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Enhancement of attrition resistance and cyclic CO_2 capture of calcium-based sorbent pellets

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ABSTRACT

Calcination/carbonation of calcium-based sorbent is considered one of the most promising technologies to capture CO_2. The attrition resistance and CO_2 uptake of Ca-based sorbent were of great concern. Efforts were made to enhance the attrition resistance of sorbents primarily by making sorbent pellets with aluminate cements and maintain high CO_2 capture capacity of sorbents by adding pore forming agents. Batch experiments were conducted in a fluidized bed to investigate the effect of parameters on sorbent attrition. CO_2 capture performance of the pellets was also examined in a calcination/carbonation reactor system. The pore structure characteristics (BET, BJH) were measured as a supplement to the attrition and reaction studies. Results showed that the mechanical property of the pellets with 10 wt.% aluminate cement was greatly enhanced. While, CO_2 capture capacity of the pellets made with 10 wt.% aluminate cement and 5–10 wt.% pores forming agent was greatly increased and displayed much slower decay during multiple cycles compared with the original limestone. This was attributed to the large number of mesopores caused by the use of chemical agents and the exposure of inner core of CaO sorbents due to the attrition, which are in favor of CO_2 capture. The pore structure showed that the BET surface area and BJH pore volume were expanded by adding pore forming agents, which benefits CO_2 uptake of the sorbents during the cycling.

1. Introduction

Energy production from fossil fuel combustion results in emission of greenhouse gases leading to global warming and climate change, with CO_2 being the dominant contributor. CO_2 capture and storage were considered a near-term meaningful reduction in CO_2 emissions. The repeated calcination and carbonation reaction (CCR) of the calcium based sorbent was widely recognized and considered as a prosperous way to capture CO_2 from flue gases with many key problems being solved. During the CCR cycles, the rapid decay in CO_2 capture capacity and great attrition of sorbents in these interconnected fluidized bed reactors are the two big problems of great concern.

Many studies have been focused on enhancing CO_2 capture performance of sorbents with different advantages and disadvantages [1–3]. However, such a treatment may not actually increase the CO_2 capture or reduce the cost of capturing CO_2 if the attrition is significant. Recently, very few studies have been focused on the attrition characteristics of sorbents after some modification treatments. Though some previous studies on particle fragmentation and attrition in fluidized beds are available, most of these early studies were reported on attrition of limestone and its derived materials in fluidized bed systems [4–6] and mainly focused on the interplay of calcination and sulfation. Scala et al. [4] studied the attrition of two limestones during calcination and sulphation in fluidized beds. Parameters of particle size and other properties: bed temperature, heating rate, superficial gas velocity, and inventory of bed materials [5–8] were found exhibiting great influence on them. The main breaking mechanism during calcination of limestone was rounding off and primary fragmentation. The study on particle attrition and SO_2 capture of limestone in a pressurized fluidized-bed combustor at 825–865 °C showed an average attrition rate (reduction rate of radius) of 0.7–2.5 μm/h. Removal of product ($CaSO_4$) layer by attrition decreased the diffusion resistance of SO_2, thereby increasing the SO_2 capture capacity [5]. Yao et al. [9] also confirmed attrition rate was abated by the formation of $CaSO_4$ over the limestone/lime particle surface when examined the primary fragmentation and attrition of limestones in a fluidized bed and other parameters such as impact velocity, impact angle, target thickness, target hardness and particle size were also found to affect the fragmentation rate by investigating the characteristics of aluminum oxide particle fragmentation [10]. Increasing the number of impacts did not have an obvious effect as the velocity investigated was below the endurance limit. Also, spherical aluminum oxide particles present great mechanical stability and they are not easy to be attrited.

However, limestone is well known to be relatively fragile, and only a few works have been done to examine its attrition during CO_2 looping cycles. Jia et al. [11] examined attrition of five limestones under calcining conditions in fluidized bed systems. Attrition varies very significantly

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from limestone to limestone, and multiple calcination/carbonation cycles resulted in severe fragmentation during the first one or two calcination periods. Coppola et al. [12,13] found that attrition was only slightly affected by the presence of SO_2 and particle size distribution of the bed material indicated limited particle fragmentation. CO_2 carrying capacity of the pelletized sorbent was higher than that of the parent limestone [14]. Sprayed water and the addition of aluminate cement could enhance sorbent strength [15]. Actually, the main factors and mechanism on the attrition of sorbents have not been well clarified, especially during calcination/carbonation for CO_2 capture. Chen et al. [16] found that attrition resistant of sorbents was enhanced by making pellets adding alumina cement, but pellets look a little compact. The aim of this paper was attempted to improve both the attrition resistance and CO_2 uptake of Ca-based sorbent by making pellets with aluminate cement and pore forming agents. Parameters such as particle size and other properties like reaction temperature (T), exposure time (t) and fluidization number (n, gas velocity is divided by the minimum fluidizing velocity) were found to strongly influence the degree of attrition experienced. Thus, effects of these parameters on the pellets fragmentation and attrition were investigated in a fluidized bed. CO_2 capture performance of CaO pellets during the calcination/carbonation cycles was also determined. The microstructure characteristics (BET, BJH) were measured as a supplement to the attrition and reaction studies.

2. Experimental

2.1. Samples

The raw materials were the natural limestone, aluminate cement and starch. The natural limestone was less than 125 μm and came from Nanjing, China. The cement with Al_2O_3 content of 58 wt.% was from Zhengzhou Ludu Refractory Material Co., Ltd., China. Starch was added into the pellets because of its great effect of forming micropores during the decomposition at about 400 °C [17]. Different mass ratio of the materials were completely mixed by hand and added into the granulator (GJ100, pelletizing Machinery Research Institute of Nanjing University of Technology, China) with a small amount of water to make pellets at room temperature. The natural limestone was made pellets and denoted as L, those mixed with 10 wt.% aluminate cement and made pellets were denoted as LC_{10}, while those mixed with 10 wt.% aluminate cement and 5 wt.% starch were denoted as $LC_{10}S_5$. Sorbent pellets with particle size ranges of 0.35–0.6 mm and 1.0–1.25 mm were used in the tests. The matrix for preparing the pellets is presented in Table 1. The compositions of the pellets are shown in Table 2. The free CaO content in the pellets was extracted with HCl and the calcium ions were titrated with EDTA (Ethylene Diamine Tetraacetic Acid).

2.2. Apparatus and procedures

The sorbent attrition test was carried out in a stainless steel fluidized bed reactor, with an internal diameter of 30 mm (which is described in detail elsewhere [16]). About 150 g of the pellets without inert bed material was preloaded in the reactor with the temperature set. Air controlled by flow meters was introduced to fluidize the sample materials. The minimum fluidizing velocity at 700 °C and 0.1 MPa for the sample size ranges of 0.35–0.6 mm and 1.0–1.25 mm was 0.25 m/s and 0.35 m/s, respectively. The fluidizing gas velocity was adjusted to maintain constant U_g/U_{mf} (gas velocity/minimum fluidization velocity) for different temperatures tested during the tests. Bag filters were fixed up to collect the elutriated fines at the exhaust. Samples before and after experiments were carefully sieved and weighed.

Table 1
Matrix for preparing the pellets.

Component/wt.%	Sample 1 (L)	Sample 2 (LC_{10})	Sample 3 ($LC_{10}S_5$)	Sample 4 ($LC_{10}S_{10}$)
Limestone	100%	90%	85.7%	81.8%
Alumina cement	0%	10%	9.5%	9.1%
Starch	0%	0%	4.8%	9.1%

Table 2
Compositions of the pellets.

Sample	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	Others	LOI
Limestone	54.98	2.07	0.21	0.08	0.048	0.021	0.271	42.32
LC_{10}	52.48	1.88	0.23	5.87	0.05	0.02	0.27	39.20
$LC_{10}S_5$	52.49	1.88	0.23	5.86	0.05	0.02	0.28	39.19
$LC_{10}S_{10}$	52.48	1.88	0.23	5.89	0.05	0.02	0.27	39.18

LOI = loss on ignition.

CO_2 capture capacity of pellets was also investigated in the calcination/carbonation reactors (which is described in detail elsewhere [1]) at 0.1 MPa and 900 °C in air for calcination and at 0.1 MPa and 700 °C in 15%CO_2/air balance for carbonation. The cold limestone was loaded into the hot reactor and heated quickly up to 900 °C and calcined for 20 min. After complete calcination, pellets were taken out and transferred into the carbonator; CO_2 and air separately controlled by means of flow meters were mixed and supplied to the reactor through the sample for 30 min. After carbonation, the pellets were taken out and weighed by a sensitive balance of an accuracy of 110 g ± 0.1 mg. During the multiple cycles, some pellets were also sampled and used for analysis.

2.3. Analysis

The microstructure of the sample pellets was measured using nitrogen as an adsorbate at −196 °C with Micromeritics ASAP 2020-M nitrogen adsorption analyzer. The Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods were applied for the determination of surface area and pore size distribution, respectively. Sorbent morphologies before and after carbonation were also observed by using scanning electron microscope (FESEM). Sauter average particle diameter was used to determine the particle size of sorbent before and after cycling. The Sauter mean diameter is defined as follows:

$$d_s = \frac{1}{\sum \frac{x_i}{d_i}} \tag{1}$$

where, d_s is Sauter mean diameters of sorbents, mm; i is the number of sieve size; d_i is the average diameter of particles; and x_i is the weight fraction of particles of average diameter d_i on the ith sieve.

The attrition rate R (mm/h), was defined to describe the attrition property of the material by Eq. (2) as follows:

$$R = \frac{d\left(d_{s,t}\right)}{dt} \tag{2}$$

where, t is the attrition time, s; and $d_{s,t}$ is the Sauter mean diameters of sorbents in the bed after reaction/attrition, mm.

Carbonation conversion was calculated by Eq. (3) as follows:

$$X_N = \frac{m_N - m_1}{m_0 A} \cdot \frac{M_{CaO}}{M_{CaCO_3} - M_{CaO}} \tag{3}$$

where, X_N is the carbonation conversion of the sample after N cycles; m_0, m_1, and m_N are the initial mass of sample, the mass of recarbonated sample after 1 cycle, and the mass of recarbonated sample after N cycle, respectively, (g); A is the CaO content in the initial sample; and M_{CaO} and M_{CaCO3} are the mole mass of CaO and $CaCO_3$, respectively, (g/mol).