COMPARING THE STRUCTURAL DEVELOPMENT OF SAND AND ROCK ILMENITE DURING LONG-TERM EXPOSURE IN A BIOMASS FIRED 12 MW_{th} CFB-BOILER

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Abstract - Oxygen Carrier Aided Combustion (OCAC) is a novel combustion concept and a spin-off from Chemical-Looping Combustion (CLC). The purpose of the concept is to increase the overall efficiency in conventional circulating fluidized bed (CFB) boilers by replacing the commonly used silica-sand bed material with an oxygen carrier (OC). The conceptual idea is to utilize the fluid dynamics in a CFB and the inherent oxygen transport supported by the OC to increase the oxygen distribution within the furnace in time and space. This is achieved as the OC can buffer oxygen in oxygen rich regions and release oxygen in oxygen poor regions of the furnace, resulting in less emissions of harmful and unburnt species as well as operation at lower air-to-fuel ratios. The OCAC concept has been successfully proven in laboratory and pilot plants and further demonstrated in full scale operation (75 MW) during more than 10'000 hours. However, as far as known to the authors no studies have been reported on the evolution in mechanical stability of an OC during continuous operation in a scale larger than 100 kW.

This work aims to make a first evaluation of how ilmenite particles used as OC are affected with regard to mechanical resistance during long-term exposure to combustion conditions in Chalmers semi-industrial scaled (12 MW) CFB-boiler. The mechanical stability of two different types of ilmenite with similar composition, a sand ilmenite and a rock ilmenite, are evaluated in experiments conducted in the Chalmers boiler. Samples of the fresh materials and samples collected during operation in the Chalmers boiler are investigated with regard to their morphology, size distribution but also to attrition in a laboratory test rig. The study shows that the two materials differ in how the mechanical degradation occurs with exposure time. Cavities are formed inside the sand ilmenite particles which are held together by an ash layer before they are shattered into numerous pieces, whereas the rock ilmenite develops distinct cracks that cause splitting of the particles.

INTRODUCTION

The utilization of different oxygen carrying materials for the purpose of combustion, so called oxygen carriers (OC), is commonly associated with the low carbon foot-print technique Chemical-Looping Combustion (CLC). In CLC, an OC is circulated between two reactors, an air reactor and a fuel reactor. In the air reactor the OC takes up oxygen, which can then be released as the OC is transported into the fuel reactor where combustion takes place. The research coupled to CLC has during more than 15 years contributed greatly to increase the understanding of OCs (Lyngfelt, 2014 and Adánez et al 2012) and their characteristics during the redox conditions presented during thermochemical fuel conversion. However, these experiences stems almost exclusively from laboratory scale units, typically in the range of 1-10 kW (Lyngfelt, 2014), operated during limited time with fuels that contain low amounts or no ash. In this manner, little is in fact known on how these OC work and are affected by the conditions presented in a large scale unit.

Oxygen Carrier Aided Combustion (OCAC) is a novel concept, sprung from CLC, which allows for increased efficiency during conversion of fuels considered as difficult, such as biomass and waste (Thunman et al., 2013). The concept has been developed as a result of close collaboration between Chalmers and the utility company E.ON and is currently available on the market by Improbed™. The concept of OCAC combines the OC used in CLC with the existing Fluidized Bed Combustion (FBC) technology where there is only one reactor and silica sand is commonly used as bed material. In OCAC, the traditional bed material in a FBC is replaced by an OC, which can take up and release oxygen inside the combustion chamber creating conditions for more effective combustion with lower emissions (Thunman et al., 2013 and Lind et al., 2016). Thus, OCAC provides a beneficial support to an already existing technology. FBC technology is sensitive to the particle size and size distribution of bed material as large particles are difficult to fluidize and fine fractions are entrained with the flue gases. Typically, a size of 100-300 μm is used (Leckner, 1998). During the last couple of years, OCAC has progressed from laboratory and pilot scale to be demonstrated on industrial scale (75 MW) for over 10'000 hours.

Both synthetic and natural materials have previously been evaluated as OCs for CLC (Adánez et al., 2012, Azis et al., 2010, Schwebel et al., 2012 and Leion et al., 2008). Although synthetic materials have given promising results with regard to oxygen carrying capacity, they so far have shown to be high cost alternatives to the existing bed materials. Among the tested natural materials, the mineral ilmenite, which is an iron-titanium oxide, has shown to be a promising alternative. Ilmenite occurs naturally both as sand and as a rock ore. Multiple studies covering the properties of both sand and rock ilmenites already exist, both with regard to their oxygen carrying capacity and interaction with ash components originating from the fuel (Adánez et al., 2010, Cuadrat et al., 2012, Knutsson and Linderholm, 2015 and Corcoran et al., 2014).

In this work, focus is put on the structural change of sand and rock ilmenite when being exposed to combustion conditions. Both sand and rock ilmenite were used as OCs during two consecutive weeks each, in Chalmers 12-MW_{th} CFB combustor while operated with biomass as fuel. The aim of this study is to map how the OC particles structure develops during long-term exposure, and further understand how the mechanical stability of the OC particles is influenced.

MATERIALS AND METHODS

Oxygen Carriers. Two types of OCs were used in the present study – a sand and a rock ilmenite. Both materials are natural occurring ilmenite ores, but have different origins. The sand ilmenite, which originated from Australia, was provided by Sibelco, while the rock ilmenite originated from Norway and was provided by Titania A/S. The elemental composition of the fresh materials are presented in Table 1, with the main crystal phase identified being $FeTiO_3$.

Table 1: Elemental specification of sand and rock ilmenite as-received from supplier

	Sand Ilmenite	Rock Ilmenite
Element	wt.%	wt.%
Fe	34.20	33.29
Ti	27.93	23.85
Mg	0.44	1.83
Si	0.15	0.94
Al	0.19	0.34
Mn	0.48	0.13
Ca	0.06	0.26
K	0.07	0.07
Na	0.04	0.08
P	>0.01	>0.01

Boiler Specification. The 12 MW_{th} CFB-boiler is situated in the Chalmers university campus and is predominantly used for district heating of campus facilities from November to April. The furnace has a cross section of 2.25 m^2 and a height of 13.6 m. A detailed description of the system is provided by Thunman et al. (2013). The system is equipped with a number of extraction ports where bed material and bottom ashes can be extracted at the dense state of the bed using a water-cooled suction probe. Bed material samples were extracted from the dense bed, the first one shortly after start-up and then on a daily basis for 15 days. In the present paper, only the results from the second and 15^{th} days are presented. During the experimental period, controlled amount of new bed material was added when required in order to keep constant operational conditions.

Experimental conditions. Two experimental runs have been performed, one with each of the OC bed materials. For both of the experimental sessions 100 % of the respective oxygen carrying bed material was used in the boiler. During the experiments, the boiler was fired with wood-chips that had a moisture content in the range of 38.5-45.3 wt. % based on the as-received fuel and the temperature was held around 850°C. Furthermore, to withhold stable operational conditions, the bed height was held constant through continuous supply of additional fresh material. The total bed inventory in the boiler was held around 3000 kg throughout the experiments.

Characterization methods. A selection of the extracted samples were immobilized in epoxy and polished to obtain a cross-sectional surface of the particles, which was evaluated with Scanning Electron Microscopy (SEM) analysis. Quanta 200FEG equipped with an Oxford EDS system was used for SEM imaging and elemental composition analysis. 50-60g of the sampled bed material was sieved during 20 minutes to obtain the size distribution. Sieving plates of the following mesh size was used; 355μm, 250μm, 180μm, 125μm, 90μm and a bottom plate for fractions below 90μm. Particles in the range of 125-180 μm were collected during the sieving, from which a sample of 5g was tested for mechanical stability in a customized jet cup, described in detail by Rydén et al. (2014). The apparatus is constructed to simulate the mechanical stress that particles undergo in a FBC. A filter collecting the fine particles that leave the device at the top, was continuously measured, providing the rate of attrition of the bed material particles.

RESULTS AND DISCUSSION

Cross-sectional SEM micrographs of fresh sand and rock ilmenite particles are shown in Fig. 1 a) and b), respectively. The materials differ in particle morphology where the sand ilmenite particles have rounded edges and the rock ilmenite particles have sharp edges.

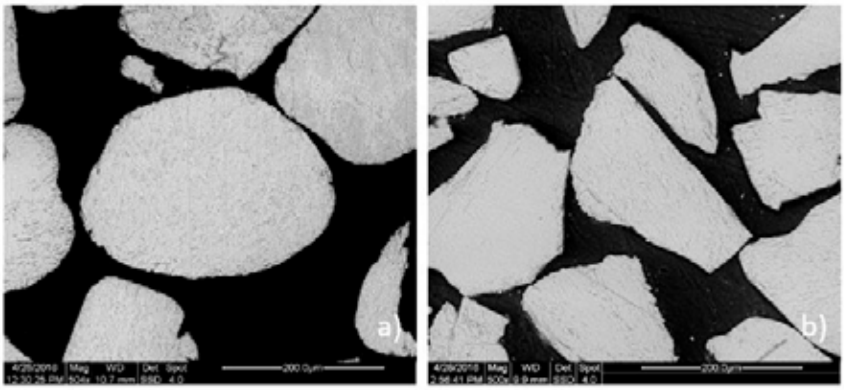

Fig. 1. SEM micrographs of ilmenite particles used as bed material during the experiments: a) sand ilmenite; b) rock ilmenite.

The difference in particle shape is influenced by the origin of the materials. The sand ilmenite, which has been used in the as-received form, has prior to collection been exposed to natural weathering, erosion and attrition, whereof the particles have obtained a rounded shape. This is not the case for rock ilmenite particles which have been mined and ground and are thus sharp-edged. Analysis with SEM-EDX show that both materials have a homogeneous distribution of Fe and Ti over the cross-section with no local enrichment of either of the elements.

The change in morphology of the particles have been followed on samples of both sand and rock ilmenite extracted after 2 and 15 days. The cross-sectional micrographs of these are presented in Fig. 2 a) - d). After 2 days of exposure, (Fig. 2 a)), small voids are formed at the outer parts of the sand ilmenite particle. This phenomenon is further developed over time and is more prominent after 15 days (Fig. 2 b)) where the voids have evolved to larger cavities that are widespread at the inside of the particles. The rock ilmenite particles have formed distinct cracks that were extended along the inside of the particles, after 2 days (Fig. 2 c)). During further exposure, the cracks in the rock ilmenite expanded further, which led to break-up of the majority of the particles (Fig. 2 d).

The different morphologies developed during exposure points on the importance that the initial structural morphology of the particles have on their mechanical performance during exposure. Small cavities are expected to form within the bed material particles, as a result of inter-diffusion of elements during high temperature exposure. Further, formation of cracks has also been reported previously as a result of the thermal and mechanical stress that the particles undergo within the reactor (Knutsson and Linderholm, 2015). During the mining and the grinding process that the rock ilmenite has undergone prior to exposure, the material has accumulated mechanical stress. The further thermal and chemical stress during exposure to the conditions in the combustion chamber, adds to this accumulated stress and leads, most probably, to cracks opening as a form of stress release. The initial material preparation, could therewith be used as an explanation for the mechanism observed for the rock ilmenite.

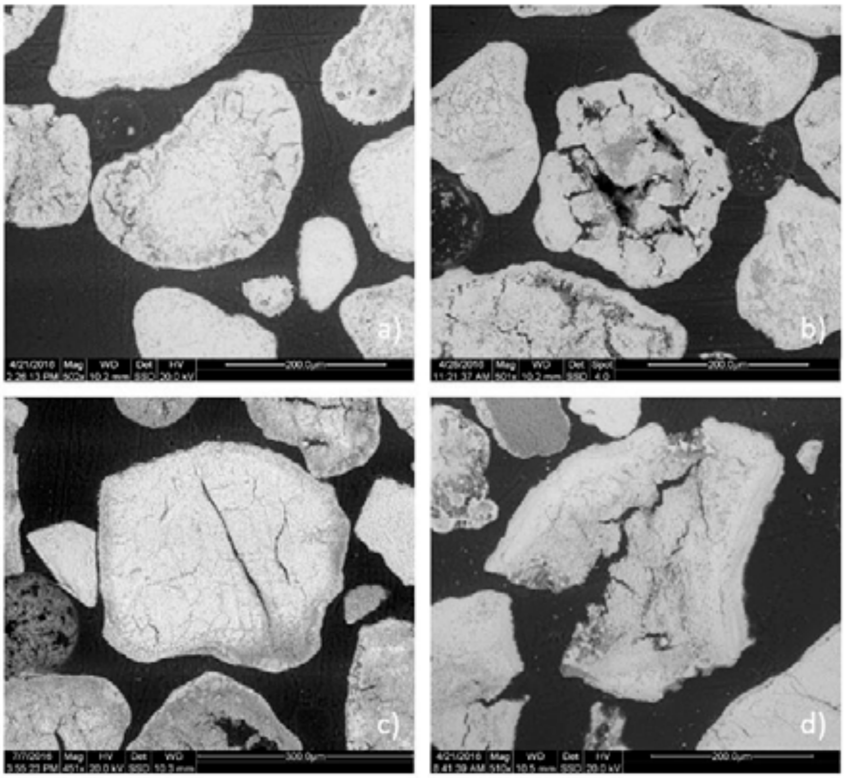

Fig. 2. SEM micrographs of cross-section of ilmenite particles extracted after 2 and 15 days of exposure where a) and b) are sand ilmenite and c) and d) are rock ilmenite.

Ash layers, similar in composition and consistent with previous research (Corcoran et al., 2014), which increase with exposure time, have been observed on both materials through SEM-EDX analysis. For sand ilmenite, the formed ash layer was found to enclose the particles, while in the case of rock ilmenite, openings in the ash layers are detected that could be a cause for particles containing cracks to fully diverge.

Particle size distributions have been obtained through sieving of the materials prior to exposure as well as sieving the collected samples that have been used in the boiler. In Figure 3, the results from the sieving of fresh sand and rock ilmenite, as well as the materials collected after 2 and 15 days, are presented. The sieving curves of the fresh materials reveal that the sand ilmenite contains considerably higher amount of finer fractions than the rock ilmenite, which is in line with the supplier´s specifications. The lower amount of fines in the case of rock ilmenite, can be explained with the more narrowed size distribution that is obtained through grinding.

After 2 days of exposure the rock ilmenite shows a noticeable increase in the amount of coarse particles (particles above 250 µm), which further expands with time. This trend is accompanied by an initial decrease in the finer particle fractions (below 125 µm), followed by a moderate increase after 15 days. For the sand ilmenite, a drastic decrease of finer fractions can be observed after two days, as well as a significant increase of particles over 180 µm. These trends are consistent and sustained after 15 days.

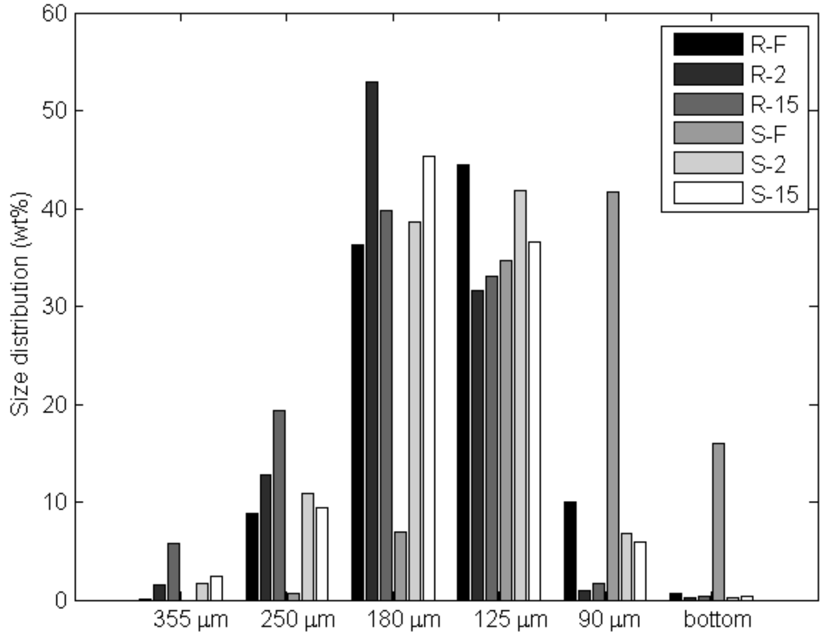

Fig. 3. Sieving curves obtained through sieving of sand and rock ilmenite in as-received condition as well as after 2 and 5 days of exposure. R stands for rock, S for sand, F for fresh material, 2 and 15 are the amount of days that the material has been used as bed material before extraction.

The enlargement of particle size for both sand and rock ilmenite, with increased time in the combustion chamber, can be explained by the ash layer growth around the particles. Increase in the porosity of the ilmenite particles (both sand and rock) has also been observed and previously reported, which would also lead to increase in the size of the bed material particles. The drastic decrease of finer fractions could mainly be explained by particle loss due to their entrainment with the flue gases and with the fly ash. Some of the particles are also expected to increase in size due to the factors described previously and thereby be accounted for in higher size fractions within the sieving curve.

Fig. 4 shows the results of the attrition tests performed on both sand and rock ilmenite. The fresh materials are worn equally in the beginning, followed by a slight increase in the measured attrition for the case of fresh rock ilmenite. The increase in the latter case was expected due to the observed sharp edged particles morphology which is thus more easily worn off than the round-edged structure of the fresh sand ilmenite particles. Accordingly, used rock ilmenite particles obtain a more rounded shape with exposure time in the combustion chamber, which is also confirmed by the results in Fig. 2. For both materials, the measured attrition is increased after exposure in the boiler. The materials show higher attrition after 2 days than after 15 days of exposure. The highest accumulated attrition is found for the rock ilmenite after 2 days, which with further exposure decreases below the attrition for the exposed sand ilmenite samples.

The attrition of both materials is highest after 2 days, which is reasonably due to that the inherent stress in the particles is released early in their exposure to boiler conditions. This is confirmed by the observation that the attrition is higher for the rock ilmenite which in its as-received form is also expected to contain a higher degree of inherent stress. With further exposure, the attrition of both materials is decreased. The reason for this could be coupled to that the particles are stabilized by the formation of ash layers. However, the rock ilmenite becomes considerably more resistant to mechanical stress with time in comparison to sand ilmenite. The reason being that cavities found in sand ilmenite are built up over time while the cracks in the rock ilmenite are formed earlier on.

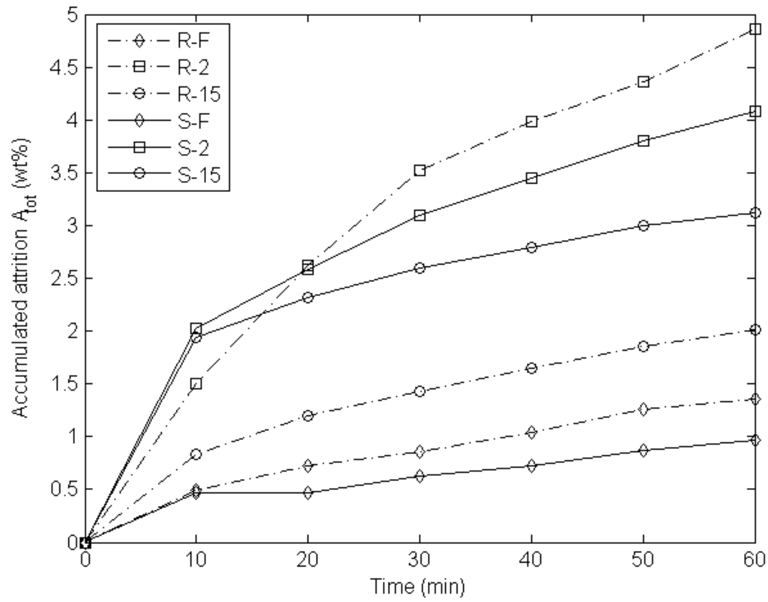

Fig. 4. Accumulated attrition measured on sand, S (solid lines) and rock, R (dashed lines) ilmenite in "as-received" conditions but also after 2 and 15 days of exposure. Diamond markers represent fresh material, F, square and circular markers represent material that has been extracted after 2 and 15 days of operation in the combustor, respectively.

Based on the results found in this study, it is proposed that the route for degradation of sand ilmenite is caused by the cavities formed inside the particles. When these become prominent enough, the particle can no longer be held together and are shattered in numerous small pieces, as shown in Fig. 5. This process is, however, delayed by the build-up of ash layers around the particles as the attrition is lower with increased exposure. Furthermore, it is suggested that the rock ilmenite decays by splitting where the observed cracks are formed, Fig. 5. It is suggested that the cracks, which induce the splitting, are caused by inherent stress in the particles originating from the mining process of the rock ilmenite. As the inherent stress in the rock ilmenite is released it causes the particles to split early in the process and after splitting withhold higher resistance to mechanical stress, which is shown by the attrition results. The sand ilmenite, on the other hand, holds less inherent stress and is thus not as sensitive early in the process and its mode of mechanical degradation is consistent with the time of exposure.

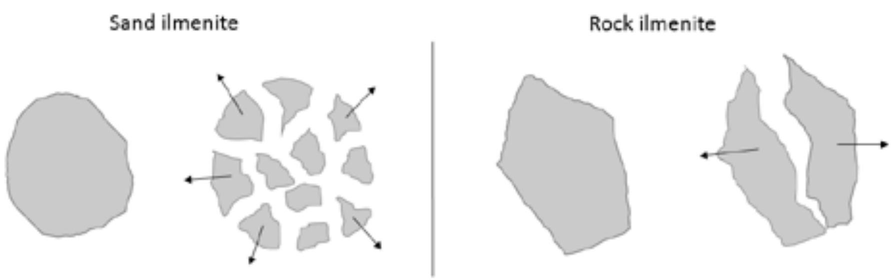

Figure 5 – Schematic sketch of the morphological change and the possible ways for particle degradation of sand and rock ilmenite particles during 15 days of exposure.

CONCLUSIONS

Two naturally occurring ilmenites, a sand and a rock ilmenite, have been used as bed material for OCAC in Chalmers 12-MWth CFB boiler during an experimental period of more than two consecutive weeks for each material. This work aimed to describe how the structure of the respective materials develop over time, with regard to mechanical stability. Both fresh samples and samples extracted from the boiler after 2 and 15 days of operation have been evaluated by means of SEM, sieving and attrition tests.

The obtained results point to that the sand and rock ilmenite differ in their structural development, which has impact on their corresponding mechanical stability. The sand ilmenite forms cavities inside the particles that are held together by an ash-layer whereas the rock ilmenite forms distinct cracks along the inside of the particles which are also influenced by the formed layer around the particles. Both materials are weakened in mechanical strength as cavities and cracks are formed. It is found that rock ilmenite is initially less resistant to mechanical stress, but with increased exposure becomes more resistant to it in comparison to sand ilmenite. Sand ilmenite is also initially less resistant, but is more consistent in its mechanical stability over time. Two different mechanisms have been proposed for the material degradation where the main difference is that the sand ilmenite is shattered into numerous small pieces while the rock ilmenite is divided by the cracks formed.

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