon, magnesium and aluminium.

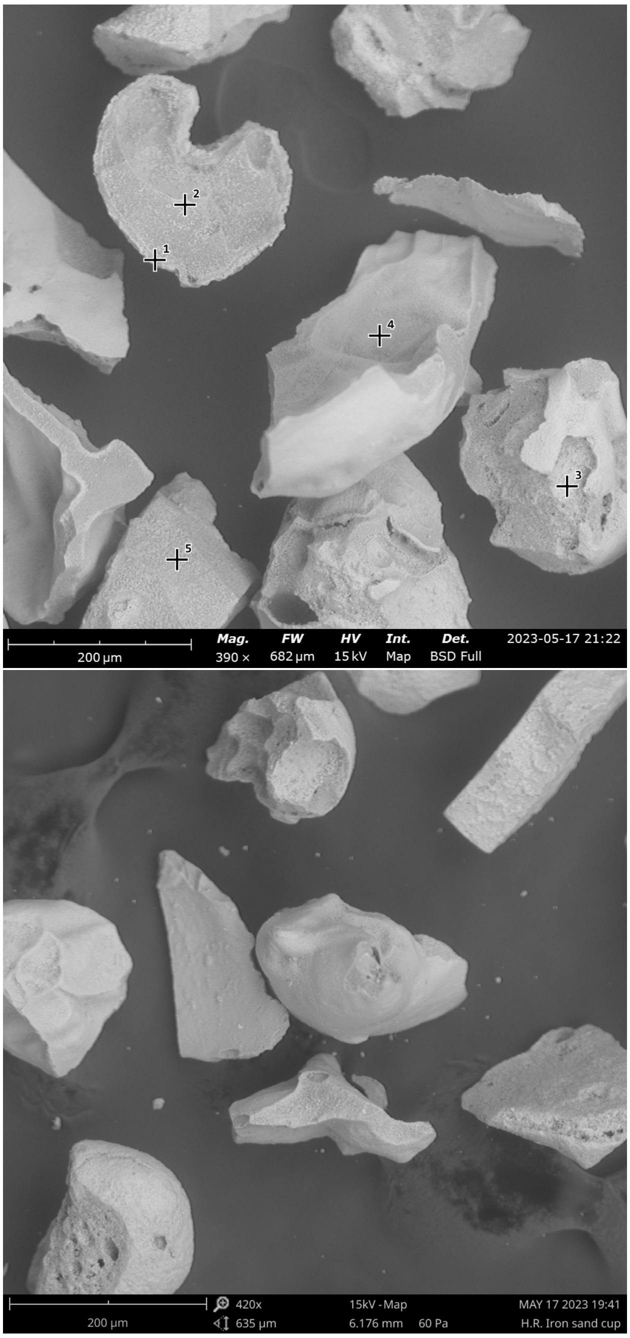

Figure 4.17: Iron sand is very hard and therefore not many fines were created

Highly Reduced LD-slag consisted of, much like its fresh calcined counterpart of mostly calcium, iron, silicon and oxygen with trace amounts of magnesium, chromium, vanadium, aluminium, titanium and manganese. Again, this elemental composition was consistent in fines and particles left in the jet cup after testing.

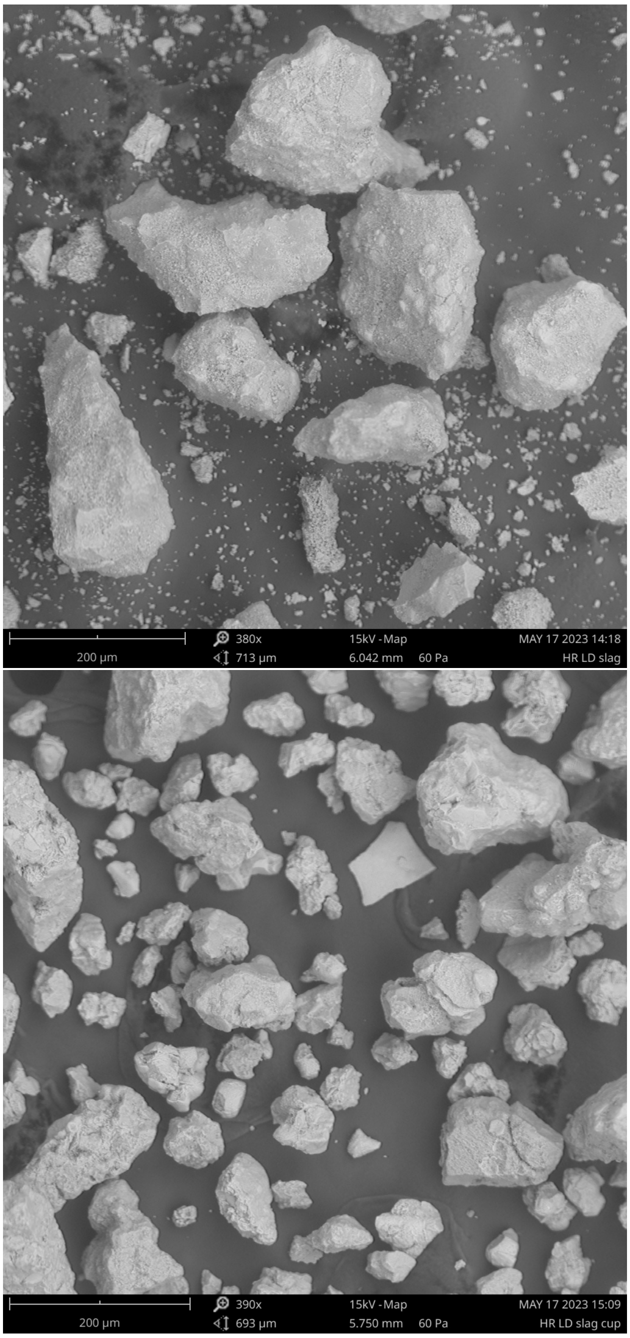

Figure 4.18: A lot of smaller pieces too large to get stuck in the filter fell down in the cup

Fines were largely similar between the different materials. Notable differences were the high amount of fines produced by synthetic ilmenite and the larger particles found in the iron sand fines.

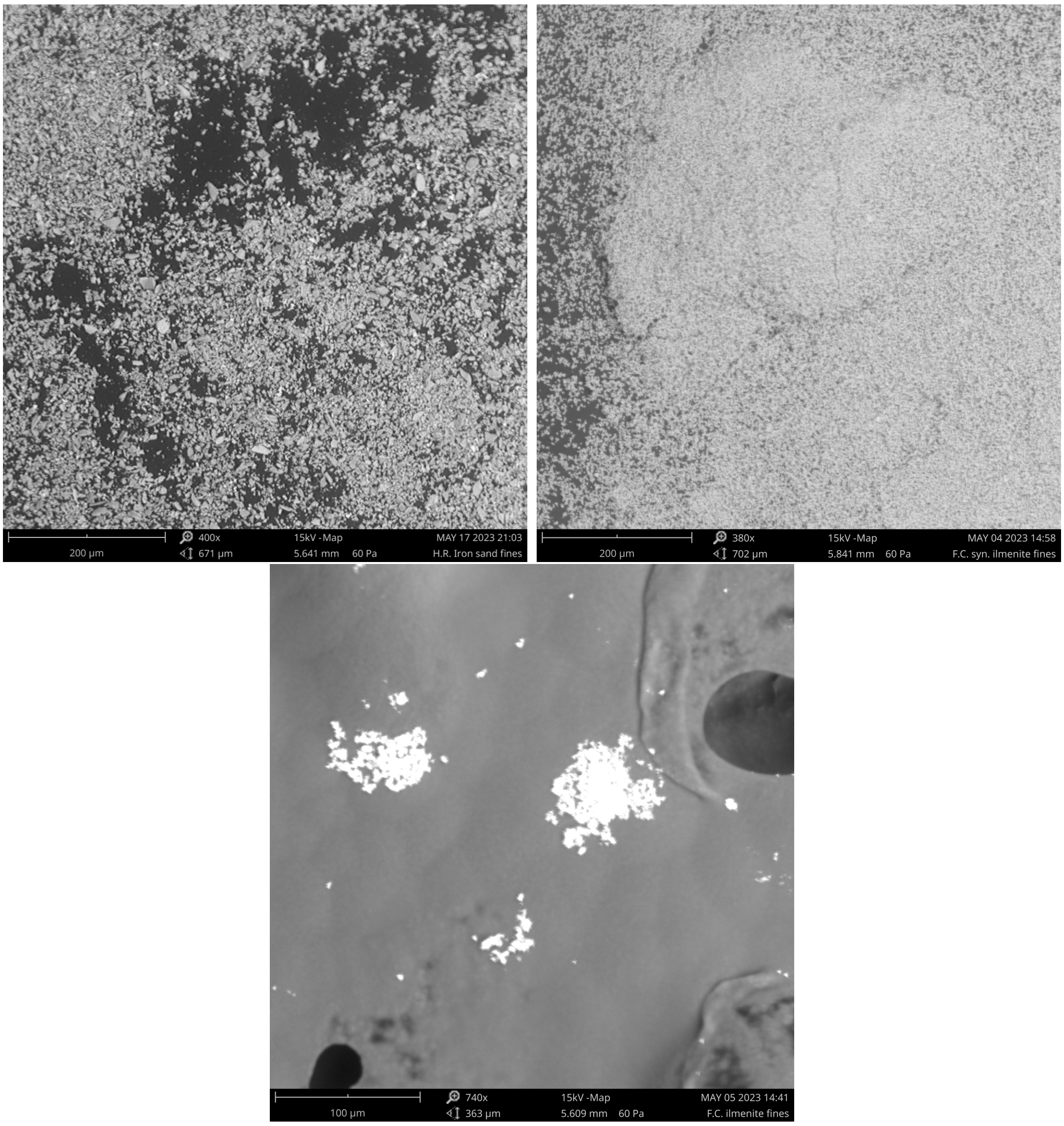

Figure 4.19: Iron sand fines (top left) were notably larger than fines produced by other materials. Synthetic ilmenite (top right) produced the most fines in the form of very fine dust and fresh calcined ilmenite (bottom) created very little fines.

5

Discussion

Crush tests was designed to measure the hardness of the particles and therefore rather a way to estimate the attrition the particles would experience in relation to each other and not as a basis for attrition rate. This is because of the difference between shock resistance and structural integrity because of the different conditions between the jet cup and crush tests, similar to how ceramic or brittle material can resist heavy loads but not shock in contrast to how metallic or soft materials can resist shock and vice versa.

The crush tests resulted in large deviations in the measurement data which made it necessary to remove the highest and lowest 10%. It is not necessarily unreliable results because of this as we are certain that the data is correct however, it is hard to pick a representative value for the sample. Therefore a standard deviation was calculated and shown in Figure 4.1.

Even though the crush test was not designed to replace or complete the jet cup experiments it overall agreed and followed the trend the jet cup tests indicated. The synthetic ilmenite and LD-slag were the softest particles and they would also lose the most weight. The same goes for iron sand, ilmenite and mill scale which were substantially harder and proved to have the most attrition resistance.

The jet cup results were quite conclusive, with a few notable exceptions. Overall, Iron sand and ilmenite showed the highest attrition resistance of the materials, while LD-slag and synthetic ilmenite were the least resistant to attrition. Mill scale would have attrition rates comparable to iron sand and ilmenite, but showed higher attrition rates in its highly reduced and partially oxidised state. In these states, the mill scale would have an attrition rate around 4 times higher than the iron sand and ilmenite and would be similar to LD-slag in its attrition rate.

Sand is not used as an OC but was tested as a reference in attrition rates due to CLT not being fully established as an alternative to traditional combustion and therefore previous testing to introduce standards was insufficient. That is why it was important that the results produced by the sand were reliable. While there were some problems with the scale a reliable result was yielded after having run the sand through 3 tests.

Iron Sand was the hardest material and lost the least amount of weight in the jet cup tests. It was by far the hardest particle to crush in the crush tests. It yielded consistent results of around 1% in attrition/h for all samples.

Mill scale performed without issues in the jet cup tests however due to its shape, there were some problems in the crush tests which is partly the reason for the removal of the top/low 10%. The particles are, as the name implies, scales which means that if a particle is standing up and then falls over in the crush tests, the crack-like sound could be mistaken for the crushing of the particle. This is what brought bigger attention to the shape of the particles even though the main focus lay on the jet cup tests and not the crush tests. In the jet cup test, the mill scale in fresh calcined and fully oxidised gave very similar results at around 1% attrition/h. While the partially oxidised and highly reduced samples were similar at around 4% attrition/h. It is of little surprise that the fresh and fully oxidised samples behaved similarly as the mill scale is an almost pure iron oxide with a high degree of oxidisation in its fresh state. The SEM images of the highly reduced mill scale show cracks in the particles that are not as notable in the fresh sample. This could be the cause of the higher attrition rate found in the highly reduced and partially oxidised samples. Due to time constraints the SEM analysis of partially oxidised samples was never made, so this is merely speculation.

Ilmenite was one of the hardest materials tested among the tested sample materials in this study and performed consistently throughout all tests. Therefore it is of high interest to use it as OC. Ilmenite was most resistant to attrition in its fresh calcined form with an attrition rate of 0,4%/h, which is the lowest of all samples. Ilmenite also seems to be consistent in attrition rate over varying oxidation degrees at around 1%/h. SEM images show cracks forming in the highly reduced particles. This is the sample that showed the highest attrition rate in the jet cup test, but it did not affect the results as much as in the mill scale. Which had similar cracks showing in the highly reduced sample.

From the SEM analysis, fresh calcined ilmenite seemed to consist of 50-80% oxygen, 10-40% iron and 0-10% titanium whereas, in a previous study, it consisted of 28% titanium which is a big difference[17]. The reason behind this is not certain but the samples could have different origins or that our sample was contaminated or not properly prepared. The iron and oxygen content varied a bit and thus a possible explanation could be because of faulty analyses of the SEM.

LD-slag was one of the samples with a higher attrition rate and in the crush tests it was expected to perform similarly to synthetic ilmenite but it held up better. This is going to be further discussed in the section below. The attrition would vary slightly from sample to sample with the fresh sample having the highest attrition at around 7,5%/h and the partially oxidised sample being lowest at 5%/h. The reason for the fresh sample being the highest in attrition could be attributed to the fact that the fresh material will produce a lot of fines initially and produce slightly less in each interval as the test went on (see figure A.1 in the appendix). As the samples of varying oxidation degrees had already been subjected to fluidization, it is possible that these samples had already released the initial amount of fines produced before being tested in the jet cup. This however does not explain why the partially oxidised sample showed the most attrition resistance, which again was not studied closer in SEM due to time constraints.

Synthetic Ilmenite was expected to act similarly to regular ilmenite, as the name implied, however, there was a significant difference between the two with synthetic ilmenite performing much worse and it was the material which experienced the most attrition.

As the synthetic ilmenite and LD-slag were equally soft particles, it was assumed they would experience roughly the same level of attrition but in every case when ran through the jet cup the synthetic ilmenite would lose at least 3 times the weight compared to the LD-slag.

The initial theory was that the OC particles would become more circular and rounded after the jet cup tests because of the abrasion between the particles in the cup. Due to the relative softness of both LD-slag and synthetic ilmenite, it was speculated that these materials would prominently exhibit this process. After comparing the particles through the SEM, it was shown that the synthetic ilmenite was the one with the roundest shape after having been run through the jet cup. And based on that information, a possible explanation could be that the jet cup chafed away the edges of the particle causing a large accumulation of fines in the filter. But there is also a possibility that this happens to LD-slag as well; being that roundness can decrease attrition, hence the stagnation in the attrition curves. Another explanation for the LD-slag not having lost as much weight when weighing the filter could be that chunks of larger particles ended up in the cup. Because of the bigger particle size, they would not get stuck in the filter and therefore not be counted as fines. Although not turned into fines, they were nevertheless shattered by the Jet cup test. In the jet cup tests the synthetic ilmenite showed an attrition of 20-25%/h depending on the oxidation degree, whereas the fresh sample had the highest attrition. This could be attributed to an initial release of fines much like previously mentioned in the LD-slag section above. Just as in LD-slag, the partially oxidised sample showed the highest attrition resistance.

The different content could be explained by the different obtaining methods as this one was created synthetically.

5.1 Possible sources of error:

The jet cup connected to the air nozzle could itself experience attrition from the particles blasted at the surface which could grind the cup and eventually cause a cavity. This cavity could influence the air vortex through the separator. The cavity growth is gradual and the only way to ensure perfectly similar scenarios would be to change the cup after each try. However, the manufacturers had made a miscalculation on the newer cups which caused them to leak air which made it impossible to use any other cup than the original. From the observed data, the cavity in the initial cup does not seem to have altered the results though it can be worth considering in the future.

As the separator was made of metals and is therefore opaque, there could exist some impurities inside of it such as, for example, corroded areas caused by the humidifier or particles stuck from previous tries due to static electricity.

The scale was not as consistent as hoped. When weighing the filter the shown weight would continuously increase. The most likely explanation is probably static electricity and to remedy this an anti-static gun was used as well as weighing the filter multiple times. To further reduce this problem a plastic bucket was placed over the filter to cover it which helped the scale to stabilize. These measures could not guarantee a perfect result but as the data yielded a reasonable trend this was accepted as credible.

SEM analyses had many trace elements which could be the result of the remains of previously tested samples when tested in the jet cup. For instance: if the mill scale was tested in the jet cup after synthetic ilmenite (which gives off a lot of fines), there could be traces of titanium which followed mill scale particles down in the cup. Similar circumstances may occur for fines in the filter.

Analyses that were made included oxygen which, in EDX, can result in many inaccuracies. Therefore a definite percentage of each material is not included as we deemed these to not be reliable. However, some differences that were significant were observed and therefore considered in the results and discussion.

6

Summary and conclusion

With both crushing strength and attrition rates considered, the conclusion is as follows:

Table 2 - From most attrition resistant to least
1. Ilmenite
2. Iron sand
3. Mill scale
4. LD-slag
5. Synthetic Ilmenite

Iron sand and ilmenite are very similar to each other in terms of attrition resistance. Iron sand was more consistent throughout all tests whereas ilmenite overall was most resistant to attrition. Mill scale was at times on par with iron sand in attrition resistance but performed worse as the material was in reduced states. Ilmenite was very consistent in crushing strength tests, only surpassed by iron sand which had the highest values in those tests. Mill scale decreased in crushing strength as the material became more reduced. Further research for implementation of these oxygen carriers is best focused on these three materials

Weighing the filter multiple times and checking very carefully for outliers in the trend was a good solution for eventual issues regarding static electricity but a sensitive scale with walls is recommended for further studies.

6.1 Further research

Because of time constraints SEM research on fully and partially oxidised samples were not conducted and can, for additional research, be inspected. This could be useful to determine if the cracks seen formed in highly reduced mill scale and ilmenite are present in other samples, as this could potentially cause higher attrition. Further analysis in SEM could be of interest to look at the cross-section of these particles to see how deep the cracks penetrate into the particles.

Other than that more jet cup and crush experiments can be made to further enhance the credibility of the study since issues regarding static electricity with the scale are probably still present. Although the removal of static electricity may seem unrelated to the actual study, it is still relevant for accuracy when weighing the filter.

It might be worthwhile to determine the efficiency of the different OC to see which material is better at transporting oxygen in a reactor. We have measured different compositions in the materials studied in this thesis, where for example LD-slag showed a lower iron content than other materials. Since iron is important for the oxygen-carrying process this might make LD-slag less suited for this purpose. Price is also a factor worth considering when upscaling to an industrial scale as small differences can multiply and grow exponentially.

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A

Appendix 1

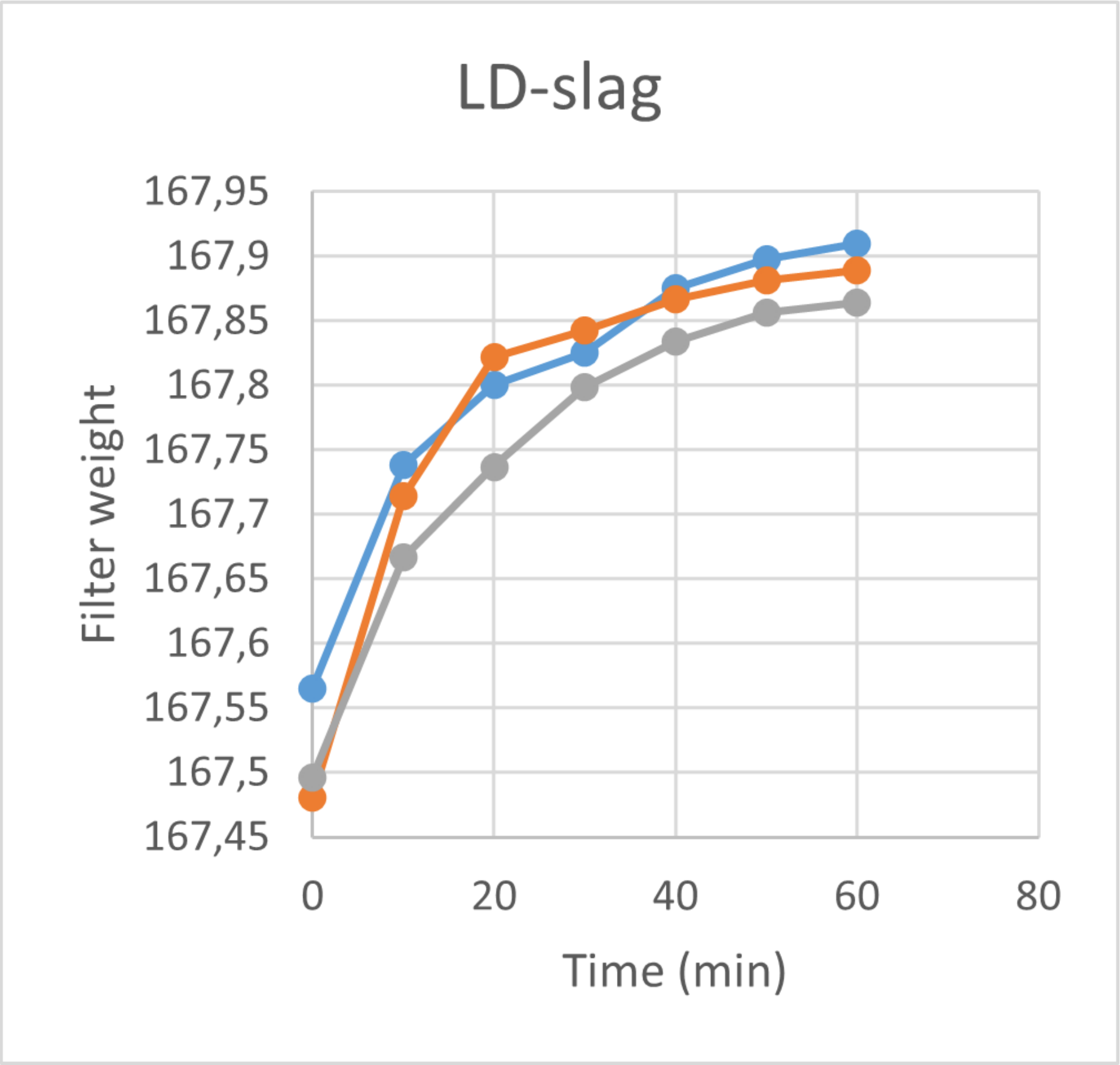

Figure A.1: Diagram that shows how the amount of fines produced by LD-slag diminishes over time.

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