



Cement bonded fine hematite and copper ore particles as oxygen carrier in chemical looping combustion



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HIGHLIGHTS

- Waste fine hematite and copper ore particles are reused by cement bonding.
- The copper ore to hematite mixing ratio is optimized at 20:80 in weight.
- Integrated merits of hematite and copper ore are achieved in a single particle.
- The $\text{CaAl}_2\text{SiO}_7$ phase acts as a perfect inert support to inhibit OC sintering.

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ABSTRACT

In this work, bimetallic oxygen carriers (OCs) were prepared from waste fine particles (<0.1 mm) of natural copper ore and hematite for possible application in chemical looping combustion (CLC) processes. The mixtures with different mass ratios of copper ore to hematite were physically bonded by 20 wt% of calcium aluminate cement to obtain OC particles with relatively high disperse structure and good mechanical strength. Cyclic isothermal redox tests were first conducted in a thermogravimetric analyzer (TGA) to optimize the copper ore to hematite mixing ratio in the bimetallic OC. Synergistic effect between copper ore and hematite was observed, and the copper ore to hematite mixing ratio was optimized at 20:80 (namely $\text{Cu}_{20}\text{Fe}_{80}\text{@C}$) based on a comprehensive consideration of OC reactivity, economic cost and auto-thermal balance in fuel reactor. Subsequently, performance of $\text{Cu}_{20}\text{Fe}_{80}\text{@C}$ and $\text{Fe}_{100}\text{@C}$ (cement bonded pure hematite) were further evaluated in a batch fluidized bed reactor, using coal as fuel. The $\text{Cu}_{20}\text{Fe}_{80}\text{@C}$ was found to be more reactive towards coal gasification products than that of $\text{Fe}_{100}\text{@C}$, which is mainly attributed to the synergistic effect attained by the coexistence of copper ore and hematite in the $\text{Cu}_{20}\text{Fe}_{80}\text{@C}$ OC. Moreover, the effects of steam concentration, oxygen to fuel ratio and coal type on the performance of $\text{Cu}_{20}\text{Fe}_{80}\text{@C}$ were investigated. It was found that both the increase of steam concentration and oxygen to fuel ratio can facilitate the coal conversion, but they are not the higher the better and should be balanced between coal conversion and operational cost when turning to industrial application. Lignite was more suitable to be converted by $\text{Cu}_{20}\text{Fe}_{80}\text{@C}$ OC in *iG*-CLC process due to its better gasification reactivity than anthracite. 30 cyclic redox tests with lignite showed that $\text{Cu}_{20}\text{Fe}_{80}\text{@C}$ exhibited superior redox reactivity, nice fluidization behavior and good anti-sintering property in fluidized bed tests. This work demonstrated that cement bonded fine particles of hematite and copper ore could be a promising and competitive OC candidate for industrial application in *iG*-CLC processes.

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1. Introduction

Growing concerns on global warming phenomenon, which most probably stems from large quantity of anthropogenic greenhouse gas emission, have resulted in worldwide research efforts to come

up with innovative and efficient combustion techniques which can reduce CO_2 emission during fossil fuel combustion processes [1–3]. Among the state-of-the-art carbon capture and sequestration (CCS) technologies [4,5], chemical looping combustion (CLC) has been viewed as one of the most promising approaches due to its inherent CO_2 separation characteristic as well as particularly low energy penalty [6]. For a typical CLC unit, it usually consists of two coupled reactors, *i.e.*, fuel reactor (FR) and air reactor (AR). A kind of solid

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Nomenclature

Cu20Fe80@C	mixed copper ore and hematite (mixing ratio of 20:80 in weight) with 20 wt% of cement	$\gamma_{H_2/C}$	the gas yield of H ₂ to total carbonaceous gas products (-)
Fe100@C	pure hematite mixed with 20 wt% of cement	Abbreviations	
F_{N_2}	the inlet flow rate of N ₂ (mL·s ⁻¹)	AR	air reactor
$F_{out, red}$	the instantaneous outlet gas flow rate (dry basis) (mL·s ⁻¹)	CCS	carbon capture and sequestration
m	the instantaneous weight of the OC (mg)	CLC	chemical looping combustion
m_o	the weight of the OC at fully oxidized state (mg)	CLOU	chemical looping with oxygen uncoupling
m_r	the weight of the OC at fully reduced state (mg)	DTA	differential thermal analysis
m_0	the weight of the OC at the beginning (mg)	ECD	electron capture detector
Me	oxygen carrier in reduced state	EDX	energy dispersive X-ray spectroscopy
MeO	oxygen carrier in oxidized state	ESEM	environmental scanning electron microscope
R_o	the oxygen carrying capacity of the OC (-)	FR	fuel reactor
t_0	the time point at the start of the reduction stage (s)	FS	full scale accuracy
t_{total}	the time point at the end of the reduction stage (s)	FTIR	Fourier transform infrared spectrometry
x_c	the carbon conversion rate (s ⁻¹)	GP	Gaoping anthracite from China
x_{inst}	the instantaneous carbon conversion rate (s ⁻¹)	iG-CLC	<i>in-situ</i> gasification chemical looping combustion
x_r	the weight loss rate of the OC with synthesis gas (s ⁻¹)	NDIR	nondispersive infrared analysis
X_c	carbon conversion (-)	OC	oxygen carrier
X_r	the weight loss ratio of the OC with synthesis gas (-)	SL	Shengli lignite from China
y_i	the instantaneous volume fraction of species i (CO ₂ , CO, CH ₄ , H ₂ and O ₂) in flue gas (-)	TCD	thermal gas conductivity
Greek symbols		TGA	thermogravimetric analyzer
Ω	the oxygen to fuel ratio (-)	XRF	X-ray fluorescence
γ_i	the gas yield of species i (CO ₂ , CO, CH ₄) (-)	XRD	X-ray diffraction

metal oxide, known as oxygen carrier (OC), circulates between FR and AR to transfer lattice oxygen needed for fuel conversion. In other words, high metal valence OC (MeO) is reduced by fuel in FR and the reduced OC (Me) regenerates itself by air oxidizing in AR. As FR and AR are structurally interconnected but atmosphere-isolated, the outlet gas of FR mainly consists of CO₂ and H₂O, highly enriched CO₂ stream can be obtained after a simple steam removal process [7].

Due to the large reserve and low price of coal, much more attention has been focused on coal-direct CLC process during recent years [8–12]. Basically, three possible ways have been proposed to realize coal-derived CLC processes, *i.e.*, *ex-situ* gasification chemical looping combustion, *in-situ* gasification chemical looping combustion (iG-CLC) and chemical looping with oxygen uncoupling (CLOU) [13]. As additional gasification and air separation units are required, the first way is considered to be economically unfavorable. For the second way, the coal gasification process and gas-solid reaction between OC and gasification products occur in FR simultaneously, so as to avoid the separated gasification unit. While for CLOU, a kind of OC which can release gaseous O₂ in FR is employed, thus direct combustion of coal with O₂ in FR is realized. In this paper, research work will be focused on iG-CLC. Fig. 1 depicts the general flow path of iG-CLC. As it can be seen that both coal and OC particles are fluidized by gasification agent (CO₂ and/or H₂O) in FR, where complicated heterogeneous and homogeneous chemical reactions, *e.g.*, coal pyrolysis, coal char gasification and OC reduction by gasification products, are taking place. Subsequently, the OC after being reduced in FR is further transported back into AR for regeneration. The possible chemical reactions for typical coal-derived iG-CLC process have been summarized in literature [14].

For industrial implementation of chemical looping processes, the selection of suitable OC matters a lot. An appropriate OC should have sufficient oxygen donating capacity, satisfactory reactivity, good resistance to sintering and agglomeration as well as being

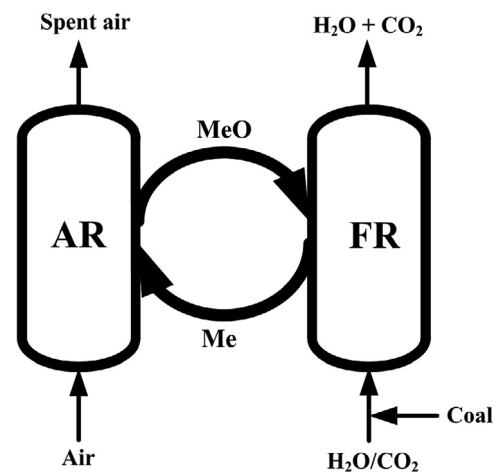


Fig. 1. General flow path of iG-CLC process.

environmentally benign and of low cost. In the last few decades, over 1000 kinds of OCs have been manufactured and tested under conditions of thermogravimetric analyzer (TGA), laboratory fluidized bed reactors as well as pilot scale chemical looping units, which have been comprehensively reviewed in Ref. [13]. During the early stage of CLC, materials for OC preparation were mostly pure chemicals, which exhibited the defect of high cost for industrial application. Additionally, due to the coal ash deposition, OC contamination by pollutants and materials loss in OC/ash separation process, the life cycle of the OC can be further reduced when being applied to coal-derived CLC process. Recently, increasing interests are being shown in natural minerals, *e.g.*, iron ore [15–21], copper ore [22–27] and manganese ore [28–31], which have been investigated and proposed to be possible OC candidates in chemical looping processes.

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