SO₃ Migration and Emission Characteristics of CFB Boilers

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Abstract. In order to study the migration and transformation of SO_3 from circulating fluidized bed boiler (CFB) in the air preheater and flue gas treatment facilities, 10 circulating fluidized bed boilers with installed capacities between 150 MW and 330 MW were measured by controlled condensation method. Ten circulating fluidized bed boilers with installed capacities ranging from 150 MW to 330 MW were measured using the controlled condensation method. It is showed that the SO_3 removal rate of the air preheater was affected by the air preheater flue gas exit temperature, which ranged from 6.7 % to 36.5 %, and the SO_3 removal rate of the rotary air preheater was higher than that of the tubular air preheater. The SO_3 removal rate of cloth bag filter and electric bag filter is above 40 %; the SO_3 removal rate of electrostatic precipitator is between 6.1 % and 10.8 %. The SO_3 removal rate of wet desulfurization method ranges from 41.7 % to 73.4 %, with the highest SO_3 removal rate of double tower double cycle. The SO_3 removal rate of off-furnace CFB semi-dry desulfurization reached 89.7 %~97.9 %, and the dry process inside the furnace + off-furnace CFB semi-dry process could reduce the SO_3 at the desulfurization outlet to below 0.3 mg/m³ under the tested conditions. The conclusions of the test analysis in this paper can provide reference for SO_3 control in circulating fluidized bed boilers and related policy formulation.

1. Introduction

As China's coal-fired units gradually enter the "post-emissions" era of ultra-low emission retrofit, SO_3 carried in coal-fired flue gas is receiving more and more attention and research [1]. For coal-fired power plants, the increase in SO_3 concentration will cause an increase in flue gas acid dew point temperature [2-3], and in order to cope with this problem, the exhaust temperature needs to be increased to prevent the corrosion of the flue and equipment by H_2SO_4 condensation, which will cause a decrease in boiler economy; secondly, SO_3 will react with NH_3 to produce ammonium sulfate and ammonia hydrogen sulfate, which is a very adhesive substance and will cause clogging of the air preheater and increase the air preheater operating pressure differential. Thirdly, SO_3 will form H_2SO_4 aerosol to be discharged into the atmosphere, and the aerosol scattered light makes the stack exhaust smoke in the form of colored plume. It is generally believed that when the concentration of SO_3 in flue gas is 17.9 mg/m³ [4], the plume will start to appear blue or yellow-brown, and under certain environmental conditions, the opacity of the flue gas will be greater than 50 % even when the volume concentration of SO_3 is only 10×10^{-6}, and only when the volume concentration of SO_3 is reduced to less than 5×10^{-6} will the blue plume phenomenon not appear [5-7]. This phenomenon is more pronounced for units burning high sulfur coal . The generation of colored plumes reduces the public's acceptance of the

environmental efforts of coal-fired power plants. In addition, SO_3 is an important component in the formation of acid rain or acid fog, which can have adverse effects on both the environment and human health. Therefore, controlling SO_3 is of great practical importance.

Compared with pulverized coal furnace, circulating fluidized bed boiler (CFB) is widely used in China, especially in areas where poor quality coal, high sulfur coal and coal gangue are burned, because it has the advantages of wide fuel adaptability, good operation adjustability and superior environmental characteristics[3]. Taking Inner Mongolia Autonomous Region as an example, the total installed capacity of CFB generating units exceeds 10 000 MW, ranking first in the country . In addition, a study showed that the standardization and universalization of SO_3 emission and control will be the focus of the thermal power industry during the 14th Five-Year Plan period, so a large amount of experimental data is needed as the theoretical support for relevant policy formulation and introduction. At present, most of the studies on SO_3 migration and emission characteristics are focused on pulverized coal furnaces, and not many reports are available for CFB boilers. Conducted SO_3 removal tests on a 300 MW CFB boiler under different operating conditions and concluded that the SO_3 removal rate was <23 % for the pre-electric precipitator and >95 % for the semi-dry desulfurization outside the furnace[6]. In order to more comprehensively study the SO_3 emission characteristics of CFB boilers and its migration in existing equipment, the research team has tested and analyzed 10 CFB boilers to provide a data base for SO_3 control and a

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technical reference for the formulation of relevant technical routes and policies.

2. Test section

2.1. Brief introduction of the test unit

The test load of the test unit, the full sulfur of coal combustion, the type of air preheater and the type of flue gas treatment facilities are shown in Table 1.

Table 1. Overview of the test unit.

Unit No.	Test Load/MW	Coal Combustion Total Sulfur （St,ar）/%	Air Prep Type	Denitrification Process	Dust Removal Facilities	Desulfurization Facilities
A1	150	1.22	Tube type	SNCR	Electric bag dust collector	Wet (single alloy tray single tower)
A2	150	0.97	Tube type	SNCR	Electric bag dust collector	Wet (double alloy tray single tower)
B1	200	1.24	Tube type	SNCR	Microfiber bag dust collector	Dry process inside the furnace + wet process outside the furnace (rotary sink coupler single tower)
B2	200	1.67	Tube type	SNCR	Microfiber bag dust collector	Dry process inside the furnace + wet process outside the furnace (rotary sink coupler single tower single cycle)
C1	330	1.21	Quadruple bin rotary type	SNCR	Electric bag dust collector	Wet (double tower double cycle)
C2	330	1.42	Quadruple bin rotary type	SNCR	Electric bag dust collector	Wet (double tower double cycle)
D1	135	0.83	Tube type	SNCR	High frequency power electrostatic precipitator	In-furnace dry process + out-of-furnace CFB semi-dry process
D2	135	1.16	Tube type	SNCR	High frequency power electrostatic precipitator	In-furnace dry process + out-of-furnace CFB semi-dry process
E1	330	1.09	Tube type	SNCR	High frequency power electrostatic precipitator	In-furnace dry process + out-of-furnace CFB semi-dry process
E2	330	1.13	Tube type	SNCR	High frequency power electrostatic precipitator	In-furnace dry process + out-of-furnace CFB semi-dry process

2.2. Calculation method

SO$_3$ mass concentration C$_{SO3}$ is calculated according to the formula in DL/T1990-2019 "Test Method for SO$_3$ in Flue Gas of Thermal Power Plants - Controlled Condensation Method".

The SO$_3$ removal rate is calculated as follows:

$$\eta_{SO_3} = \frac{C_{SO_3,in} - C_{SO_3,out}}{C_{SO_3,in}} \times 100\% \tag{1}$$

Where: η_{SO3} indicates the SO$_3$ removal rate; C$_{SO3}$,in indicates the facility inlet SO$_3$ mass concentration; C$_{SO3}$,out indicates the facility outlet SO$_3$ mass concentration.

3. Results and Discussion

3.1. Removal of SO$_3$ by air preheater

The test uses the SO$_3$ concentration at the air preheater inlet as the original SO$_3$ concentration in the flue gas. From Table 2, it can be seen that the sulfur content of the combustion coal of the test units is relatively close, except for A2 and D1 units, which are all medium sulfur coal, but the difference in the original SO$_3$ concentration is large. This is because in addition to the coal combustion sulfur content, SO$_3$ generation is also influenced by various factors such as combustion temperature, excess air coefficient, flue gas residence time, fly ash accumulation catalysis and metal oxide film catalysis on the heated surface . Compared to pulverized coal furnaces, the raw SO$_3$ concentration in CFB boilers is also influenced by SNCR and dry desulfurization in the furnace: it has been suggested that SNCR denitrification has a removal effect on gaseous SO$_3$, and the higher the ammonia to nitrogen molar ratio, the higher the removal of SO$_3$ by SNCR. When the dry desulfurization process is used, the molar ratio of calcium to sulfur in the furnace is >1. The calcination of limestone produces calcium oxide, magnesium oxide, and other metal oxides that react with sulfur dioxide and SO$_3$ in the flue gas, reducing the concentration of SO$_3$.

Table 2. Air preheater SO₃ removal rate

Unit No.	Inlet SO$_3$ concentration/ （mg/m^3）	Outlet SO$_3$ concentration/ （mg/m^3）	Air preheater flue gas outlet temperature/°C	Ŋ SO$_3$/%
A1	31.38	22.62	124.2	27.9
A2	25.80	19.94	119.9	22.7
B1	93.59	83.48	144.4	10.8
B2	60.71	52.70	143.9	13.2
C1	60.71	40.98	126.4	36.5
C2	78.32	54.67	119.3	30.2
D1	10.32	9.63	152.8	6.7
D2	12.55	11.32	162.0	9.8
E1	18.20	16.03	167.7	11.9
E2	22.30	20.23	166.6	9.3

The effect of air preheater flue gas outlet temperature on the SO₃ removal rate is shown in Figure 1.
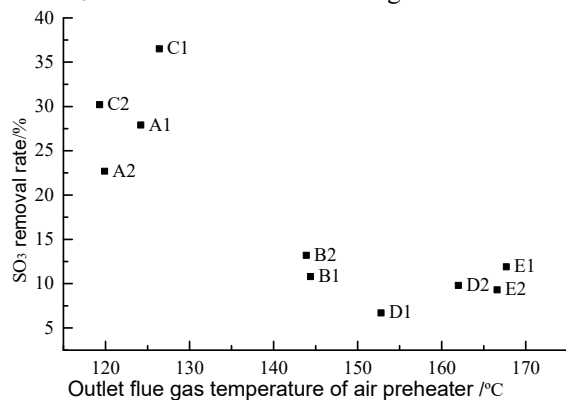

Figure 1. The relationship between SO₃ removal rate and air preheater flue gas outlet temperature

The flue gas outlet temperatures of the air preheater of the test units ranged from 119.3 °C to 167.7 °C, and it can be seen that the higher the flue gas outlet temperature, the lower the SO₃ removal rate. the flue gas outlet temperatures of D1, D2, E1, and E2 ranged from 152.8°C to 167.7°C, and the SO₃ removal rates were around 10%. the flue gas outlet temperatures of A1, A2, C1, and C2 were lower, ranging from 119.3 °Cto 126.4 °C, and the corresponding SO₃ removal rates were higher, 27.9 %, 22.7 %, 36.5 % and 30.2 %, respectively. This is because SO₃ exists mainly in the form of H₂SO₄ aerosol in the operating temperature range of the air preheater. When the metal wall temperature at the cold end of the air preheater is lower than the flue gas acid dew point temperature, H₂SO₄ aerosol will form liquid H₂SO₄ condensation on the heated surface, and the lower the outlet flue gas temperature of the air preheater, the greater the possibility of H₂SO₄ aerosol condensation and the higher the air preheater removal rate of SO₃ ; in addition, when there is NH₃ present in the flue gas escaping from the denitrification system, NH₃ will react with SO₃ to form ammonium sulfate or ammonia hydrogen sulfate, and the amount of ammonium sulfate or ammonia hydrogen sulfate generated is mainly affected by the SO₃ concentration, NH₃ escape and reaction temperature , and the more drastic the change of flue gas temperature in the air preheater, the easier the ammonia hydrogen sulfate is deposited , and the higher the SO₃ removal rate. It can also be seen from Figure 2 that the SO₃ removal rate is higher for the rotary air preheater of C1 and C2 compared to the tubular air preheater of A1 and A2. This may be due to the fact that for rotary air preheaters, the H₂SO₄ already condensed at the air preheater inlet evaporates and is carried away in the air as the flue gas and air alternately pass through the heated surface, and the rate of evaporation depends on the moisture content in the air and the metal wall temperature.

3.2. Removal of SO₃ by dust collectors

The SO₃ removal rate of the dust collector is shown in Table 3, which shows that the SO₃ removal rate of the dust collector is from high to low in the order of cloth bag filter > electric bag filter > electrostatic precipitator. The SO₃ removal rates of the test units D1, D2, F1, and F2 ranged from 6.1 % to 10.8 %, which is due to the fact that under normal conditions, the ESP flue gas temperature is above the acid dew point of the flue gas and the amount of SO₃ condensation is very low, so the removal of SO₃ from the ESP is mainly due to the ability of the fly ash to adsorb a small amount of SO₃. However, when the operating conditions fluctuate, the flue gas temperature may be lower than the acid dew point, at which point SO₃ condenses on the soot and is removed, and the removal rate increases. The removal rate of SO₃ depends on the fly ash concentration, surface area, flue gas temperature, and soot composition .

Table 3. Dust collector SO₃ removal rate

Unit No.	Inlet SO₃ concentration/ （mg/m^3）	Outlet SO₃ concentration/ （mg/m3）	Ŋ $_{SO3}$/%
A1	22.62	11.56	48.9
A2	19.94	11.90	40.3

B1	83.48	34.06	59.2
B2	52.70	21.45	55.8
C1	40.98	21.64	47.2
C2	54.67	30.23	44.7
D1	9.63	8.59	10.8
D2	11.32	10.28	9.2
E1	16.03	15.05	6.1
E2	20.23	18.27	9.8

3.3. Removal of SO$_3$ by the desulfurization facility

The removal rates of SO$_3$ by the desulfurization facilities are shown in Table 4.

Table 4. Desulfurization facilities SO$_3$ removal rate

Unit No.	Inlet SO$_3$ concentration/ （mg/m^3）	Outlet SO$_3$ concentration/ （mg/m^3）	η SO$_3$/%
A1	11.56	6.70	42.0
A2	11.90	5.26	55.8
B1	34.06	19.86	41.7
B2	19.22	10.13	49.3
C1	21.64	7.10	67.2
C2	30.23	9.00	73.4
D1	8.59	0.59	93.1
D2	10.28	＜0.30	＞97.1
E1	15.05	1.55	89.7
E2	18.27	0.39	97.9

From Table 4, the SO$_3$ removal rate of wet desulfurization is from high to low in the order of double tower double cycle > double alloy tray single tower > single alloy tray single tower > spin sink coupler single tower, except for the SO$_3$ removal rate of double tower double cycle process which is around 70 %, the difference between the removal rates of the other three processes is not large, ranging from 41.69 % to 55.8 %.

The removal of SO$_3$ in the wet FGD system is achieved by mass transfer between flue gas and slurry, so the magnitude of SO$_3$ removal depends on the arrangement and pressure drop of the system . The mass transfer between flue gas and slurry is usually classified as inertial collision, gravitational settling, Brownian diffusion, diffusion electrophoresis and thermophoresis. The flue gas containing H$_2$SO$_4$ aerosol is rapidly cooled below the acid dew point upon entering the absorption tower, and the cooling rate is greater than the absorption rate of H$_2$SO$_4$ vapor by the slurry, resulting in the formation of submicron droplets in the H$_2$SO$_4$ acid mist. For submicron droplets with diameters less than 0.05 μm, Brownian diffusion plays a dominant role in mass transfer . Due to the relative velocity between the submicron droplets and the slurry, the mass transfer due to Brownian motion is not sufficient for the slurry to capture the submicron droplets efficiently . Therefore, the larger droplets in the flue gas can be removed in the absorption tower, but the submicron droplets will follow the flue gas out of the stack. It has been shown that the SO$_3$ removal rate of conventional single-tower wet desulfurization is about 30 % to 60 %;

while the wet desulfurization system with ultra-low emission modification (e.g., double-tower double-circulation system) increases the contact time between H$_2$SO$_4$ aerosol and slurry, which helps to enhance the SO$_3$ removal rate; and the two processes of adding trays and rotary sink couplers in the absorption tower increase the slurry and H$_2$SO$_4$ aerosol Both processes increase the contact probability between slurry and H$_2$SO$_4$ aerosol and strengthen the mass transfer process between flue gas and slurry, which is also beneficial to SO$_3$ removal, and the higher SO$_3$ removal rate of double trays than that of single trays confirms this conclusion.

It can also be seen from Table 4 that the removal rate of SO$_3$ by the off-furnace CFB semi-dry process is 89.7 %~97.87 %, which is significantly higher than that by the wet process. The principle of off-furnace CFB semi-dry desulfurization is as follows: the flue gas from the dust collector enters the absorption tower from the bottom, and after accelerated by the venturi section, it reacts with slaked lime, recycled ash and water to remove sulfur dioxide, SO$_3$ and other acidic components. When the flue gas flows through the absorption tower, the flue gas turbulently mixes with the bed material from the bottom to the top, and flocs are formed continuously in the process of rising, and the flocs fall down due to their own weight, and are continuously disintegrated in the process of falling and driven by the flue gas to rise again, while the top structure of the absorption tower further strengthens the bed material. This series of processes increases the density of the bed in the absorption tower

(average density of 4 kg/m^3, in the dense phase flow area at the bottom of the bed density can reach 10 kg/m^3 ~ 20 kg/m^3). In addition, the small particle size of calcium hydroxide (2 μm to 5 μm) gives the bed material a huge specific surface area (20 m^2/g). These two points together make the bed material have a strong adsorption effect on H$_2$SO$_4$ aerosol; on the other hand, the relative slip velocity between gas and solid phases in the absorption tower can reach tens of times of the single particle slip velocity due to the acceleration of the venturi section, and the gas-solid two-phase flow mechanism greatly enhances the mass and heat transfer between gas and solid, which can ensure the full reaction between SO$_3$ and absorber in the high temperature section of the absorption tower .

4. Conclusion

(1) As measured, the original SO$_3$ production of CFB boiler ranged from 10.32 mg/m^3 to 93.59 mg/m^3, and the original SO$_3$ production was affected by various factors together, and the furnace denitrification and dry desulfurization also had the effect on SO$_3$ removal.

(2) The air preheater ranges SO$_3$ removal rate is from 6.7 % to 36.5 %, the lower the air preheater flue gas outlet temperature, the higher the SO$_3$ removal rate, and the corresponding higher the risk of air preheater corrosion cavitation or blockage. Due to the structural characteristics, the SO$_3$ removal rate of tubular air preheater is lower than that of .rotary air preheater.

(3) Because of the combined effect of physical adsorption and chemical adsorption, the SO$_3$ removal rate of bag filter and electric bag filter is above 40 %; the SO$_3$ removal rate of electrostatic precipitator is lower, between 6.1 %~ 10.8 %.

(4) The wet desulfurization SO$_3$ removal rate is between 41.7 % ~ 73.4 %, with the highest SO$_3$ removal rate of 67.2 % to 73.4 % for double tower double cycle.

(5) The highest SO$_3$ removal rate of external CFB semi-dry desulfurization is 89.7 %~97.9 %, and the dry process inside the furnace + external CFB semi-dry desulfurization process can reduce the outlet SO$_3$ to below 0.3 mg/m^3 under the test conditions.

References

1. WANG Hongliang, XUE Jianming, XU Yueyang, et al. Formation and control of SO$_3$ from coal-fired power plants[J]. Electric Power Technology and Environmental Protection,2014,30(5):17-20;

2. LIU Yu, SHAN Guangbo, YAN Song, et al. Progess in Research on Formation,Harm and Control Technique of SO$_3$ in Flue Gas of Coal-Fired Boiler[J]. Environmental Engineering,2016,34(12):93-97;

3. HUANG Zhong.Optimization Technologies of circulating fluidized bed boiler[M]. Version 1.Beijing: China Electric Power Press, 2019: 11-12(in Chinese);

4. MIN Wei, HU Haifang.Discussion on the semi-dry process technical route of flue gas advanced treatment based on thermoelectric CFB boiler[J].Cogeneration Power Technology,2015,2:54-56;

5. ZHAN Weiquan.Analysis of SO$_3$removal performance by dry and wet desulfurization process[C]. Chinese Society of Environmental Sciences. 2014 Annual Meeting of the Chinese Society of Environmental Sciences (Chapter 6). Chinese Society of Environmental Sciences: Chinese Society of Environmental Sciences, 2014:207-212(in Chinese);

6. PAN Danping, WU Hao, JIANG Yezheng, et al. Improvement in removal of fine particles and SO$_3$ acid mist from desulfurized flue gas with heterogeneous condensation[J].Journal of Fuel Chemistry and Technology,2016,44(01):113-119;

7. WANG Dingbang, LEI Ming, YU Fusheng, et al. SO$_3$ migration and emission characteristics of coal-fired power units[J].Thermal Power Generation,2018,47(11):96-101.