Fuel Processing Technology 177 (2018) 200–209

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

The effects of water vapor and coal ash on the carbonation behavior of CaO-sorbent supported by γ-Al_2O_3 for CO_2 capture

Liangyong Chen[a,*], Neng Qian[b]

[a] School of Energy and Environment, Southeast University, Nanjing 210096, China
[b] School of Energy, Nanjing Tech University, Nanjing 211816, China

ARTICLE INFO

Keywords:
CO_2 capture
Calcium sorbent
Carbonation
Water vapor
Coal ash

ABSTRACT

Coal ash and water vapor are usually present in the flue gas derived from coal combustion, which inevitably impact the performance of calcium sorbents in a Calcium-Looping process for CO_2 capture. This study investigated the influence of high-temperature water vapor and coal ash on the carbonation behavior of γ-Al_2O_3-supported calcium sorbent in a fluidized-bed reactor and a TGA apparatus. It was found that the presence of water vapor during carbonation induced the extensive formation of large voids on the sorbent surface and the decomposition of inert mayenite ($Ca_{12}Al_{14}O_{33}$) into CaO and Al_2O_3. As a result, the reactivity and carrying capacity of the synthetic sorbent were significantly increased. During the significant exothermic carbonation reaction, the enhanced cooling effects of sorbent particles by water vapor in flue gas may provide a better equilibrium condition for higher carbonation rate and capture capacity. Coal ash impurities caused severe decay of the sorbent surface, but high-temperature water vapor exerted a very strong activation function to the ash-contaminated synthetic sorbents for better carbonation.

1. Introduction

Calcium-Looping (CaL) is a promising carbon capture technology applicable to coal-fired boilers for large-scale power generation. This technology is based on the reversible reaction between CaO and CO_2 to capture CO_2 from flue gas and produces a pure CO_2 stream for sequestration [1]. CaL can be deployed using two interconnected fluidized-bed reactors: a Carbonator for CO_2 capture and a Calciner for sorbent regeneration. While low-cost natural materials such as limestone or dolomite are attractive CO_2 sorbents, their poor carrying capacity (~10 wt% in long term operation) and high attrition rate hinder their use in the fluidization regime [2]. Carbonation of the calcium sorbent involves an initial fast stage dominated by chemical reaction on the sorbent surface, and a slow second stage controlled by CO_2 diffusion through the product layer over unreacted sorbent [3]. The initial fast stage is practically useful, which determines the cyclic flux and solid inventory of the CaL system. However, this process occurs in a very limited interval of conversion, and the CO_2 uptake of each cycle decreases quickly with cycle number [4,5]. High sorbent loss caused by substantial attrition in fluidized-bed system and the decreased performance is another serious concern [6]. A multi-cycle test conducted in a demonstration unit of dual fluidized-bed reactors showed that significant sorbent attrition led to a material loss of 60% in only 25 cycles, which together with sorbent deactivation further resulted in a decrease of CO_2 capture efficiency from 90% to 75% [7]. One of the strategies is to fabricate a synthetic sorbent with inert materials to improve Tammann temperature, mechanical strength, and the dispersity of active ingredients. These inert materials tested include Al_2O_3, SiO_2, MgO, and CeO_2 et al. [8–11], among which Al_2O_3 seems to be the most studied support. Another strategy is sorbent pretreatments prior to CO_2 capture cycles, such as thermal and chemical treatment or doping [12,13]. External hydration at low temperature (200–400 °C) or higher (500 °C) appears to be an effective method for the reactivity restoration of calcium sorbents [14–16].

In general, 10–15 vol% water vapor exists in the flue gas of coal combustion. A few previous works examined the enhanced CO_2 uptake of the natural calcium sorbents, mainly limestone, as water vapor was present during calcination and/or carbonation at high temperature (> 600 °C) [17–22]. There is still no consensus about the mechanism. The interpretations for the enhanced carbonation include the acceleration of solid state diffusion [23], the catalytic improvement in CO_2 capture [24], and the reduction in diffusion resistance [17,25]. For the synthetic calcium sorbents, the carbonation behaviors in flue gas with the presence of water vapor had not been well understood. John Blamey et al. [26] observed that the presence of high temperature steam in flue gas could improve cyclic CO_2 capture capacity of the

---

[*] Corresponding author at: School of Energy and Environment, Southeast University; Sipailou 2#, Nanjing 210096, China.
E-mail address: 101012271@seu.edu.cn (L. Chen).

https://doi.org/10.1016/j.fuproc.2018.04.028
Received 19 February 2018; Received in revised form 6 April 2018; Accepted 22 April 2018
0378-3820/

calcined limestone pelletized using a small amount of calcium aluminate cement as binder, but the mechanism needed to be further revealed for their synthetic sorbent. On the other hand, about 50–80 wt% solid residues from pulverized coal combustion are carried out of the boiler with the flue gas in the form of fly ashes. These fly ashes derived from pulverized coal are very fine particles (65–90% of them < 10 μm) composed of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, and a small amount of alkali metal oxides (Na_2O, K_2O) [27]. They will be present in CaL circulation if there is no high-temperature filtration prior to CaL system. In addition, because of highly endothermic calcination reaction, low-cost coal is typically proposed to be the fuel for the regeneration process and, therefore, the physical mixing of coal ash with calcium sorbent is inevitable. If 850–950 °C is the typical temperature for regeneration, there is a great potential for chemical interaction between fine coal ashes and calcium sorbent in the Calciner. Thus, the performance of the calcium sorbent in the subsequent carbonation will be altered, which also need to be evaluated prior to CaL process development.

The goal of this research is to gain an initial understanding the influences of high temperature water vapor and coal ash on the carbonation behaviors of γ-Al_2O_3-supported calcium sorbent which is proposed to be used for CO_2 capture for the coal-fired power generation. The effects of water vapor concentration and coal ash loading were first investigated for the fresh sorbent, and then the influence of water vapor or coal ash on the cyclic carbonation behaviors. The activation function of water vapor for the carbonation reaction of the coal ash-contaminated sorbents was validated. This work also investigated into the physicochemical mechanism of activation function from water vapor in a TGA apparatus.

2. Experimental

2.1. Material preparation

The γ-Al_2O_3-supported calcium sorbent had also been proved, in a screening test performed previously in our lab, to be a promising material for CaL process as compare to the lime sorbent derived from calcination of limestone and the synthetic sorbents supported by TiO_2 and SiO_2. The improved mechanical strength, effective capture capacity, and carbonation kinetics in long term operation for γ-Al_2O_3-supported calcium sorbent would greatly reduce the attrition tendency, sorbent mass flow rate and residence time needed for the operation of a CaL system. The γ-Al_2O_3-supported sorbent used in this study was prepared in a batch mode using calcium oxide (CaO, Sigma-Aldrich, $d_{50} = 5$ μm) and alumina (γ-Al_2O_3, Sigma-Aldrich, $d_{50} = 2$ μm). 180 g of CaO was pre-mixed with 120 g of γ-Al_2O_3 and stirred in a stirring tank for 6 h. Then deionized water was continuously sprayed into the tank during stirring to make a dense paste, which was then extruded through a 2.0 mm sieve to produce pellets. The pellet materials were subsequently dried at 75 °C for 36 h, crushed and calcined at 850 °C for 2 h. The calcined particles in the range of 350–700 μm were sieved out for experimentation. The effects of coal ash were investigated using the combustion residue of pulverized coal (Xuzhou bituminous coal, China). The majority of the coal ash particles were smaller than 15 μm, and its softening temperature (ST) was 1335 °C. The ash analysis can be found in Table 1.

2.2. Experiments and data evaluation

The carbonation/calcination experiments were performed in a fluidized-bed facility (See Fig. 1), which consists of a fluidized-bed reactor, gas feeding system, filtration, condenser/moisture trap, and a gas analyzer. The fluidized-bed reactor (ID = 42 mm, which is big enough to avoid slug flow for fluidized bed operations) was fabricated from a stainless steel tube. A porous ceramic plate, mounted at a 250 mm height from the bottom of reactor, was used as a gas distributor and sample holder. The heating zone, 600 mm long, was heated by an electronic furnace during the experiment. The feeding system allowed the accurate supply of N_2 and CO_2 via two mass flow controllers (DO7-7B, Beijing Sevenstar Electronics CO., LTD). A constant flow pump (TAUTO TBP-1002, Shanghai, China) fed the desired amount of deionized water into a steam generator, where the feed water was vaporized into steam. Then steam and carrier gas were mixed and pre-heated to 600 °C before entering the heating zone. The CO_2 concentration (dry based) in the off-gas was continuously measured using the gas analyzer. The bed temperature, pressure drop, and gas concentration were recorded by a computerized data acquisition system.

Six series of batch tests, named ST1 to ST6, were performed in the fluidized-bed facility. The testing conditions are listed in Table 2. All tests were repeated for high reliability, and the CO_2 concentration in the simulated flue gases for carbonation reaction was 20 vol%. In ST-1, 0, 15, 25, and 50 vol% of water vapor were adopted to investigate the effects of water vapor concentration. Here, highly concentrated water vapor (50 vol%) was tested to see if there were significant improvement in sorbent reactivity with the additional water vapor. ST-2 investigated the effects of coal ash at 0, 5, and 15 wt% loadings (relevant to the weight of sorbent sample).

Cyclic carbonation/calcination reactions were performed in ST-3 to ST-6. ST-3 was used as a benchmark experiment, where a flue gas stream containing 20 vol% CO_2 balanced by N_2 was applied for carbonation. In ST-4, the effects of 25 vol% water vapor during the carbonation step of each cycle were investigated. ST-5 determined the effects of coal ash at 15 wt% loading on cyclic reactions. For each test from ST-3 to ST-5, fresh sorbent was used to perform 10 cycle consecutive reactions. The carbonation and calcination were conducted at 650 °C and 900 °C, respectively. For each cycle, the sorbent was first exposed to the flue gas stream at 650 °C until full carbonation. Then the atmosphere was switched to 3.0 NL/min pure N_2, meanwhile the bed temperature was increased to 900 °C at a rate of 20 °C/min for the calcination reaction. The calcination duration, including the period for heating and holding, was 60 min in total. Here N_2 atmosphere and the prolonged calcination were used to ensure full de-carbonation before the next carbonation reaction. After that, the bed materials were cooled down to 650 °C in N_2 flow for the new cycle. ST-6 was to validate the activation function of water vapor for the decayed sorbent, in which the used sorbents in ST-5 were tested for an additional 10 cycles of carbonation–calcination with wet flue gas.

20.0 g of sample was used in each test from ST-1 to ST-6. The superficial velocity in the fluidized-bed reactor was 0.185 m/s, approximately 3.0–4.0 times the minimum fluidizing velocity of the sorbent particles. In ST-2 and ST-5, the fresh sorbents were thoroughly premixed with the required amount of coal ashes and then baked at 650 °C for 2 h prior to the real experiments. This pretreatment step ensured interaction between coal ashes and sorbents occurring to some extent, and established a starting point for experiments.

The results of the six series of tests showed a varied set of carbonation conversions depending on operational conditions and cycle number. As examples, the CO_2 breakthrough curves for ST-1, ST-3, and ST-4 are shown in Fig. 2. This study is focusing on the detailed

Table 1
Coal ash analysis (wt%).

Item	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	P_2O_5	SO_3	Balance
Content	48.96	27.27	8.24	1.35	6.09	0.98	0.4	1.87	0.08	3.23	1.53