Research article

Impacts of water vapor and AAEMs on limestone desulfurization during coal combustion in a bench-scale fluidized-bed combustor

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ABSTRACT

Limestone is normally added into fluidized bed boiler furnace as sulfur sorbent. Water vapor, alkali and alkaline earth metals (AAEMs) within coal have great influence on desulfurization mechanism. In this paper, the impacts of water vapor and AAEMs on limestone desulfurization during coal combustion are studied. In the experiments, Jincheng anthracite (JCA) and Zhundong lignite (ZDL) were used as fuel with limestone addition under different concentrations of water vapor in a bench-scale fluidized-bed combustor (FBC). SEM, ICP-AES and XRD techniques were employed to analyze the micro-morphology and chemical compositions of deposited ash to understand the mechanism. The results show that water vapor and AAEMs within coal accelerate the limestone desulfurization during coal combustion. ZDL has a stronger propensity of self-desulfurization than JCA. The grain size of coal ash grows with water vapor addition, and this phenomenon is further intensified under the condition of desulfurization or ZDL combustion. The mechanism is probably that water vapor and AAEMs improve the solid state diffusion during desulfurization and improve growth of ash grains.

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1. Introduction

The pollutant SO_2 produced by coal combustion not only damages the human health but also causes acid rain. To address this problem, desulfurization technologies have been developed. According to the different positions for desulfurization, there are before-, in- and after-furnace methods. Among them the in-furnace desulfurization with limestone addition has been widely used in the circulating fluidized bed (CFB) boiler. The temperature of 800–950 °C in the CFB boiler is considered as the optimum temperature window for desulfurization by limestone which will at least reduces 80% of SO_2 emissions [1].

For coal-fired CFB boilers, water vapor accounts for a high concentration in the fuel gas. For example [2], there is 8.4% water vapor by burning East Kentucky bituminous; and under the same condition there is 12.4% water vapor after the combustion of Sack lignite; besides, CFB boiler is often used for burning low-quality fuels such as high-moisture lignite which may produce nearly as high as 20% water vapor.

The high concentration of water vapor in fuel gas will influence limestone desulfurization. Stewart [3,4] et al. studied on the issue. The results show that the conversion of samples with 15% water vapor is equivalent to a 45% increase as compared to desulfurization without water vapor. This tendency has also been proved by Wang [2,5] and Jiang [6]. About the mechanism they point out water vapor can accelerate the solid state diffusion which leads to faster reaction rate and more crystal defects. As a result, the CaO inside the product layer will have more chances to react with SO_2 and the desulfurization reaction can go deeper, this in turn increases the degree of conversion. For further confirming the mechanism, Manovic [7] et al. conducted experiments on CaO sulfurization with water vapor addition. The results show that water vapor can greatly increase the rate of agglomeration. Agglomeration after 100 days in the absence of water vapor was found to be similar with that in the presence of water vapor. They also studied the agglomeration of residues after desulfurization by SEM, and their surfaces and profiles were analyzed by EDX spectroscopy. The mechanism was also stated as water vapor can accelerate solid state diffusion during CaO sulfurization, which can in turn strengthen agglomeration of particles and finally forms fouling. The connections between particles due to desulfurization are often stronger than the original strength of the particles. Finally, they confirm that both chemical reaction and water vapor are required for appreciable agglomeration to occur, having one or the other does not suffice.

Above studies approved that the reaction rate increase and the degree of conversion becomes higher with increasing of water vapor. However, higher water vapor can also bring negative effect of serious sintering [8]. Therefore, it is speculated that there is an optimal concentration of water vapor for limestone desulfurization, but the issue has not been highly focused. In addition, the mechanism mentioned above has not been confirmed exactly. That makes the study necessary.

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After all, the reactants are all in the fixed state in the above studies, and the flue gas is all provided by cylinders of different gases, which means the experimental conditions are different from the actual conditions in the CFB boilers. To study CaO desulfurization under fluidized state, Stewart et al. [4] conducted experiments on the desulfurization of CaO calcined in a pilot-scale circulating fluidized bed combustor using two coals with the presence of water vapor. The results show that there is no obvious change in the releasing amount of SO_2 during coal combustion with 15% water vapor addition, but the existence of water vapor can promote the limestone desulfurization by increasing Ca utilization from 41 to 47%. In addition, water vapor has different influence on the desulfurization for different coals, that is, the limestone desulfurization for high-sulfur coal has been greatly improved with water vapor addition, while no obvious effect found for low-sulfur coal, which might be due to its low releasing amount of SO_2.

In fluidized desulfurization process, water vapor showed different effect. The alkali metal and alkali earth metals (AAEMs) also have influence, especially for low-rank coal, such as Victoria lignite [9] and Zhundong coal [10]. But the research on it is scarce, not to mention in presence of water vapor. Many researchers focus on the effect of AAEM additive to limestone desulfurization. Davini et al. [11] pointed out that the desulfurization efficiency had been enhanced obviously with 2 wt% NaCl addition. Fuertes et al. [12] studied on the effect of more different kinds of metallic salt additives. The results show that the inorganic additives, such as Na_2CO_3, Li_2CO_3, K_2CO_3, Na_2SO_4, NaF and NaC1, could promote the reaction. The mechanism is that the presence of AAEM additive lowers the resistance of solid state diffusion which is similar to the influence of water vapor. For further study of the mechanism, Hu et al. [13] focused on the influence of various Li^+-, Na^+-, and K^+-containing inorganic salts. The results show that all of them could promote the reaction. Specifically, Li^+- and Na^+-containing salts enhance the desulfurization process by increasing solid state diffusion in both the solid reactant (limestone) and the solid product (anhydrite), whereas K^+-containing salts promote the reaction only by increasing solid state diffusion in the solid reactant. The significant increase in the solid state diffusion causes serious deformation and coalescence of the product grains. The results of Chen [14] and Wang et al. [15] also proved the above mechanism. They further pointed out that the incorporation of Na^+ ions (Na_2CO_3 addition) in solid product $CaSO_4$ lattice structures results in formation of more extrinsic point defects in the crystal lattices of $CaSO_4$ and a significant increase of solid state diffusion in the solid product. From the solid-state physics point of view, Li et al. [16] also propose that the defect formation caused by the additive may explain the enhanced desulfurization and therefore establish a new desulfurization model. The relationship between the solid state diffusion coefficient and the additive fraction is integrated into the model which can be used to describe the product island formation and the product layer growth.

The studies above are mainly concerned about the limestone itself during desulfurization rather than the influence of water vapor and AAEMs within coal on SO_2 release and removal during coal combustion in fluidized bed. And the mechanism for the influence of water vapor and AAEMs on limestone desulfurization remains unclear. Therefore, experiments in this paper were conducted in a bench-scale FBC for Jincheng anthracite (JCA) and Zhundong lignite (ZDL) combustion with limestone addition under the condition of 0–15% water vapor. The change of SO_2 concentration was monitored by FTIR. SEM. ICP-AES and XRD techniques were employed to analyze the impacts of water vapor and AAEMs on limestone desulfurization.

2. Experimental section

2.1. Samples

JCA and ZDL were obtained and sieved, with their ultimate and proximate analyses are listed in Table 1. The chemical compositions of their ash are provided in Table 2. It can be seen from Table 1 that there are obvious differences in the contents of moisture, volatile and ash between them. And the S content of JCA is higher than that of ZDL. Table 2 shows that the content of AAEM oxides within the ZDL ash is much higher than those in JCA ash. From the two tables shown above, it can be speculated that the two coals could show different characteristics, such as combustion and desulfurization.

The particle size of the sieved coal ranged from 0 to 2.36 mm. Quartz sand with a particle size range of 0.18–0.55 mm and a mean particle diameter of 0.235 mm was used as the bed material with an initial quantity of approximately 150 g. Limestone from Heilongjiang (HLJ) province in China was used as sorbent for capturing SO_2. The particle size ranged from 300 to 450 μm and the components are listed in Table 3. The particle size distribution was measured by a Malvern Mastersizer 2000, and the result is shown in Fig. 1.

Coal and limestone were separately dried beforehand in a vacuum drying oven for at least 2 h at 110 °C to eliminate the intrinsic liquid water.

2.2. FBC facility: description, experimental procedure and operating conditions

The experiments of limestone desulfurization were conducted in a FBC facility. The main body of the combustor consisted of a preheating section, a furnace section (containing both dense phase and dilute phase portions), a cyclone and a filter bag. The furnace section was equipped with a screw feeder, which allowed for a steady coal feed rate between 5 and 20 g/min. The flows of air into the facility were controlled by a mass flow control. The details of the experimental setup were discussed in detail elsewhere [17,18]. In addition, the facility was retrofitted with adding a water-vapor generator and a nozzle to study the influence of water vapor. The water-vapor generator, as shown in Fig. 2, consisted of the water source (Ulupure, 18.25 MΩ cm), peristaltic pump (LEAD LIUID-BT50S), heater with PID controller and stainless steel U-shaped vaporization pipe. To prevent water vapor from condensing, heating tapes (200 °C) which were covered with thermal insulation materials and high temperature resistance tinfoil were wrapped around the pipe. The water vapor produced in the generator was carried by air with the rate of 0.5 m³/h through the nozzle into dense phase portion of the combustor. In order to satisfy the requirement of testing the concentration of water vapor and other gaseous products during coal combustion on line, a sampling pipe which was made of 304 stainless steel with the diameter of 10 mm was installed to a port on the top of the furnace (see Fig. 2). The furnace was wrapped by heating tapes to prevent water vapor in the pipe from condensing. FTIR (GASMET-DX4000, Finland), of which the wavelength range is 900–4200 cm^{-1} with the resolution power of 8 cm^{-1}, was applied to monitor the changes of all gaseous products in the furnace on line. To prevent the ash

Table 1
Ultimate and proximate analyses of JCA and ZDL.

Sample	Proximate analysis (%)				Ultimate analysis (%)					Heating value
	M_{ar}	V_{ar}	A_{ar}	FC_{ar}	C_{ar}	H_{ar}	O_{ar}	N_{ar}	S_{ar}	$Q_{net,ar}$ (kJ/kg)
JCA	4.00	6.72	30.24	59.04	59.35	2.56	1.29	0.72	1.84	20,480
ZDL	16.40	25.00	3.24	55.36	65.69	3.13	9.81	1.30	0.43	23,460