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Study on the limestone sulfation behavior under oxy-fuel circulating fluidized bed combustion condition

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ABSTRACT

In order to investigate the behavior of limestone sulfation under oxy-fuel circulating fluidized bed (CFB) combustion condition, experiments were conducted in a 50 kW oxy-fuel CFB system under the O_2/CO_2 and air combustion conditions. A small cage, containing limestone particles, was dipped into the dense zone of the CFB combustor during the experiments. The calcination of limestone, pore structure of the product layer, and calcium conversion were studied. It was found that the increasing of temperature would promote the calcination of limestone and the high concentration of CO_2 would inhibit calcination of limestone. The formation process of the product layer was completely different between the direct and indirect sulfation, while it was almost the same during the indirect sulfation under the oxy-fuel and air combustion. However, both the temperature and gas compositions played important roles in determining the pore structures of the product layer during the limestone indirect sulfation process. Under the O_2/CO_2 combustion condition, the calcium conversion of indirect sulfation was always higher than that of direct sulfation. The highest final calcium conversion after 60 min was found at 900 °C under the O_2/CO_2 combustion condition.

1. Introduction

The combustion of fossil fuels for power generation is a main contributor to greenhouse gas emissions. Oxy-fuel combustion is widely considered as one of the most promising technologies to address the emissions of greenhouse gas [1–3]. With this technology, the CO_2 concentration in the flue gas may be up to 90%. Therefore, an easy CO_2 capture and storage becomes possible.

Compared with pulverized coal (PC) oxy-fuel combustion, oxy-fuel circulating fluidized bed (CFB) combustion is believed to be a better choice for CO_2 capture because of several unique advantages. Some well-known advantages include fuel flexibility, low NO_x emission, and efficient sulphur removal. For the above reasons, oxy-fuel CFB combustion technology has attracted further attention from investigators [4–14].

During the typical oxy-fuel combustion process, a part of flue gas would be recycled to the furnace, thus SO_2 in the flue gas would gradually accumulate. The experimental results of the 0.8 MW oxy-CFB units at Canmet Energy [15] showed that the high SO_2 concentration would cause the corrosion of the tube and device due to the sulphate deposition after a long period operation. In addition, the high SO_2 concentration would be harmful for CO_2 compression, purification and transportation [16]. The removal of the SO_2 is necessary during the oxy-fuel CFB combustor operation. Limestone sorbent injection is a relatively simple and low-cost process for SO_2 capture.

The operating temperature of CFBCs can vary greatly with fuels used. For example, more reactive fuels such as lignite are fired at 800–850 °C, and fuels such as char are fired at 900–950 °C. Moreover, because circulation of solids in the combustor can help to an effective control of the temperatures, an oxy-fuel CFB boiler can be operated under the oxygen concentration of range from 21% to above 50%. Therefore, the limestone can be surrounded by CO_2 concentration ranging from 50% to above 90% during their stage in the CFB combustor. Thus, according to the equilibrium CO_2 pressure over limestone on temperature, as suggested by Baker [17], the sulfation reaction of limestone can proceed via two different routes under the oxy-fuel CFB combustion condition, as shown in Fig. 1.

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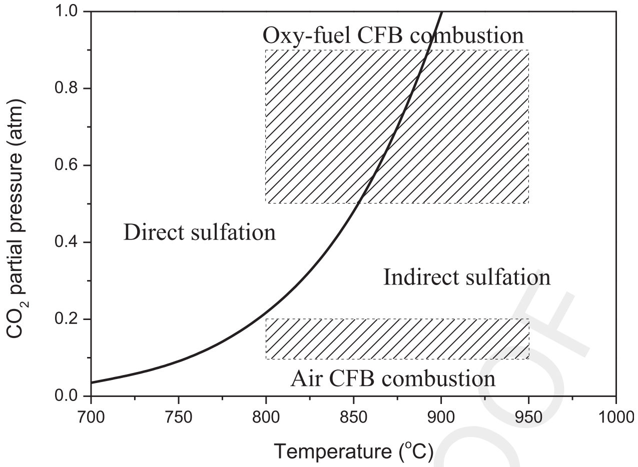

Fig. 1. Equilibrium CO_2 partial pressure over limestone.

In the zone under the curve in the figure, the operating condition leads to a previous calcination of $CaCO_3$, and then sulfation of CaO, which is known as the indirect sulfation:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \quad (1)$$

$$CaO(s) + SO_2(g) + 0.5\ O_2(g) \rightarrow CaSO_4(s) \quad (2)$$

In the zone above the curve, the sulfation of limestone will occur between $CaCO_3$ and SO_2 directly, being necessary lower temperatures to operate under indirect sulfation for the certain CO_2 concentration. The direct sulfation step can be represented by the following formula:

$$CaCO_3(s) + SO_2(g) + 0.5O_2(g) \rightarrow CaSO_4(s) + CO_2(g) \quad (3)$$

Some works about the sulfation of limestone under oxy-fuel combustion condition have been done with TGA and fix-bed combustor. Most of them are related with direct sulfation. Liu et al. [18] suggested that the direct sulfation reaction can often proceed at a fairly high rate even at high conversions and consequently enables better sorbent utilization. However, Garcia-Labiano et al. [19] hold the contrast opinion, the sulfation conversion reached by the limestone under the indirect sulfation was always higher than that under the direct sulfation.

The TGA and fix-bed combustor has many limitations owing to its absence of those existing in fluidized bed, such as simultaneous calcination and sulfation, attrition, thermical shock, and crackle. Up to now, only few works have been done about the sulfation of limestone with the fluidized bed reactors [20,21]. These studies are concerned with the effects of the operation parameters, such as temperature, inlet oxygen concentration, particle size etc., on the limestone desulfurization characterization, but there are still many unknowns.

The aim of the paper is to study the limestone sulfation behavior under oxy-fuel circulating fluidized bed combustion condition. The calcination of $CaCO_3$, pore structure of product layer, and calcium conversion under the air and oxy-fuel combustion conditions were investigated in an oxy-CFB combustor.

2. Experimental

2.1. Experimental system

The experimental system consisted of a circulating fluidized bed combustor, a cyclone, a U-valve, a flue gas cooler, a bag filter, a fuel and sorbent feed unit, a gas supply unit, and a measurement and data acquisition system. Fig. 2 shows a schematic diagram of the installation.

The stainless steel combustor has a height of 3250 mm and an inside diameter of 100 mm. The combustor is equipped on the outside with three electrical heaters and a solid cooler to adjust the heat duty of 30–50 kW.

Coal is fed to the combustor by means of a screw feeder located just above the distributor. Another screw feeder controls the sorbent fed to the combustor.

The reactant gases, air, CO_2 and O_2, are supplied from cylinders by mass flow controllers to simulate typical gas compositions (O_2/CO_2, O_2/N_2) entering into the combustor in oxy-fuel combustion conditions. The oxygen concentration of inlet gas ranges from 21% to 50%.

The measurement system consists of thermocouples, pressure sensors, flow meters, and gas analyzers. The temperatures and pressures in the system are measured at distances of 125 mm, 475 mm, 825 mm, 1525 mm, 2925 mm, and 3100 mm along the combustor above the distributor, and at the cyclone and the loop seal. The oxygen concentration of the flue gas is measured by a zirconia oxygen analyzer. The concentration of CO_2, CO, SO_2, and NO_x in the flue gas is monitored on-line by an FTIR analyzer (GASMTE DX4000) located after the cyclone.

2.2. Procedure

In order to investigate the limestone sulfation behavior for oxy-fuel circulating fluidized bed combustion, a small cage made from stainless steel net containing limestone particles was dipped into the dense zone of the CFB combustor during the experiment, as can be seen in Fig. 3. The cage has a height of 20 mm and a diameter of 20 mm. The aperture mesh of the stainless steel is 1 mm. All the limestone

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