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Synergistic effects of mixtures of iron ores and copper ores as oxygen carriers in chemical-looping combustion

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Abstract

Iron ore is a cheap and nontoxic oxygen carrier in chemical-looping combustion (CLC). However, it performs good recyclability while low reactivity in the CLC of solid fuels. Copper ore exhibits very high reactivity and oxygen uncoupling behavior, while suffers from tendency towards sintering and agglomeration during consecutive redox cycles at a higher temperature (e.g., 900–1000 °C). In this work, mixtures of hematite and copper ore were used as oxygen carriers for CLC of syngas and coal. Through the isothermal redox experiments at 950 °C in a thermogravimetric analyzer, it is found that there are synergistic effects between iron ore and copper ore, and copper ore could be more efficiently utilized when the mixing ratio of copper ore is maintained 10–20 wt%. As the mixing ratio of copper ore is 20 wt%, the reduction reaction of the mixer OC is no longer endothermic, which is beneficial to the controllability of the fuel-reactor temperature. The fluidized-bed experiments were carried out to verify the reactivity of the mixing ore OCs at 950 °C. It is observed that the mixing OC with 20 wt% copper ore has a better reactivity with the gasification products (especially H₂) of low-volatile anthracite than the pure hematite, and leads to a higher fuel conversion rate and CO₂ yield. The mixtures of iron ore and copper ore are expected to address simultaneously reactivity, recyclability, cost and environmental concerns of oxygen carriers. © 2014 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

Keywords: Hematite; Copper ore; Oxygen carrier; Chemical-looping combustion; Coal

1. Introduction

The present CO_2 capture technologies have the disadvantage of the large energy penalty while separating CO_2 from flue gas. Chemical-looping combustion (CLC) is an innovative combustion

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technology for heat and power production with inherent CO_2 capture [1], thereby avoiding the need for costly separation processes. In a CLC system, fuel-reactor (FR) and air-reactor (AR) are interconnected while isolated from each other in reaction atmosphere [2]. The oxygen required for the fuel combustion is provided by an oxygen carrier (OC) which is reduced in the FR and regenerated by oxidation with air in the AR. The flue gas leaving the FR just consists of CO_2 and H_2O while the fuel is oxidized by OC

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completely, then pure CO_2 is obtained for storage or application after steam condensation.

The OC is critically important for CLC. Suitable OCs for gaseous and solid fuels should have the following characteristics: high reactivity to convert fuel to CO_2 and H_2O ; sufficient oxygen transport capacity to reduce the solid inventory in the reactors; high resistance to agglomeration, sintering, fragmentation and attrition; low cost and environmental friendliness [3]. At present, the OC is usually manufactured by pure chemicals whose cost is too high to be used in the large-scale CLC plants. Iron ore (e.g., hematite, ilmenite), which is inexpensive, abundant, environmental friendly, has been widely studied as OC in CLC [4–6], however it still exists several disadvantages, i.e., if Fe_2O_3 (the main component of iron ore) is only reduced to Fe₃O₄, its oxygen transport capacity will be lower; if the reduction phase contains FeO or Fe, thermodynamic limitation for FeO and Fe will prevent full conversion of CO and H_2 into CO_2 and H_2O [7,8]. Additionally, the reduction rate between iron ore and fuels is not rapid enough, which in return contributes to the increase of bed inventory. Thus it is necessary to improve the reactivity of iron ore through, e.g., doping with high-reactivity metal oxides (e.g., CuO [9,10], NiO [11]). However, the modified iron ore OCs were limited by complex preparation process and high price of the active metal. On the other side, in the case of CLC of coal, the char gasification is a rate-limiting step [12], resulting in a low CO₂ capture efficiency and coal combustion efficiency using iron ore as OCs. Therefore, accelerating the char gasification is important to fast and complete conversion of solid fuels in the FR. Some researches aimed to improve the char gasification rate through adding catalysts into OC. The catalysts are usually alkali metals or alkaline earth metals [13–15]. However, the loss of catalysts during the multiple redox process and the sintering/agglomeration of OC particles due to the low melting points of alkali components should be in particularly solved.

Copper ore, which is a respectively cheaper material compared with chemicals of active metal oxides, exhibits very high reactivity and oxygen uncoupling behavior (which is able to release gaseous O_2 in the oxygen-deficient FR to avoid the rate-limiting gasification step in the in-situ gasification CLC processes), which leads to higher overall reaction rate, higher carbon conversion, higher CO₂ capture and combustion efficiencies, and much less OC inventory and lower solid circulation rate. Furthermore, the reaction of copper ore and coal gasification products is exothermic (by the way, the reaction of iron ore and fuels is endothermic), which will helps to fulfill the heat balance over the system. However the copper ore is still more expensive than iron ore and copper materials have rather low melting points

(1083 °C for Cu, 1235 °C for Cu₂O and 1326 °C for CuO) [9,16], which is easy to sinter and agglomerate at high temperatures.

The mixtures of iron ore and copper ore as OCs may exhibit synergistic effects in improving reactivity of iron ore and resistance to sintering/ agglomeration of copper ore. The synthetic mixed copper-iron oxides OCs have been studied by different researchers [9,17,18]. The mixed OCs showed favorable performance and synergistic effects. The objective of this study was to design a natural combined OC with optimized mixing ratio of iron ore and copper ore to attain high reactivity and stable reaction performance in CLC. The mixture of iron ore and copper ore was also expected to address cost and environmental concerns of OCs.

2. Experimental

2.1. Experimental material

In this work, the OCs were prepared from a hematite and a nature copper ore of China. In order to improve the mechanical strength, they were calcined at 500 °C for 5 h and then 1000 °C for 10 h in an air-atmosphere muffle oven. Finally, the ore particles after calcination were ground and sieved to 0.18–0.28 mm to obtain the fresh OC products. Based on the X-ray fluorescence (XRF, EDAX EAGLE III) measurement and X-ray diffraction (XRD, X' PertPRO) analysis, the chemical analysis of the two ores is shown in Table 1. The coal used in this work was GaoPing (GP) anthracite from China. The particle size of coal was in the range of 0.3–0.5 mm and the proximate and ultimate analyses of coals are shown in Table 2.

2.2. Experimental procedure and fluidized-bed reactor

At first, the copper ore and hematite were mixed with the mass ratio of 0/10, 1/9, 2/8, ..., 10/0 as the primary samples. The samples were labeled as Hem, 1Cu9Hem, 2Cu8Hem, ..., Cu-ore, respectively. Then, the isothermal redox experiments were conducted in a thermogravimetric analysis (WCT-1D, TGA) with these samples.

 Table 1

 Chemical analysis of the hematite and copper ore OC.

Hematite w	t%	Copper ore wt%			
Fe ₂ O ₃	81.89	CuO	21.04		
SiO ₂	8.42	CuFe ₂ O ₄	70.05		
Al_2O_3	8.37	SiO ₂	5.53		
Others	1.32	Al_2O_3	1.08		
		Others	2.29		

Table 2 Proximate and ultimate analyses of GP coal.

Solid fuels	Proximate (wt%, ad)			Ultimate (wt%, ad)					
	Moisture	Volatiles	Ash	Fixed carbon	С	Н	Ν	S	0
GP coal	2.25	10.69	20.62	66.44	70.04	3.54	1.90	1.24	0.41

Eighteen reduction–oxidation cycles were conducted at atmospheric pressure to determine the stability of each mixed samples. The reaction temperature was 950 °C in all tests. In the reduction periods, syngas was introduced to react with the OC for 1 min. The syngas composition is based on typical coal gasification products, which is a gas mixture of 25% H₂, 35% CO and 40% CO₂ (volume based). In the oxidation periods, air was used to re-oxidize the OC for 3 min. To avoid the mixing of reduction gases and air, the system was flushed with argon for 4 min before and after each reduction.

Moreover, the screened mixed ore particles that have a reasonable mixing proportion were conducted in a batch fluidized-bed reactor with GP anthracite. The reaction temperature was still 950 °C. The fluidization gas was 50% $H_2O + 50\%$ N_2 (750 ml/min $N_2 + 0.6$ g/min H_2O) in the reduction and air (900 ml/min) in the oxidation. Nitrogen was used to sweep the reactor between the two periods. A total amount of about 60 g 2Cu8Hem or 71 g hematite particles were first placed on the stainless porous plate, exposing to the air for 30 min at a set-point temperature to ensure complete oxidation. A batch of 0.9 g coal was added into the reactor which corresponds to a supply oxygen coefficient of 1.0. The supply oxygen coefficient is defined as the ratio of the active oxygen provided by OC to the oxygen required for the full combustion of coal. We defined here FeO as the reduced form for hematite, and FeO and Cu₂O for 2Cu8Hem OC.

A schematic view of the batch fluidized-bed reactor is shown in Fig. 1. It consists of a gas feeding unit, a fluidized-bed reaction unit, and a gas



Fig. 1. Schematic view of the fluidized-bed reaction system.

detection unit. The gas feeding unit provides air or nitrogen, which is introduced into the reactor from the bottom to simulate the AR or FR. A straight stainless steel tube with a height of 890 mm and an inner diameter of 26 mm was used as the reaction chamber, and it was electrically heated by a furnace. The off gas from the top of the reactor was first led to a filter to remove particulate matter and an electric cooler to remove the steam carried by gas, and then to an on-line gas analyzer (Gasboard Analyzer 3100) to detect the concentrations of CO₂, CO, CH₄, H₂ and O₂.

3. Data evaluation

The weight loss ratio of the OC at the reduction period, X_r (wt%), and at the oxidation period, X_o (wt%), can be calculated as:

$$X_{\rm r} = (m_{\rm o} - m)/m_{\rm initial} \times 100\% \tag{1}$$

$$X_{\rm o} = (m - m_{\rm r})/m_{\rm initial} \times 100\%$$
⁽²⁾

where m_0 and m_r represent the weight of OC at the oxidized state and reduced state; *m* is the weight of the OC at time *t*; m_{initial} is the weight of the OC at the beginning. The oxygen transport capacity, R_o (wt%), was defined as $R_o = (m_o - m_r) \times 100/m_{\text{initial}}$. Additionally, the oxygen releasing capacity is defined as the mass fraction of the gaseous oxygen can be released from the OC in inert atmosphere of the OC.

To study the enhancement effects of the unit mass copper ore on the oxygen transport capacity, the reaction rate and oxygen releasing capacity of the mixed ore, the contribution degrees of the oxygen capacity, reaction rate and oxygen releasing capacity of the copper ore, $Con(R_o)$ (-), $Con(r_{avg})$ (min⁻¹) and $Con(M_o)$ (-) are defined as

$$Con(R_{o}) = (R_{o,Cu} - R_{o,iron})/\beta_{Cu}$$
(3)

$$Con(r_{\rm avg}) = (r_{\rm avg,Cu} - r_{\rm avg,iron})/\beta_{\rm Cu}$$
(4)

$$Con(M_o) = (M_o - 0)/\beta_{Cu}$$
⁽⁵⁾

where $R_{o,Cu}$, $r_{avg,Cu}$ and $R_{o,iron}$, $r_{avg,iron}$ represent the oxygen transport capacities and average weight loss rates of the mixed ore and pure iron ore, respectively, M_o is the weight loss ratio of the mixed ore at the stage of oxygen releasing with argon. β_{Cu} is the mass fraction of the copper ore in the mixed ore. The contribution degrees indicate how much copper ore contributes to the reactivity of mixed ore OCs.

In the fluidized-bed experiments, the carbon conversion, $X_{\rm C}$, was calculated as

$$X_{\rm C} = \frac{\int_{t_0}^{t} F_{\rm exit}(y_{\rm CO} + y_{\rm CO_2} + y_{\rm CH_4}) dt}{\int_{t_0}^{t_{\rm total}} F_{\rm exit}(y_{\rm CO} + y_{\rm CO_2} + y_{\rm CH_4}) dt}$$
(6)

where y_{CO} , y_{CO_2} and y_{CH_4} are the molar fraction of CO, CO₂ and CH₄ at each second in the gas products, respectively; F_{exit} is the molar flow rate of the flue gas in the outlet, determined by N₂ balance between the inlet and the outlet of the reactor; t_0 and t_{total} represent the start time and the end time of the reaction.

In order to further study the reaction process, gas yields of each component (CO₂, CO, CH₄ or H₂) exiting the reactor, γ_i were calculated as

$$\gamma_{i} = \frac{\int_{t_{0}}^{t_{\text{total}}} [y_{i}F_{\text{exit}}] \mathrm{d}t}{\int_{t_{0}}^{t_{\text{total}}} [(y_{\text{CO}} + y_{\text{CO}_{2}} + y_{\text{CH}_{4}})F_{\text{exit}}] \mathrm{d}t}$$
(7)

Especially, γ_{H_2} could be understood as the ratio of hydrogen to carbon in the flue gas.

4. Results and discussion

4.1. Synergy between the hematite and copper ore

Isothermal redox experiments with different mixing ratio of the copper ore and hematite were first conducted. Figure 2 shows the weight loss curve of different samples during the cycles. The weight loss ratio of the OC, TG, was calculated as TG (%) = $(m/m_{\text{initial}}) \times 100\%$. By comparing Fig. 2(a)-(c), it can be found that copper ore and 2Cu8Hem have a slow weight loss curve before the reaction with syngas, which is due to the oxygen release of the copper ore. Hematite did not have such weight loss curve since it cannot release oxygen at 950 °C. Furthermore, it is found in Fig. 2(b) that the mass of the oxidized and reduced state of copper ore declined gradually with the cycle numbers and stabled finally. From Fig. 2(a), the mass of the hematite in the oxidized state declined only after the first cycle and its reactivity maintained stable during subsequent cycles. The mass of the mixed ore 2Cu8Hem in the oxidized state also declined only after the first cycle and then it kept stable in subsequent cycles. The mass of the mixed ore in the reduced state basically maintained stable after the 8th cycle. For more details see Figs. S1 and S2 in Supplemental material. Moreover, based on the comparisons of theoretical and actual oxygen transport capacities of the samples (Table S1 in Supplemental material), in all samples, part of Fe_3O_4 is reduced only to FeO and part of FeO is reoxidized only to Fe₃O₄. It is also found that CuO reduced to Cu is easier than Fe_2O_3 reduced to FeO or Fe. The



Fig. 2. Mass loss ratio of (a) Hem, (b) Cu-ore and (c) 2Cu8Hem vs time.

XRD result (Fig. S3 in Supplemental material) shows that the main reduzates for 2Cu8Hem after TGA experiments are Fe_3O_4 , FeO and Cu. No copper oxides or Fe_2O_3 is found in the XRD pattern, which agrees with the result discussed above.

Figure 3(a) and (b) show the change of oxygen transport capacity of different samples during multiple cycles. Some of the experiments were repeated 3 times and the oxygen transport capacity of Cu-ore and 2Cu8Hem during multiple cycles is shown in Fig. S4 in Supplemental material. The error ranges in Figs. 3(b) and 4 are all less than 1%. The oxygen transport capacity of all the samples kept steady after multiple cycles, and with the increase of the copper ore content in the mixed ore, the oxygen transport capacity of the mixed ore increased as well. As the reactivity of the OCs maintained stable after 18 cycles, the data of the 18th cycle was used to analyze the reactivity performance of the OC. It is clear from Fig. 3(b) that the oxygen transport capacity of the mixed ore increased with the copper ore content in the mixed ore. If the synergy of the hematite and the copper ore does not exist, the oxygen transport capacity will increase in a linear relationship with the copper ore content. However, from Fig. 3(b), when the copper ore content was in 20-40 wt%, 60-70 wt% and 80-90 wt%, the increase in oxygen transport capacity does not have a linear relationship with the copper ore content. Therefore, it can be concluded that synergy of the hematite and the copper ore indeed exists in the mixed ore.

The synergistic effect for the oxygen transport capacity is controlled by the following two factors: first, hematite can alleviate the sintering of copper ore at a high temperature (e.g., 900– 1000 °C), which improves the oxygen transport capacity of copper ore; second, Fe_2O_3 on the surface of hematite can react with CuO on the surface of copper ore to form $CuFe_2O_4$ as mixing these two ores together. The oxygen transport capacity of $CuFe_2O_4$ is higher than the sum of



Fig. 3. Evolution of the oxygen transport capacity of different OCs during (a) multiple cycles and (b) the 18th cycle.



Fig. 4. The average weight loss rate of OCs at different mass fraction of copper ore.

the oxygen transport capacity of Fe_2O_3 and CuO with same mass. The stepwise synergistic effects (Fig. 3b) are the result of a combination of these two factors. As the first factor is dominant, there is a peak when 20 wt% copper ore. As the second factor dominates, there is a peak when 60 wt% copper ore. Finally, the stepwise synergistic effects are observed. The synergistic effect for the second factor is also proved by analyzing the XRD result of 2Cu8Hem sample as well as the HSC Chemistry simulation (Figs. S3 and S5 in Supplemental material).

To study the reaction rate of the OC with the syngas, the average weight loss rate of the OC during 4–5 min, r_{avg} (wt%/min), is calculated as $r_{avg} = (X_{r,t=5} - X_{r,t=4})/(5-4)$, where $X_{r,t=4}$ and $X_{r,t=5}$ represent the weight loss ratio of the OC in the reduction phase at 4 and 5 min (one-minute reduction for syngas after 4-min argon sweeping) in each cycle, respectively. It can be seen in Fig. 4, the average weight loss rate of the OC increased with the copper ore content, i.e., the reaction rate of the OC with the syngas is

improved as the increase of the copper ore ratio. Similar with the analysis of the oxygen transport capacity, the average weight loss rate of the mixed ore in the reduction period did not comply with a linear relationship with the copper ore ratio. For instance, the average weight loss rates in the reduction stage were nearly the same when the copper ore ratio was 20 wt% and 30 wt%, respectively. Once again, the existence of the synergy between the hematite and copper ore was proved (see Fig. S6 in Supplemental material).

4.2. Optimizing of the mixing ratio

From the studies above, adding copper ore into the hematite can improve the oxygen transport capacity, reaction rate and oxygen release ability of the OC. However, the high price of copper ore and the risk of sintering and agglomeration at high temperatures limit the copper ore content in the mixed ore. In addition, there exists synergy between hematite and copper ore, i.e., they may affect each other in the reaction. So the copper ratio in the mixed ore could be optimized, i.e., there exists certain mixing ratios which can lead to more sufficient use of copper ore in the mixed ore. The contribution degree of unit mass copper ore was introduced to evaluate this mixing ratio, which can be used to analyze the enhancement effect of unit mass copper ore in the OC with different mixing ratios on the oxygen transport capacity, reaction rate and oxygen release ability.

From Fig. 5, all the contribution degrees of the copper ore varied with the copper ore content in the mixed ore, which also proved the synergy between copper ore and hematite again. From Fig. 5(a) and (b), $Con(R_o)$ and $Con(r_{ave})$ both reached maximum value when the copper ore ratio was 20 wt%, which means that the contribution of unit mass copper ore to the oxygen transport capacity and reaction rate reached the maximum under this copper ore ratio. From Fig. 5(c), $Con(M_o)$ reached the maximum value



Fig. 5. The contribution degree of the (a) oxygen transport capacity, (b) reaction rate and (c) oxygen releasing capacity of copper ore at different mass fraction.

when the copper ore ratio was 10 wt%. Therefore, when the mixing ratio of copper ore maintained 10–20 wt%, the copper ore could be more efficiently utilized. In addition, by calculating $Con(M_o)/Con(R_o)$, it was found that all values are between 0.5–0.6, which indicates that the enhancement effect of the oxygen transport capacity of the mixed ore was mainly due to the oxygen release of the copper ore (see Fig. S7 in Supplemental material).

Figure 6 shows the differential thermal analysis (DTA) of copper ore, iron ore and 2CuHem8, respectively in the last four cycles. In Fig. 6, the peak upward indicates exothermic reaction, the peak downward indicates endothermic reaction and the area of the peak means heat absorption/release capacity. As shown in Fig. 6, copper ore released heat in the reduction stage with the syngas. Copper ore also released heat during the oxidation stage, and the heat was greater than that in the reduction stage. While for hematite, the reac-



Fig. 6. The DTA curves of OCs vs time.



Fig. 7. Heat release capacity of the OCs at different mass fraction of copper ore.

tion was endothermic in the reduction stage and exothermic in the oxidation stage. For 2Cu8Hem, in the reduction stage, it was first exothermic and then endothermic, moreover, the endothermic peak and the exothermic peak just balanced, which indicates that if adding 20 wt% of copper ore into the iron ore, the mixed ore will not absorb heat in the reduction stage, which could be benefit to control the temperature of the reactor. The heat absorption and release of all the OCs kept steady during the last four cycles, which again indicates that the reactivity of the OCs reached stable after repeated cycles.

To further study the effect of the copper ore content in the mixed ore on the heat release capacity of the OC during the reduction stage, the heat release capacity of different OCs during the 18th reduction stage were calculated, as shown in Fig. 7. When the copper ore content was higher than 20 wt%, the reduction stage was an exothermic reaction, and the releasing heat increases with the copper ore content. Therefore, by considering the efficient utilization of the copper ore and the controllable reactor temperature, it can be regarded that a 20 wt% copper ore content in the mixed ore was the most suitable.

4.3. Reaction performance verification of the mixing ore OC

The reaction between OCs and coal was further studied by the fluidized-bed experiments to verify the reactivity of the pure hematite and 2Cu8Hem. Figure 8 shows the outlet gas concentrations as a function of time for the reduction period where GP coal was used as fuel. It can be seen that there was almost no CH₄ in the outlet gas. A small CO and H₂ peak appeared in the initial phase, which is due to the devolatilization of coal. Subsequently, the remaining char was gasified by the steam into syngas, i.e., CO and H₂, which reacts further with the OCs to CO₂ and H₂O, leading to descending concentrations of CO and H₂. As the reaction



Fig. 8. Concentration profiles of outlet gas using (a) Hem and (b) 2Cu8Hem.

proceeds, the reactivity of the OC decreased, which led to an increase of H₂ and CO concentrations. Then, the concentrations of H₂ and CO decreased again due to the consumption of coal. By comparing the CO₂, CO and H₂ peaks for Hem and 2Cu8Hem as shown in Fig. 8(a) and (b), it can be seen that the CO₂ peak for 2Cu8Hem was higher than that for Hem. However, the CO and H₂ peaks for 2Cu8Hem was lower than these for Hem. It verifies a better reaction performance of 2Cu8Hem while reacting with the coal. It should be noted that coal was introduced into the reactor when the oxygen concentration was stable for 2Cu8Hem. During the N_2 purging period, it is hard to avoid oxygen releasing of OC. Therefore, the actual reaction performance of 2Cu8Hem must be better in a real CLC system than the experimental result.

Figure 9 shows the instantaneous rate of fuel conversion for Hem and 2Cu8Hem. The instantaneous rate of fuel conversion, x_{inst} , based on the remaining non-reacted carbon was determined as $x_{inst} = (dX_C/dt)/(1 - X_C)$. It can be found that the rate of fuel conversion for 2Cu8Hem is higher than that for Hem. The average value of this rate



Fig. 9. Instantaneous rate of fuel conversion as function of carbon conversion for Hem and 2Cu8Hem.

Table 3 Gas yields using Hem and 2Cu8Hem.

	$\gamma_{\rm CO_2}$	γсо	γ_{CH_4}	γ_{H_2}
Hem	0.69	0.31	0.005	0.27
2Cu8Hem	0.79	0.21	0.002	0.075

was calculated in a char conversion interval of 0.2–0.8, and the results for 2Cu8Hem and Hem are 15.9 and 13.8%/min, respectively. As known, the good reactivity of OC can accelerate the rate of fuel conversion [19,20]. Thus it can be concluded that 2Cu8Hem has a better reactivity with the GP coal than Hem.

In this work, the gas yields of CO₂, CO, CH₄ and the ratio of hydrogen to carbon were calculated, which presented in Table 3. As seen, γ_{CO_2} for 2Cu8Hem is higher than that for Hem, γ_{CO} , γ_{CH_4} and γ_{CH_4} for 2Cu8Hem are all lower than theses for Hem. It indicates that 2Cu8Hem has a better reactivity with the gasification gases than Hem. There was almost no CH₄ in the flue gas. By comparing the values of γ_{CO} and γ_{H_2} when 2Cu8Hem was used in the experiments, we found that the value of γ_{H_2} is much higher than that of γ_{CO} , which means that 2CuHem has a better reactivity with H₂ than CO.

The XRD result of the 2Cu8Hem after experiment was analyzed (Fig. S3 in Supplemental material). It was found that the main reduzates for 2Cu8Hem were Fe₃O₄ and Cu, while no FeO was found. This means that the Fe₂O₃ in the fluidizedbed experiment was mainly reduced to Fe₃O₄. Some unreacted Fe₂O₃ was also found in the XRD pattern. In addition, by testing the 2Cu8Hem samples after fluidized-bed experiment, the attrition rate of the 2Cu8Hem OC is about 1.71%/h.

5. Conclusion

The mixture of iron ore and copper ore as OC is studied in this work. It is found that there is a

synergy between iron ore and copper ore. Through the TGA analysis, it is concluded that the copper ore could be more efficiently utilized when the mixing ratio of copper ore maintained within 10-20 wt%. In consideration of the controllability of the FR temperature, 20 wt% copper ore content in the mixed ore is the most suitable ratio. Subsequently, the results of fluidized-bed experiments verified the good reaction ability of 2Cu8Hem. It is also found that 2Cu8Hem has a better reactivity with H₂ than CO.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.proci.2014.07.010.

References

 T. Mattisson, A. Lyngfelt, P. Cho, *Fuel* 80 (2001) 1953–1962.

- [2] A. Lyngfelt, B. Leckner, T. Mattisson, *Chem. Eng. Sci.* 56 (2001) 3101–3113.
- [3] J. Adánez, P. Gayán, J. Celaya, L.F. de Diego, F. García-Labiano, A. Abad, *Ind. Eng. Chem. Res.* 45 (2006) 6075–6080.
- [4] T. Song, T. Shen, L. Shen, J. Xiao, H. Gu, S. Zhang, Fuel 104 (2013) 244–252.
- [5] H. Leion, A. Lyngfelt, M. Johansson, E. Jerndal, T. Mattisson, *Chem. Eng. Res. Des.* 86 (2008) 1017–1026.
- [6] J. Adánez, A. Cuadrat, A. Abad, P. Gayán, L.F. de Diego, F. García-Labiano, *Energy Fuels* 24 (2010) 1402–1413.
- [7] S.A. Scott, J.S. Dennis, A.N. Hayhurst, T. Brown, *AIChE J.* 52 (2006) 3325–3328.
- [8] E. Jerndal, T. Mattisson, A. Lyngfelt, Chem. Eng. Res. Des. 84 (2006) 795–806.
- [9] R. Siriwardane, H. Tian, T. Simonyi, J. Poston, *Fuel* 108 (2013) 319–333.
- [10] W. Yang, H. Zhao, J. Ma, D. Mei, C. Zheng, *Energy Fuels* 28 (2014) 3970–3981.
- [11] H. Zhao, L. Liu, B. Wang, D. Xu, L. Jiang, C. Zheng, *Energy Fuels* 22 (2008) 898–905.
- [12] H. Leion, T. Mattisson, A. Lyngfelt, Fuel 86 (2007) 1947–1958.
- [13] S. Zhang, R. Xiao, J. Liu, S. Bhattacharya, Int. J. Greenhouse Gas Control 17 (2013) 1–12.
- [14] H. Gu, L. Shen, J. Xiao, S. Zhang, T. Song, D. Chen, *Combust. Flame* 159 (2012) 2480–2490.
- [15] D.M. Quyn, H. Wu, C. Li, Fuel 81 (2002) 143-149.
- [16] D. Mei, H. Zhao, Z. Ma, C. Zheng, *Energy Fuels* 27 (2013) 2723–2731.
- [17] B. Wang, R. Yan, H. Zhao, Y. Zheng, C. Zheng, *Energy Fuels* 25 (2011) 3344–3354.
- [18] S. Wang, G. Wang, F. Jiang, M. Luo, H. Li, *Energy Environ. Sci.* 3 (2010) 1353–1360.
- [19] H. Leion, T. Mattisson, A. Lyngfelt, Int. J. Greenhouse Gas Control 2 (2008) 180–193.
- [20] T.A. Brown, J.S. Dennis, S.A. Scott, J.F. Davidson, A.N. Hayhurst, *Energy Fuels* 24 (2010) 3034–3048.