Sulfur Fate During Bituminous Coal Combustion in an Oxy-fired CFB Combustor
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Oxy-fuel combustion is considered as one of the most promising technologies for capturing CO\textsubscript{2} from power plant. Many works have been done on the sulfur transformation behavior during oxy-fuel combustion, however the results are discrepant. In this paper, SO\textsubscript{2} emission characteristics during oxy-fired circulating fluidized bed (CFB) combustion were studied in a 50kWth CFB combustor. Results show that without limestone injection, SO\textsubscript{2} emission in 21%O\textsubscript{2}/79%CO\textsubscript{2} atmosphere is smaller than that in air atmosphere, but SO\textsubscript{2} emission increases with O\textsubscript{2} concentration. The reason is that the elevated bed temperature under high O\textsubscript{2} concentration weakens the sulfur retention ability of the coal matrix mainly through removing more organic sulfur. With Ca/S=2.5, SO\textsubscript{2} emission in 21%O\textsubscript{2}/79%CO\textsubscript{2} atmosphere is also smaller than that in air atmosphere, but SO\textsubscript{2} emission decreases with O\textsubscript{2} 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 O\textsubscript{2} concentration increases from 21% to 40%.

Keywords: Oxy-fuel combustion, CFB, SO\textsubscript{2} emission, desulfurization efficiency

1. Introduction

Oxy-fuel combustion in circulating fluidized bed combustor (CFBC) has attracted large attention in recent years due to its extensive advantages such as fuel flexibility, in-furnace desulfurization, low NO\textsubscript{x} emission and compact boiler size, etc. Czakiet et al found that the carbon conversion ratio and the sulfur conversion ratio can be promoted by elevating O\textsubscript{2} concentration on a laboratory scale CFB apparatus. Lawrence et al studied the oxy-coal combustion in a small-scale CFB and found the CO\textsubscript{2} 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 has done the bench and pilot experiment at VTT. CANMET has carried the oxy-CFB experiment with full flue gas recycled. However the published paper contains contradictory results on the SO\textsubscript{2} emission characteristics of oxy-CFB combustion. Lawrence found even without lime injection the SO\textsubscript{2} emissions were dramatically decreased with oxy-CFB combustion. VTT’s pilot experiment showed that the desulfurization efficiency of limestone during oxy-CFB combustion can get to 98%, much higher than that in air combustion. Jia et al 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 increases 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. Pyrite sulfur and organic sulfur release as SO$_2$ at the CFB temperature while sulfate sulfur are quite stable. Also, the operation parameters of different experiment are different, such as the gas velocity, temperature, Ca/S molar ratio, etc. Whatever, 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 50kWth 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.

2. Experimental

The experiments were conducted in a 50kW$_{th}$ CFB apparatus, as shown in Fig.1. The inner diameter of the primary zone is 122 mm and that of the secondary zone is 150mm. The total height of the riser is 4200mm. The system is equipped for various types of 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.
3. Discussion

Fig. 4 shows the SO\textsubscript{2} emission under oxy-fuel and air-fired conditions without limestone addition. SO\textsubscript{2} emission in air atmosphere is a little higher than that in 21%O\textsubscript{2}/79%CO\textsubscript{2} atmosphere while SO\textsubscript{2} emission increases with the increase of O\textsubscript{2} concentration in O\textsubscript{2}/CO\textsubscript{2} atmosphere.

The desulfurization efficiency of limestone with Ca/S molar ratio of 2.5 is shown in Fig. 7. The desulfurization efficiency in air atmosphere is lower than that in 21%O\textsubscript{2}/79%CO\textsubscript{2} atmosphere while it increases with the increase of O\textsubscript{2} concentration in O\textsubscript{2}/CO\textsubscript{2} atmosphere.

4. Preliminary results

SO\textsubscript{2} 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 SO\textsubscript{2} emission originates from the organic sulfur in the parent coal. The desulfurization efficiency of limestone in O\textsubscript{2}/CO\textsubscript{2} 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.