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Characteristics of hematite and fly ash during chemical looping combustion of sewage sludge

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HIGHLIGHTS

- CLC is an attractive technology for processing sewage sludge.
- No char bypassed to air reactor during CLC of sewage sludge.
- The reactivity of hematite shows a slight decrease during 10 h operation.
- Phosphorus speciation in CLC fly ash is beneficial to agriculture.

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ABSTRACT

Chemical looping combustion (CLC) of sewage sludge is an appropriate solution of how to manage the continuously increasing sewage sludge production and at the same time, how to rationally use renewable resource. This work attempted to investigate the combustion performance of sewage sludge in a continuous CLC unit based hematite oxygen carrier. Besides, the characteristics of hematite and fly ash during chemical looping combustion of sewage sludge were elaborated. Compared to either bituminous coal or anthracite, sewage sludge was a unique solid fuel in the term of high combustion efficiency even at 800 °C. Additionally, there were no char particles bypassed to air reactor during CLC of sewage sludge. During 10 h continuous operation, hematite shows a slightly decrease reactivity, indicating a good long-term reactivity of the oxygen carrier used. Although some ash particles deposited on the surface of hematite, no reaction between sludge ash and hematite were identified. The only phosphate identified incinerated sludge ash was $Ca_2P_2O_7$. However, the form of phosphorus in fly ash based on CLC was $CaH_2P_2O_7$ and $CaHPO_4$. The presence of steam in flue gas and the reduction atmosphere can significantly accelerate the generation of $CaH_2P_2O_7$ and $CaHPO_4$. Then, possible options of utilizing sludge ash on agriculture were discussed.

1. Introduction

Sewage sludge is one of the major solid wastes generated from municipal wastewater treatment [1,2]. It is a complex heterogeneous mixture of micro-organisms, synthetic organic compounds, inorganic materials and moisture. Additionally, it contains heavy materials and essential nutrients (like N, P, S and Mg) [1,3]. The surge of industrialization and urbanization coupled with increasingly stringent sludge reuse regulations and increasing public pressure, is forcing both public and private sludge generators to develop environmental friendly sewage sludge treatment routes [4,5]. It is anticipated that upcoming sludge treatment should accentuate upon reuse energy and recovery phosphorus from sludge.

Among various options, chemical looping combustion (CLC) is one of the feasible alternatives. Sewage sludge treatment using CLC technology has been successfully tested using Ni-based oxygen carrier [6]. CLC is a novel combustion technology based on transfer oxygen from air to fuel by a metal oxide, named oxygen carrier, which is continuously circulating between air and fuel reactor. It is an innovative combustion technology with inherent separation of CO_2 [7]. When solid fuel (coal, biomass or sewage sludge) is used, *in situ* gasification chemical looping combustion (*i*G-CLC) is one of the feasible options [8]. In this process, solid fuel is directly introduced to fuel reactor where the gasification of solid fuel and subsequent reactions with oxygen carrier particles will occur simultaneously [7,9]. Then, the reduced oxygen carrier circulates to air reactor where it is re-oxidized by air.

The adequate oxygen carrier is a cornerstone in the successful development of a CLC system, which should have high reactivity,

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environmentally harmless and high resistance to attrition and agglomeration [7,10,11]. Additionally, low cost materials as oxygen carriers are relevant option to process a solid fuel in *i*G-CLC because the system will lose some oxygen carrier particles during separation of ash out of the fuel reactor [7,11]. Although Ni-based oxygen carrier shows high reactivity and good performance when combustion sewage sludge [6], nickel is more expensive than other metal oxides and it is harmful to environment. Considering this, hematite, composed of Fe_2O_3, is preferred for use in sewage sludge combustion in a CLC process. Mattisson et al. demonstrated that hematite showed superior rate of both reduction and oxidation which made it feasible to be employed in a CLC system [12]. Furthermore, different solid fuels were tested using iron ore as oxygen carrier in CLC process [9,13]. The results show that both iron ore and the oxide scale work well as oxygen carrier for combustion pet coke, char-coal, lignite and two kinds of bituminous coals. Moreover, both oxygen carriers increase their reactivity with time. Additionally, the continuous operation has been accomplished to evaluate the performance of iron ore as oxygen carrier for combustion solid fuels [13,14]. It can be found that hematite shows good behavior as an oxygen carrier in a CLC process for combustion coal or biomass.

Ash accumulation is an important problem in the CLC process of solid fuel that requires special attention and analysis. Although ash can be separated by a cyclone because it has a much lower density than oxygen carrier, there are still some residual ash left in the system, especially using high ash content fuels [15]. The effect of ash on oxygen carrier can vary depending on the ash content, the nature of ash, the experimental conditions and the oxygen carrier used [16,17]. Most of ashes are detrimental and reduced the reactivity of oxygen carrier, except the lignite ash enriched in CaO [15,17,18]. For example, Azis et al. [17] found that an increase in gas conversion for lignite and coal gasification ash was obtained at relatively high ash loading because of the beneficial effect of Ca (in lignite ash) and Fe (in coal gasification ash) acting as a catalyst or an oxygen carrier. Bao et al. also demonstrated that the ash mainly composed of $CaSO_4$ and Fe_2O_3 could act as oxygen carrier and increase the reactivity of carrier [15]. Besides, Ksepko [19] reports that sludge ash can be effectively used as a low-cost, valuable oxygen carrier in CLC process. In addition, it should be mentioned that a large amount of Ca is presented in sludge ash [20], which has been shown to be an efficient additive in oxygen carrier to promote the reactivity of carrier and catalyze gasification process [21,22]. Thus, the interaction between sludge ash and oxygen carrier cannot be ignored.

Furthermore, phosphorus (P) is enriched in sludge fly ash during sewage sludge combustion in a fluidized bed reactor [23]. Additionally, P is indispensable as an essential nutrient for all living organisms and cannot be replaced [24]. Thus, recovery P from sludge ash is especially important in the light of the shrinking global phosphate rock reserves and increases in demand for P fertilizer in agriculture [25]. The reaction atmosphere had a significant effect on the crystalline structure in sludge ash. The phosphorus speciation in fly ash based on CLC is $CaHPO_4$ and $CaH_2P_2O_7$, which are not detectable based on air combustion [6].

In this work, the combustion of sewage sludge using chemical looping technology based on hematite oxygen carrier was carried out in a continuous CLC unit. The effect of fuel reactor temperature on gas distribution was analyzed. Subsequently, the CLC performances of both Shenhua bituminous coal and Huaibei anthracite were used for comparison. This work also characterized the morphologies of the fresh and used hematite after 10 h operation by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), scanning electron microscope (SEM) and X-ray fluoroscopy (XRF) analyses. Furthermore, the characteristic of sludge ash from the outlet of fuel reactor was analyzed and the behavior of phosphorus in fly ash was determined.

2. Experimental

2.1. Oxygen carrier and sewage sludge

Hematite was supplied by Nanjing Steel Manufacturing Company. Samples were crushed and sieved to 0.1–0.3 mm. After this, the samples were calcined at 980 °C for 3 h in a muffle oven to completely oxidize and increase the mechanical strength. Table 1 shows the chemical compositions of the fresh material.

De-watered sewage sludge supplied by Jurong wastewater treatment plant was used as solid fuel in the experiment. Table 2 shows the proximate and ultimate analyses of the sewage sludge together with the lower heating value, as well as Shenhua bituminous coal and Huaibei anthracite. The sample was sieved to a size range of 0.2–0.45 mm.

2.2. Experimental setup and procedure

2.2.1. 1 kWth continuous unit

Experiments were conducted in a 1 kWth continuous unit made of stainless steel, as shown in Fig. 1. The facility has been described in detail in our previous work [26]. This unit is composed of two interconnected fluidized bed reactors connected by a loop-seal and a cyclone. The fuel reactor is a rectangular spout-fluid bed, with a cross section of 50×30 mm^2, and a height of 1000 mm. Sewage sludge is fed by a screw feeder at the bottom of this bed with an Ar stream in order to avoid gas backflow from the reactor. Steam is used as gasifying gas. The loop-seal, with a cross section of 34×30 mm^2 and a height of 370 mm, transfers reduced oxygen carrier particles to the air reactor. The fluidizing gas in loop-seal is steam, which also acts as gasifying agent. The oxidation of carrier takes place in air reactor, consisting of a fast fluidized bed with 25 mm inner diameter and 1600 mm height. Air is introduced to the bottom of air reactor to oxidize carrier.

The unit is electrically heated in an oven to supply heat for start-up and compensate heat loss during operation. Temperatures in the bed of air reactor and fuel reactor are monitored as well as the pressure drops in important locations of the system. The outlet gas from air reactor and fuel reactor is sampled by gas bags for off-line analysis. CO, CO_2, H_2, CH_4 and O_2 concentration in flue gas is analyzed by a NGA2000 type gas analyzer (EMERSON Company, USA) measuring 0.00–20.00 vol.% CO, 0.00–100.00 vol.% CO_2, 0.00–10.00 vol.% CH_4, 0.00–25.00 vol.% O_2 and 0.0–50.0 vol.% H_2. The concentrations of C_2–C_4 hydrocarbons are analyzed by a gas chromatograph (GC).

In this test, the gas flow introduced to air reactor was 0.84 m^3/h. The steam flows supply for loop-seal and spout-fluid bed were 0.21 kg/h and 0.15 kg/h, respectively. The Ar stream for the pneumatic medium for conveying sewage sludge particles into fuel reactor was 0.27 m^3/h. The sludge flow rate was 100 g/h, corresponding to a thermal power of 278 Wth.

2.2.2. Fixed bed reactor

A batch fixed bed reactor made of stainless steel was used to investigate the reactivity of both fresh hematite and the one

Table 1
Compositions of the fresh hematite (wt.%).

Fe_2O_3	SiO_2	Al_2O_3	P_2O_5	CaO	SO_3	Others
83.21	7.06	5.13	0.38	0.24	0.21	3.77