### **ARTICLE IN PRESS**

#### [Applied Energy xxx \(2015\) xxx–xxx](http://dx.doi.org/10.1016/j.apenergy.2015.06.023)



Contents lists available at [ScienceDirect](http://www.sciencedirect.com/science/journal/03062619)

# Applied Energy



journal homepage: [www.elsevier.com/locate/apenergy](http://www.elsevier.com/locate/apenergy)

## Cement/CaO-modified iron ore as oxygen carrier for chemical looping combustion of coal

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#### highlights

- Iron ore as oxygen carrier was modified with CaO by two different methods.

- Fuel conversion was enhanced with the CaO-modified iron ore.

• Formation of Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> in Cement/CaO-combined iron ore prevented sintering.

#### article info

Article history: Received 2 December 2014 Received in revised form 4 June 2015 Accepted 14 June 2015 Available online xxxx

Keywords: Oxygen carrier Chemical looping combustion Iron ore Coal

#### abstract

Chemical looping combustion (CLC) of solid fuels is considered as a potential technology to reduce the energy penalty and the cost for  $CO<sub>2</sub>$  capture. However, the low efficiency of carbon conversion and gasification products conversion is a big concern for the in-situ gasification chemical looping combustion (IG-CLC) process with the low-cost natural iron ore as an oxygen carrier. This paper evaluates the enhanced fuel conversion with a new CaO-modified iron ore as oxygen carrier during the continuous coal CLC in a 1  $kW_{th}$  reactor. Both CaO-mixed iron ore and cement/CaO-combined iron ore were tested. The effect of oxygen carrier on the gaseous products was evaluated in the fuel reactor temperature range of 880–980 °C. The samples of oxygen carrier were characterized using BET, SEM–EDX and XRD. The results indicate that compared with the pure iron ore oxygen carrier, the utilization of both CaO-mixed iron ore and the cement/CaO-combined iron ore could efficiently enhance coal conversion and gaseous conversion in the fuel reactor. However, when the CaO-mixed iron ore was used, some CaO powder due to the attrition during continuous operation adhered to the particle surface of iron ore. The Ca-containing compounds, i.e., potential eutectic of a low melting point caused sintering on the particle surface of iron ore. As a result, it caused the reactivity deterioration of oxygen carrier at a high fuel reactor temperature. To avoid the occurrence of sintering on the particle surface of the oxygen carrier, an improvement of cement/CaO-combined iron ore as oxygen carrier was proposed. A stable structure of  $Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>$  was formed during the calcination process of the cement/CaO-combined iron ore. The sintering resistance of the iron ore was improved and the oxygen carrier after experiments maintained the porous structure. Reactivity deterioration of the combined oxygen carrier did not occur during the 5 h continuous operation even at the fuel reactor temperature of  $980 °C$ . Overall, the Cement/CaO-combined iron ore is a competitive oxygen carrier in the coal CLC process.

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#### 1. Introduction

Chemical looping combustion (CLC) is an emerging promising combustion technology with inherent separation of  $CO<sub>2</sub>$  without extra energy penalty  $[1]$ . Basically, the CLC process contains two reactions in cycle, i.e., the oxidation and the reduction of oxygen carrier, as is shown in [Fig. 1.](#page-1-0) The reduced oxygen carrier is first

<http://dx.doi.org/10.1016/j.apenergy.2015.06.023> 0306-2619/© 2015 Elsevier Ltd. All rights reserved. oxidized in the air reactor to obtain molecular oxygen from the air and then, the oxidized oxygen carrier is reduced in the fuel reactor to provide lattice oxygen for the fuel. Through the repeated oxidation and reduction of oxygen carrier, the oxygen is transformed from air to fuel avoiding direct contact between them, and the flue gas from the fuel reactor is not mixed with  $N_2$ . Therefore, the flue gas from the fuel reactor after water removal is, ideally, pure  $CO<sub>2</sub>$ . By this means,  $CO<sub>2</sub>$  is inherently captured during the fuel conversion without energy penalty.

Please cite this article in press as: Gu H et al. Cement/CaO-modified iron ore as oxygen carrier for chemical looping combustion of coal. Appl Energy (2015), <http://dx.doi.org/10.1016/j.apenergy.2015.06.023>

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Fig. 1. Schematic of chemical looping combustion.

For the solid fuel CLC process, the most common approach is the in-situ gasification chemical looping combustion (IG-CLC) [\[2\].](#page--1-0) In this approach, reaction patterns in the fuel reactor involve the fuel pyrolysis/gasification and the subsequent oxygen carrier reduction by the gaseous products, as is shown in Fig. 2. The feasibility of the IG-CLC technology has been successfully demonstrated in continuous reactors scaled from 500 W to 100 kW<sub>th</sub> with different solid fuels [\[2\]](#page--1-0). However, it is important to note that loss of oxygen carrier due to the ash removal process is inevitable in the IG-CLC process. The addition of oxygen carrier is then necessary to maintain the normal operation of the CLC process, and it would increase the capital cost. Therefore, increasing investigations have recently focused on the inexpensive Fe-based oxygen carrier, including synthetic materials  $[3-5]$ , natural iron ores  $[6-8]$  and industry byprod-ucts [\[9–11\].](#page--1-0) Unfortunately, these Fe-based oxygen carriers often exhibited a relatively poor performance during the IG-CLC process, i.e., low efficiency of coal conversion and gas conversion [\[12\].](#page--1-0) Therefore, larger bed inventory or reactivity improvement of the Fe-based oxygen carrier is necessary to realize high fuel conversion efficiency.

To promote the solid fuel conversion, some investigations were conducted to modify the Fe-based oxygen carriers with common gasification catalysts. One way is to mechanically add NiO [\[13\]](#page--1-0) or CaO [\[7,14,15\]](#page--1-0) into the Fe-based oxygen carrier. These mixtures as oxygen carrier created a synergistic effect on enhancing the fuel conversion due to the inevitable contact among char, catalysts and oxygen carrier. The other way is to develop a combined Fe-based oxygen carrier with carbonates [\[16,17\]](#page--1-0) and cement [\[18,19\].](#page--1-0) Commonly, these combined oxygen carriers involve the creation of new compounds, which promote the reaction between gaseous products and oxygen carrier [\[19–21\].](#page--1-0) The enhanced gas– solid reaction could further promote the char gasification due to



Fig. 2. Fuel conversion path in the fuel reactor in the IG-CLC process.

the reaction equilibrium. Among these additives, CaO seems to have a broader application prospect than other materials, e.g., NiO,  $K_2CO_3$  and Na<sub>2</sub>CO<sub>3</sub> due to its low cost. The CaO-modified oxygen carrier includes a mixture of lime and ilmenite and cement-combined oxygen carrier. For the mixed oxygen carrier, the CaO or lime may face with some potential problems at a high temperature, e.g., attrition and sintering, which could cause the reactivity deterioration of oxygen carrier during long-time operation. Addition of aluminate cement as a binder can improve the mechanical strength, chemical properties and sintering resistance of the particles [\[22–24\]](#page--1-0). Then, the cement-combined oxygen carrier was developed and the new stable formation of  $Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>$ was formed with enhanced sintering resistance. However, the performance of the combined oxygen carrier has not been tested in a continuous reactor, which was the most likely CLC reactor [\[25\]](#page--1-0).

Accordingly, the present investigation aims at evaluating the performance of CaO-modified Australia iron ore with different modification methods in a 1 kW $_{\text{th}}$  interconnected fluidized bed. A series of characterization analysis were conducted to explore the behavior of the CaO-modified iron ore, including X-ray diffraction (XRD), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM–EDX).

#### 2. Experimental

#### 2.1. Fuel

In the present investigation, Shenhua coal from China was selected as a feed stock. The proximate analysis and ultimate analysis are listed in Table 1. The coal was crushed into small size and double-sieved into the size range of 0.1–0.3 mm.

#### 2.2. Preparation of oxygen carrier

According to the X-ray Fluorescence (XRF) analysis results in [Table 2,](#page--1-0) the raw iron ore after calcination at 950  $\degree$ C mainly consists of 83.08% Fe<sub>2</sub>O<sub>3</sub>, 6.8% Al<sub>2</sub>O<sub>3</sub> and 9.13% SiO<sub>2</sub>. The chemical compositions of the involved raw materials, i.e., calcined dolomite and cement are also displayed in [Table 2](#page--1-0).

The dolomite after calcination was used as the CaO decoration. Two different methods were employed to add CaO into iron ore, i.e., mechanically mixed CaO/iron ore and cement/CaO-combined iron ore, noted as CIO and CCIO, respectively. For the CIO, the iron ore and the dolomite were initially calcined at 950 and 900  $\degree$ C, respectively. Afterwards, the particles were sieved to 0.1–0.3 mm and mixed at the iron ore/dolomite mass ratio of 4/1. The CCIO involved the utilization of a high alumina cement to combine the iron ore and dolomite. Dolomite was added to make use of the excess  $Al_2O_3$  and  $SiO_2$  in cement and iron ore to maximize the fraction of  $Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>$  in the oxygen carrier. The particles of these raw materials were first crushed to the size range below 0.03 mm. The fine powder was mixed with the mass ratio of iron ore/cement/ dolomite at 7/1/2 in a dry condition. Afterwards, some water was added to make a wet mixture, and it was then fed into a two-gear-roller granulator to extrude to form particles, as is displayed in [Fig. 3.](#page--1-0) The combined oxygen carrier was then calcined





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