

Sulfur fate during bituminous coal combustion in an oxy-fired circulating fluidized bed combustor

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Abstract—To clarify the sulfur transformation behavior during oxy-fired circulating fluidized bed (CFB) combustion, experiments on SO₂ emission characteristics were carried out in a 50 kWth CFB combustor. Results show that SO₂ emission is quite dependent on the bed temperature in different atmospheres without limestone injection. With Ca/S=2.5, SO₂ emission in 21%O₂/79%CO₂ atmosphere is smaller than that in air atmosphere, but SO₂ emission decreases with the increase of O₂ concentration. The calcium forms in the ash prove the combination of calcination/carbonation and direct sulfation mechanism of limestone under oxy-combustion conditions. And the desulfurization efficiency of limestone (as deducting the self-retention efficiency from the total sulfur removal efficiency) increases from 40% to 52% as the O₂ concentration increases from 21% to 40%.

Key words: Oxy-fuel Combustion, CFB, SO₂ Emission, Desulfurization Efficiency

INTRODUCTION

Oxy-fuel combustion is considered as a competitive technology for CO₂ capture from coal-fired power plant due to its technical feasibility and economical advantages [1,2]. The SO₂ emission characteristics from oxy-coal combustion has been extensively studied and summarized by Toftegaard [2]. Two main different conclusions were obtained. Some investigators [3-6] observed that the conversion of sulfur in coal to SO₂ decreased in O₂/CO₂ combustion compared with traditional air combustion because high SO₃ concentrations in the flue gas during O₂/CO₂ combustion resulted in sulfur retention by ash or deposits in the furnace. Whereas, Zheng and Furimsky argued that CO₂ plays no insignificant role for the sulfur release compared oxygen by equilibrium calculations [7].

Meanwhile, the in-furnace desulfurization by injection of limestone has been suggested for oxy-fuel combustion because larger desulfurization efficiency could be expected [8-10]. They explained direct sulfation of limestone will occur because the high CO₂ partial pressure and the calcium conversion under direct sulfation is usually higher than that under calcination/sulfation due to the higher porosity of the product layer.

Oxy-fuel combustion in circulating fluidized bed combustor (CFBC) has attracted large attention in recent years due to its extensive advantages [11,12] such as fuel flexibility, in-furnace desulfurization, low NO_x emission and compact boiler size. Czakiert et al. [13] found that the carbon conversion ratio and the sulfur conversion ratio can be promoted by elevating O₂ concentration on a laboratory scale CFB apparatus. Lawrence et al. [14] studied the oxy-coal combustion in a small-scale CFB and found the CO₂ concentration in the flue gas was more than 85% (dry basis). Foster Wheeler and VTT

are developing the near zero emissions oxy-CFB boiler and have done the bench and pilot experiments at VTT [15]. CANMET has carried the oxy-CFB experiment with full flue gas recycled [16]. However, the published paper contains contradictory results on the SO₂ emission characteristics of oxy-CFB combustion. Lawrence [14] found even without lime injection the SO₂ emissions were dramatically decreased with oxy-CFB combustion. VTT's pilot experiment showed that the desulfurization efficiency of limestone during oxy-CFB combustion can reach 98% [15], much higher than that in air combustion. Jia et al. [16] observed that the sulfur capture was lower in oxy-CFB combustor at 850 °C than air-fired, ranging from 65% to 78.2%. For petroleum coke, a 20% improvement in sulfur capture efficiency can be obtained when the temperature is increased to 950 °C. The different conclusions may be caused by the different fuel types and operation conditions. Generally, there are three forms of sulfur in the coal: pyrite sulfur, organic sulfur and sulfate sulfur. And the forms of sulfur are coal-dependent. Different sulfur forms have different release behaviors [17,18]. Pyrite sulfur and organic sulfur release as SO₂ at the CFB temperature, while sulfate sulfur are quite stable. Also, the operation parameters of different experiments are different, such as the gas velocity, temperature, and Ca/S molar ratio. In any event, the sulfur transfer mechanism during oxy-CFB combustion is still not clear now.

In this paper, the sulfur release and desulfurization behaviors during oxy-fired and air fired combustion are investigated in a 50 kWth CFB combustor. Tests with limestone injection and without limestone injection are arranged to differentiate the desulfurization efficiency of limestone from the self-retention efficiency of parent coal.

EXPERIMENTAL

The experiments were conducted in a 50 kWth CFB apparatus, as shown in Fig. 1. The inner diameter of the primary zone is 122 mm and that of the secondary zone is 150 mm. The total height of the riser is 4,200 mm. The system is equipped for various types of

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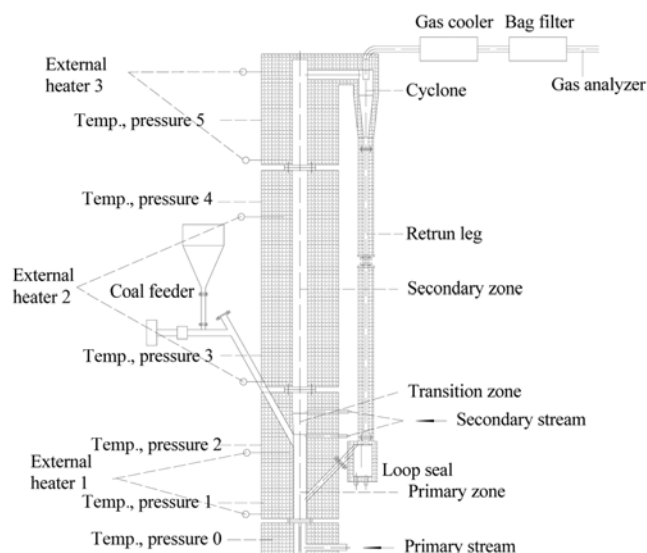


Fig. 1. 50 kWth CFB setup diagram.

measurements and has facilities that make it possible to vary parameters independently and in a wide range. The detailed description of the setup can be found elsewhere [19].

In this study, one Chinese bituminous coal was used and sieved as the coal sample. The ultimate analysis and proximate analysis are listed in Table 1. The sulfur forms in the parent coal are listed in Table 2. The analysis of the limestone used is shown in Table 3. The particle size distribution of the coal and limestone are shown in Fig. 2. O_2 and pure CO_2 mixture were used to simulate the oxy-CFB combustion with recycle flue gas (RFG) purified. Four atmospheres including air, 21% O_2 /79% CO_2 , 30% O_2 /70% CO_2 and 40% O_2 /60% CO_2 were conducted and the same excess oxygen was fixed at 0.2. Conditions without limestone injection were used to study the sulfur-retention ability of coal, while conditions with Ca/S molar ratio of 2.5 were employed to study the desulfurization ability of limestone. SO_2 concentrations in the flue gas are measured online by an IR analyzer. The calcium forms in the ash were measured by EDTA complexometric titration (for total calcium), Barium sulfate precipitation gravimetric method (for calcium sulfate), neutralization volumetric method (for calcium carbonate) and gravimetric

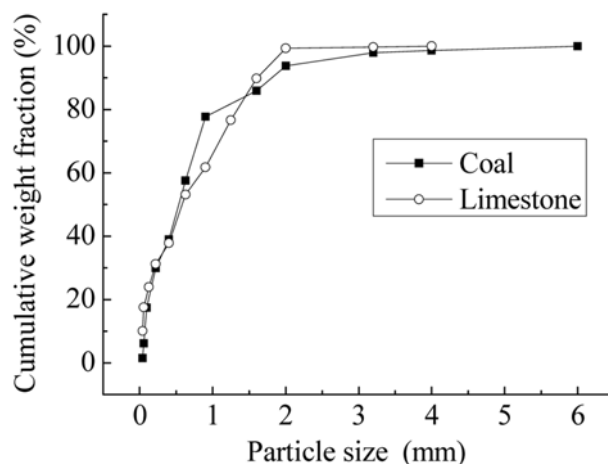


Fig. 2. Particle size distribution of the coal and limestone samples.

differentiate method (for calcium oxide). The self-retention efficiency η_s (%) of parent coal was calculated as:

$$\eta_s = \frac{SO_{2,t} - SO_{2,wo}}{SO_{2,t}} \times 100$$

Where $SO_{2,t}$ means the total SO_2 emission when the pyrite sulfur and organic sulfur in the parent coal convert to SO_2 completely and sulfate sulfur does not decompose, mg/MJ; $SO_{2,wo}$ means SO_2 emission measured without limestone injection, mg/MJ.

The desulfurization efficiency η_L (%) of limestone was calculated as:

$$\eta_L = \frac{SO_{2,t} - SO_{2,wi}}{SO_{2,t}} \times 100 - \eta_s$$

Where $SO_{2,wi}$ means SO_2 emission measured with limestone injection, mg/MJ.

RESULTS AND DISCUSSION

1. SO_2 Emission Characteristics Under Different Atmospheres

Fig. 3(a) shows the SO_2 emission under oxy-fuel and air-fired conditions without limestone addition. SO_2 emission in air atmo-

Table 1. Ultimate analysis and proximate analysis of coal sample

Sample	Ultimate analysis/wt%					Heating value/ MJ/kg	Proximate analysis/wt%			
	C_{ad}	H_{ad}	O_{ad}	N_{ad}	S_{ad}		FC_{ad}	V_{daf}	A_{ad}	M_{ad}
Bituminous coal	58.97	3.65	7.30	0.67	1.76	23.54	47.33	25.02	25.55	2.10

Table 2. Sulfur forms of coal sample

Sample	Total sulfur	Pyrite sulfur	Organic sulfur	Sulfate sulfur
Bituminous coal	1.76	0.30	1.11	0.35

Table 3. Analysis of limestone (wt%)

CaO	SiO_2	MgO	Al_2O_3	Fe_2O_3	K_2O	TiO_2	S	Cl	LOI
53.01	1.98	1.05	0.80	0.20	0.12	0.03	0.03	0.01	42.62

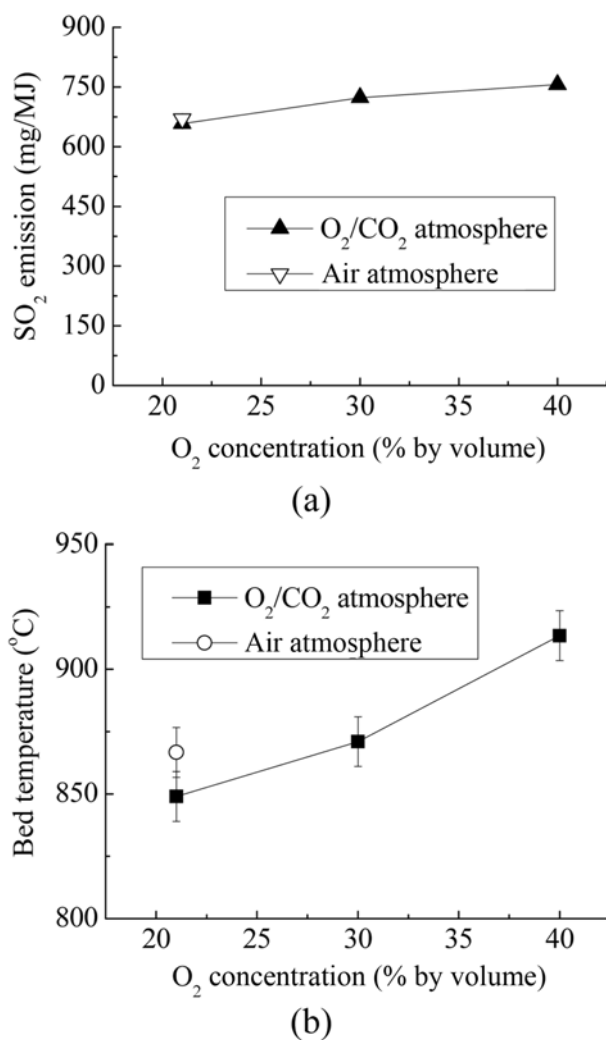


Fig. 3. (a) SO₂ emission under different atmospheres, (b) Bed temperature in different atmospheres.

sphere is a little higher than that in 21%O₂/79%CO₂ atmosphere, while SO₂ emission increases with the increase of O₂ concentration in O₂/CO₂ atmosphere. There are two possible reasons for this: first, the sulfur release is closely related to the temperature. Different forms of sulfur in the coal start to release at different temperature. Pyrite will decompose at around 400 °C [20]. The decomposing temperature of inorganic sulfate is usually over 1,000 °C [21]. The release of organic sulfur is very complex for the varied type. The aliphatic sulfur and aromatic sulfur are decomposed at different temperatures ranging from 400–1,000 °C. The bed temperature in different atmosphere is shown in Fig. 3(b). Temperature in air atmosphere is higher than that in 21%O₂/79%CO₂ atmosphere and lower than those in high O₂ concentration. The SO₂ emissions are in good agreement with the temperature. Pyrite sulfur should be release completely [20] and sulfate sulfur will not decompose [21] at the temperature. Organic sulfur which is bonding into the coal matrix will be partly retained in the ash due to the incompletely burnt condition. Fig. 4 shows the unburnt carbon content in the solid samples (fly ash and bottom ash) and self-retention efficiency under different atmospheres. Good agreement between unburnt carbon in ash

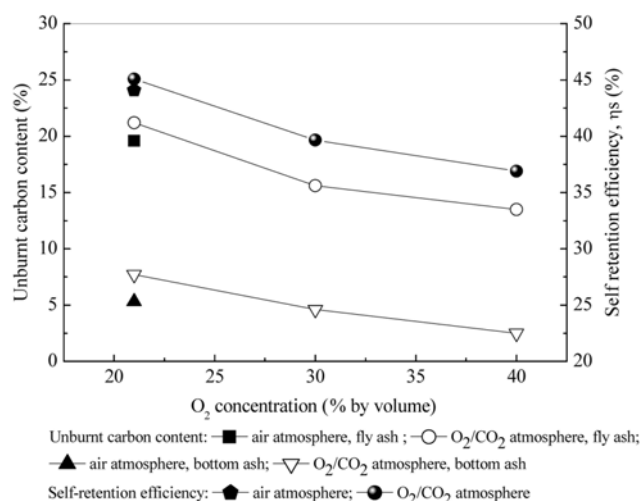


Fig. 4. Unburnt carbon content and self-retention efficiency under different atmospheres.

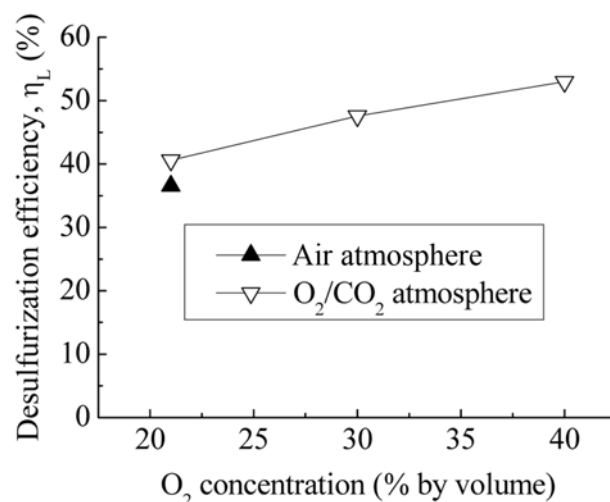


Fig. 5. Desulfurization efficiency of limestone under different atmospheres.

and self-retention efficiency indicates that the temperature is the most important factor for SO₂ emission and the elevated bed temperature under high O₂ concentration weakens the sulfur retention ability of the coal matrix, mainly through removing more organic sulfur. Secondly, oxy-fuel may promote the sulfur capture-ability by alkali and alkaline earth metals (Na, K, Mg, Ca) in the ash due to the high CO₂ concentration in the atmosphere, but it is not clarified in the paper.

2. Desulfurization Efficiency of Limestone Under Different Atmospheres

The desulfurization efficiency of limestone with Ca/S molar ratio of 2.5 is shown in Fig. 5. With limestone injection, the bed temperature is slightly influenced. The desulfurization efficiency in air atmosphere is lower than that in 21%O₂/79%CO₂ atmosphere, while it increases with the increase of O₂ concentration in O₂/CO₂ atmosphere. To examine the desulfurization mechanism of limestone in oxy-CFB combustion, the calcium forms in solid samples were analyzed and the results are shown in Table 4. The experimental error

Table 4. Calcium forms in the ash (wt% of Ca)

Atmosphere	Fly ash			Bottom ash		
	CaSO ₄	CaCO ₃	CaO	CaSO ₄	CaCO ₃	CaO
Air	30.3	4.3	65.4	28.8	7.9	63.3
21%O ₂ /79%CO ₂	33.7	39.4	26.9	35	37.4	27.6
30%O ₂ /70%CO ₂	35.6	34.9	29.5	37.7	36.1	26.2
40%O ₂ /60%CO ₂	39.2	34.5	26.3	38.4	34.3	27.3

is $\pm 0.5\%$. In air atmosphere, CaO and CaSO₄ are the main forms of calcium, which indicates that CaCO₃ decomposes into CaO first and then part of CaO reacts with SO₂ to form CaSO₄. The calcium conversion to CaSO₄ is about 30%, which is close to the results in the references [15,16]. In O₂/CO₂ atmosphere, CaO, CaCO₃ and CaSO₄ are all main forms in the ash. According to the relationship [10] between CO₂ partial pressure and calcination temperature of CaCO₃, CaCO₃ decomposition will be prohibited under the oxy-CFB combustion conditions. At the same time, direct sulfation will occur. Based the calcium form under O₂/CO₂ atmosphere, a combination of calcination/carbonation and direct sulfation exists during the oxy-CFB combustion. At direct desulfurization, the desulfurization efficiency is higher than indirect desulfurization and increases as the temperature increases, as summarized in reference [22]. Jia et al. [16] reported the sulfur capture efficiency increases from 64.5% to 87.3% as bed temperature increases from 842 °C to 946 °C when burning petroleum coke in a oxy-fired CFB. Also, the superficial gas velocity at higher O₂ concentration is lower when keeping the same fuel and excess oxygen ratio in this experiment, which may prolong the residence time of limestone in the combustor and promote sulfur capture. As shown in Fig. 5, the desulfurization efficiency increases from 40.6% to 53.0% as O₂ concentration increases from 21% to 40%.

CONCLUSIONS

SO₂ emission characteristics from an oxy-fired CFB combustor with and without limestone injection were investigated to distinguish the self-retention efficiency of parent coal and desulfurization efficiency of limestone. Results show that self sulfur retention efficiency under different atmospheres is in good agreement with the unburnt carbon content in the ash, indicating that the difference of SO₂ emission originates from the organic sulfur in the parent coal. The desulfurization efficiency of limestone in O₂/CO₂ atmosphere is higher than that in air atmosphere. The calcium forms in the ash prove the combination of calcination/sulfation mechanism and direct sulfation mechanism during oxy-CFB combustion.

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