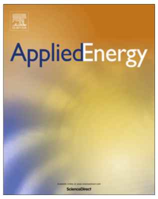
Applied Energy xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy



Characterization of ilmenite used as oxygen carrier in a 100 kW chemical-looping combustor for solid fuels

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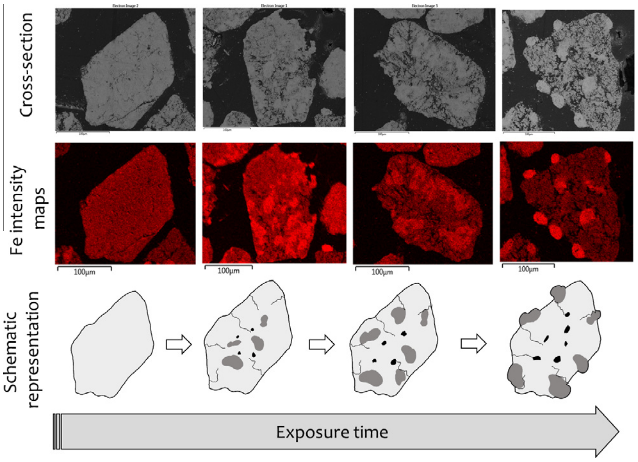
HIGHLIGHTS

- The ilmenite particles exposed in 100 kW unit does not form an iron shell.
- Fe segregates first within the ilmenite particles and further diffuses outwards.
- Difference in mechanical and chemical stress in larger units is suggested as cause.
- Mechanism for the microstructure development and material break down is suggested.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 December 2014
Received in revised form 22 April 2015
Accepted 25 May 2015
Available online xxxx

Keywords:
Chemical-looping combustion
100 kW CLC unit
Oxygen carrier
Ilmenite
Fe segregation

ABSTRACT

Chemical-looping combustion (CLC) is considered to be the most promising and economically viable process for carbon dioxide capture. The oxygen carrier has a central role in the chemical-looping combustion process. Ilmenite, a natural mineral composed of $FeTiO_3$, has been extensively used as oxygen carrier in CLC systems due to its availability, relatively low cost and demonstrated reactivity. During the looping process ilmenite undergoes a series of chemical and mechanical transformations that eventually lead to the break-down of particles into smaller fragments, which are unfit for use in circulated fluidized bed (CFB) applications.

In the present study a 100 kW chemical-looping system was operated with ilmenite particles as oxygen carrier and with biomass char as fuel. Ilmenite particles were collected at the end of the run. The collected particles were characterized by X-ray diffraction (XRD) and Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS). Thermodynamic predictions of the expected compounds at the given conditions were also used to compare with the experimentally obtained results.

The aim of the study was to understand the change in morphology and chemical compositions of the collected ilmenite particles and to relate them to the exposure conditions in the CLC reactor.

It was found that the aging of the ilmenite particles could be distinguished based on the particle morphology. Furthermore, a possible mechanism for the transformation of the ilmenite particles during the cyclic chemical-looping process was proposed.

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http://dx.doi.org/10.1016/j.apenergy.2015.05.122
0306-2619/© 2015 Published by Elsevier Ltd.

Please cite this article in press as: Knutsson P, Linderholm C. Characterization of ilmenite used as oxygen carrier in a 100 kW chemical-looping combustor for solid fuels. Appl Energy (2015), http://dx.doi.org/10.1016/j.apenergy.2015.05.122

1. Introduction

The oxide that transports oxygen to the fuel has a central role in the chemical-looping combustion (CLC) process. In order for a transient oxide to be considered a good candidate for oxygen carrier in a CLC process it has to fulfill a list of criteria, such as:

- to be reactive both towards fuel and oxygen;
- to have sufficient oxygen transport ability;
- to be mechanically robust at high temperatures;
- to have high melting temperature;
- to have low production cost;
- not to be environmentally harmful [1].

Based on the ability of the oxides to convert the fuel, their melting point, as well as the formation of undesired side products the oxides based on copper (CuO), manganese (Mn_2O_3), iron (Fe_2O_3) and nickel (NiO) have been considered as best suited for the process [2,3]. Their suitability has been successfully demonstrated for syngas conversion in continuous CLC units [4–8]. With the introduction of the CLC concept to solid fuels the observed deactivation of the chosen systems caused by ash or by the loss of material when separated from the ash has put more weight on the necessity of a lower price and high availability of the oxide sources [9].

Investigations of low cost materials containing the desired transient oxides have been conducted in a series of studies [9–15]. Among the tested materials, ilmenite, iron–titanium mineral has been most widely tested within the performed CLC research [12,16–22].

Ilmenite is a natural mineral found in metamorphic and igneous rocks composed mainly of $FeTiO_3$, which nowadays represents mainly a source of TiO_2 for pigment industry. When ilmenite is used as oxygen carrier in a CLC system, $FeTiO_3$ represents the most reduced form, and Fe_2TiO_5 ($Fe_2O_3 + TiO_2$) the most oxidized form. During the redox cycling in the CLC system, other compositions are still possible [16].

Fresh ilmenite shows a slow conversion of the used fuel in the beginning with further gain in reactivity with the number of redox cycles and reaches at the end a value of reactivity similar to a synthetic Fe_2O_3 [16,23,24]. The gain in reactivity with the number of redox cycles has been explained previously by the formed Fe_2O_3 layer around a TiO_2 core that was suggested to enhance the availability of Fe_2O_3 for further transport of oxygen.

In the present study, ilmenite particles have been characterized after their use in a 100 kW CLC pilot plant. The investigated particles showed no formation of an iron rich surface layer. Instead, some particles displayed the formation of denser regions in an otherwise porous particle matrix. This unexpected finding led to the present study, which – based on the observed morphology and the chemical phase distribution within the particles – aims at exploring and clarifying the mechanism behind the activation and aging of ilmenite particles used as oxygen carrier in a chemical-looping process. Once properly understood, the mechanisms behind oxygen-carrier aging can provide important perspectives on the expected particle lifetime, and hence, on some design and cost aspects of a full-scale CLC system.

2. Materials and methods

2.1. Materials

The ilmenite used in this study is supplied by Titania A/S and originates from Norway. The particles have been ground and sieved to size interval 100–300 μm, with an average diameter of 171 μm. The used ilmenite contains 65.5 wt% $FeTiO_3$, 14.8 wt% Fe_2O_3 and 14 wt% TiO_2.

Used particles investigated in this study have been exposed for an interval of up to 70 h of fuel operation, and have been exposed for a longer interval in hot conditions. Particles are continuously elutriated from the reactor system, and therefore make up material has to be added with regular intervals. Hence, some of the investigated particles have experienced much less than 70 h of fuel operation.

The fuel used in this study is Swedish wood char produced by subjecting wood chips of both hard- and soft wood to 450 °C for 20 h in the absence of oxygen.

2.2. CLC reactor

The ilmenite characterized in the present study has been used as oxygen carrier in a 100 kW CLC unit consisting of an air reactor and a fuel reactor, as well as a four-chambered carbon stripper, four loop seals, and a circulation riser. The particles have different variation in conversion in the air and in the fuel reactor. The material in the air reactor are fully or almost fully oxidized, given the long residence time and the fast oxidation kinetics. In the fuel reactor, the particles have different residence time, and therefore different conversion. Some particles may dwell in the fuel reactor for several minutes, and leave the fuel reactor as highly reduced particles with $FeTiO_3$ as dominating phase, whereas other particles may remain for only a brief period of time, and exit the fuel reactor only slightly reduced. After the fuel reactor, particles enter the carbon stripper, where char is gasified and reactions between syngas and oxygen carrier occur, thus reducing the ilmenite further. The carbon stripper serves an important function and has a well-documented ability to increase the carbon capture efficiency [25]. However, the carbon slip from the fuel reactor is small and therefore the conversion difference of in- and outbound oxygen-carrier particles to and from the carbon stripper is also small. The particles returning to the air reactor display therefore a varying degree of oxidation.

The design of the 100 kW unit has been described in detail by Markström et al. [25,26]. Operational results from the 100 kW unit using ilmenite as oxygen carrier and wood char as fuel can be found in [27]. In this work, the gas conversion was 89–95%, and the carbon capture efficiency was 93–97% at a fuel power of 67 kW.

2.3. Methods for characterization

The crystal phase characterization of all the materials has been performed by X-ray powder diffraction (XRD), Siemens D5000 with Cu Kα characteristic radiation. Step size of 0.05° and an extracted profile between 20° and 90° (2θ) have been used as selected conditions.

For the morphological changes and chemical evaluation of the ilmenite particles a Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS), Quanta 200FEG with an Oxford EDS system have been used.

Porosity changes in the materials were evaluated using Image J software [28] and by contrast adjustments of SEM micrographs of cross-sections as well as Fe-maps of the same areas.

The specific surface area (the Brunauer–Emmett–Teller (BET) specific surface area) was measured by N_2-adsorption (Micromeritics, TriStar 3000).

FactSage, version 6.3 has been used for prediction of the phases that are thermodynamically stable under the present conditions. FactSage has been run in its Equilib module and FTsalt, FToxid and FACT53 have been used as databases [29].

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