Study on SO₃ Cooperative Removal Effect of Ultra-low Emission Technology in Coal-fired Power Plants

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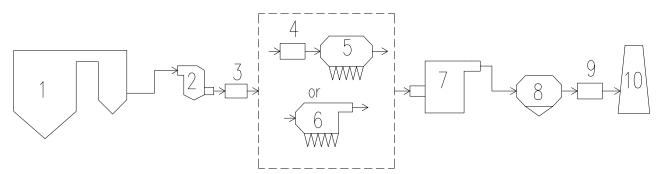
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Abstract. SO₃ is one of the main precursors of atmospheric PM_{2.5}, and its emission has attracted more and more attention in the industry. This paper briefly analyzes the harm of SO₃ and the method of controlled condensation to test SO₃. The effect of cooperative removal of SO₃ by ultra-low emission technology in some coal-fired power plants has been tested by using the method of controlled condensation. The results show that the cooperative removal of SO₃ by ultra-low emission technology in coal-fired power plants is effective. The removal rate of SO₃ by low-low temperature electrostatic precipitators and electrostatic-fabric integrated precipitators can be exceeded 80%, while the removal rate of SO₃ by wet flue gas desulfurization equipment displays lower than the above two facilities, and the wet electrostatic precipitator shows a better removal effect on SO₃. With the use of ultra-low emission technology in coal-fired power plants, the SO₃ emission concentration of the tail chimney reaches less than 1 mg / Nm³.

1 Introduction

The production and consumption of Chinese coal account for more than 70% of the total energy, of which about 50% of the raw coal is directly used to generate power and heat^[1]. Because some sulfur dioxide (SO₂) can be oxidized to sulfur trioxide (SO₃) in the process of coal combustion, the concentration of SO₃ in the flue gas is further increased after the large-scale application of Selective Catalytic Reduction (SCR) denitrification technology, and about 0.8% to 1.5% of the SO₂ can be converted to SO₃ in the flue gas^[2]. SO₃ concentration is relatively low, but it can also cause severe harm. Firstly, SO₃ reacts with escaping ammonia (NH₃) to generate ammonium sulfate ((NH₄)₂SO₄) and ammonium bisulfate (NH₄HSO₄). And these two reaction products can block micro-pores on the surface of the catalyst, which can shorten the service life of the catalyst. Secondly, the phenomenon that the flue gas acid dew point raises with the increase of SO₃ content^[3-5] can improve the corrosion risk of the tail flues, such as air pre-heater, deduster and chimney^[6-9]. Thirdly, after the wet flue gas desulphurization (WFGD), SO3 in the flue gas will combine with water vapor to form acid mist, which can decrease opacity of flue gas, leading to the phenomenon of blue feather happen^[10-11]. According to the report of USEPA, SO3 is one of the main precursors of atmospheric PM2.5^[12], and the secondary particle(sulfate) contributes about 26% for PM2.5 formation^[13]. Therefore SO3 and sulphate aerosols may cause a series of health problems.



1-Boiler; 2-Selective catalytic reduction (SCR) denitrification equiment; 3-Air pre-heater; 4-Flue cooler; 5-Electrostatic precipitator; 6-Electrostatic-fabric integrated precipitator; 7-Wet flue gas desulfurization equipment; 8-wet electrostatic precipitator; 9-Gas-gas heater; 10-Chimney

Fig.1. Ultra-low emission technical route for coal-fired power plants

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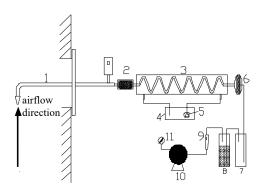
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In American 14 states, the SO₃ emission standard limit is under 6 mg/m³, but according to Emission Standard of Air Pollutants For Thermal Power Plants in China, there is no requirement for the SO₃ emission standard limit^[15], except that sulphuric fog should be lower than 5mg/m³ in Shanghai local standard^[16]. With the increasing of critical environmental standards, the control of SO3 will become more and more standardized in coal-fired power plants. At present, most of the coal-fired power plants in China are considering the removal of SO₃, during the reconstruction of ultra-low emission. The typical ultra-low emission technical route is shown in Fig.1. This paper analyzes the effect of cooperative removal of SO₃ by the ultra-low emission technology, by means of testing the SO₃ concentration in inlet and outlet of the low-low temperature electrostatic electrostatic-fabric precipitator, the integrated precipitator, the wet flue gas desulfurization equipment and the wet electrostatic precipitator.

2 Experimental section

2.1 The sampling technology of SO₃ in flue gas

Due to the stable aerosol system and very active chemical nature of SO₃ in flue gas, SO₃ is easy to combine with water vapor to form acid mist. Because of the low concentration, SO₃ is difficult to capture, and easily disturbed by SO₂. There are some sampling and analytical standards of SO₃ at home and abroad, such as EPA Method 8, JIS K0103-2005, Modified Method of ASTM 3226-73T, DL/T998-2006, ISO 4221-1980^[17-25]. The main sampling methods are isopropanol absorption method and controlled condensation method(CCM). To avoid the loss of SO₃ during sampling, the isopropanol absorption method improves the temperature of the sampling system. However, when the high-temperature sampling gas goes into the absorption bottles with the low-temperature isopropanol, it will cause isopropanol to volatilize and SO₃ to escape, which makes the a bsorption efficiency lower^[26]. CCM is that the flue gas passes through the sampling gun with heating and quartz filter in turn, and enters the condenser tube in the water bath. Then SO₃ condenses into ideal acid mist particles under the action of a certain flow rate under a certain moisture and temperature conditions. Due to the effect of centrifugal motion, the acid mist is controlled in the condenser tube wall^[27]. Then clean the condenser tube with deionized water or 80% isopropanol, test the concentration of SO42- in the cleaning solution, and finally calculate the SO₃ concentration in the flue gas. CCM is the main domestic method for the optimum capture efficiency, and it should control the sampling heating temperature and the water bath temperature of the condensing tube, including the reasonable control of condenser tube's parameters, such as the pipe diameter, the curvature radius, the extension length and so on.



1-Sampling gun with mouth; 2-Particulate filter; 3-Condenser tube Controlled; 4-Water bath heater; 5-Circulating water pump; 6-Secondary catcher; 7-Droplet separator; 8-Dryer; 9-Flow gauge; 10-Air pump; 11-Pressure gage

Fig.2. Schematic diagram of the control condensation sampling process

3 Results and discussion

3.1 The removal effect of SO₃ by low-low temperature electrostatic precipitators

With two sets of 660 MW low and low temperature electrostatic precipitators under different loads as the test object, the test results of collaborative removal of SO₃ are shown in Table 1. The test results show that, under different loads, the two sets of low-low temperature electrostatic precipitators have stable performance and the collaborative removal rate of SO₃ is above 80%. The analysis suggests that SO₃ is easy to combine with water vapor to form acid mist, and it is actually the coexistence of the gas mixing system formed by SO₃, H₂O and sulfuric acid (H₂SO₄). The Fig.3 shows that the proportion of SO3 converted to acid mist depends on the temperature of the flue gas^[28]. Above 220 °C, SO₃ and H₂O are both in the gaseous state, and there is no acid mist to form. SO₃ and H₂O are gradually converted to acid mist from 110 °C to 220 °C. Below 110 °C, they are completely converted into acid mist. After cooling, the import temperature of flue gas of low-low temperature electrostatic precipitators is mostly about 90 °C, and SO₃ in the gaseous state is converted to acid mist at this time. In the area, the dust concentration is high, the total surface area of dust is large and most of the acid mist is adsorbed on the porous surfaces of fly ash. With the decreasing of temperature, the adsorption and the chemical reactions between fly ash and alkalis are both strengthened. Therefore, the removal effect of SO₃ displays better by low-low temperature electrostatic precipitators.

 Table 1. Test results of collaborative removal of SO3 by low-low temperature electrostatic precipitators

Generator	Installed capacity MW	Load rate %	Import concentration of SO ₃ mg/m ³	Export concentration of SO ₃ mg/m ³	Removal rate %
А	660	83	11.72	2.17	81.46

		100	12.27	2.25	81.64
В	660	76	8.66	1.12	87.07
		96	7.47	0.94	87.42

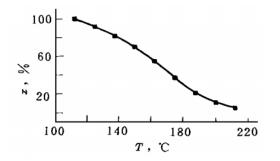


Fig. 3. Relationship between the fraction of SO₃ converted to sulfuric acid vapor and temperature

3.2 The removal effect of SO₃ by electrostatic-fabric integrated precipitators

With three sets of electrostatic-fabric integrated precipitators with different generators as the test object, the SO₃ concentration is separately tested in the inlet and outlet of the equipment, and the results are shown in Table 2. According to the results, the removal rate of SO₃ can basically reach above 80 %. The analysis suggests that smoke can be used as adsorbent, because it can form powder with a larger specific surface area. SO₃ and acid mist are adsorbed when they are penetrating into powder. Adsorption is divided into physical adsorption and chemical adsorption. For the physical adsorption, when the molecular structure is more complex and the boiling point is higher, the substance is adsorbed more easily. Because of the higher boiling point, H₂SO₄ and SO₃ belong to substance which is easy to be adsorbed. Chemical adsorption is more efficient and more stable than physical adsorption, so the alkali metal oxides, such as CaO, NaO, Fe₂O₃ and so on, have a certain of adsorption effect on SO3^[29,30]. However, according to the test results of unit C, the removal rate of SO₃ tends to be stabilized and has no big change, when the resistance of the equipment is increased, subsequently the amount of dust on the filter-bag is increased, by adjusting the spraying time.

 Table 2. Test results of collaborative removal of SO₃ by electrostatic-fabric integrated precipitators

Gener-at or	installed capacity MW	Load rate %	Resis-ta nce Pa	Import concentra-tio n of SO ₃ mg/m ³	Export concentra-tio n of SO ₃ mg/m ³	Remo-v al rate %
А	350	100	880	4.32	1.11	74.31
В	350	100	680	26.4	3.72	85.91
C 660		660 95	650	8.5	1.5	82.35
	660		900	8.39	1.36	83.79
			1000	8.99	1.59	82.31

3.3 The removal effect of SO₃ by wet flue gas desulfurization equipment

With three sets of wet flue gas desulfurization equipment with different generators as the test object, the SO₃ concentration is separately tested in inlet and outlet of the equipment, and the results are shown in Table 3. According to the results, the removal rate of SO₃ is from 37.8% to 40%, which agrees with the conclusions in literatures^[31-33]. The analysis suggests that part of the SO₃ can be removed by wet flue gas desulfurization equipment, but the effect is limited. This reason is that flue gas containing SO3 and gaseous acid mist passes the desulfurization towers, then it is rapidly cooled to below the acid dew point. The cooling speed is much faster than the speed of the gaseous acid mist be absorbed by the absorbent in the absorption tower, leading to form the sub-micron acid mist which is difficult to capture^[34,35]. Part of the large size of acid mist can collide with the slurry droplets in spray tower, and can be absorbed by serosity. However, the sub-micron acid mist has very good fluidity in the gas streams and is difficult to capture, so it can escape easily.

 Table 3. Test results of collaborative removal of SO₃ by Wet flue gas Desulfurization equipment

Generator	Installed capacity MW	Load rate %	Import concentration of SO ₃ mg/m ³	Export concentration of SO ₃ mg/m ³	Removal rate %
А	660	100	1.5	0.85	43.33
В	660	100	1.36	0.84	38.24
С	350	100	1.11	0.69	37.84

3.4 The removal effect of SO₃ by wet electrostatic precipitators

The wet electrostatic precipitator is a kind of gas cleaning equipment, which is set up in the inlet of chimney and after wet flue gas desulfurization equipment. The wet electrostatic precipitator is the lastest device which makes flue gas meet the stardard of ultra-low emission in coal-fired power plants. With five sets of wet electrostatic precipitator with different generators as the test object, the SO₃ concentration is separately tested in inlet and outlet of the equipment. The collaborative removal effect of SO3 is obtained by wet electrostatic precipitators, and the results are shown in Table 4. According to the test results, SO₃ emission concentration is less than 0.5mg/m³ with the five sets of wet electrostatic precipitator, respectively. It shows that the wet electrostatic precipitator plays a good role. The removal rate of SO₃ with different unit has a large fluctuation which is low to 50% and higher than 80%. The main reason is that the inlet concentration of SO₃ has a great influence on its removal efficiency. The relationship between the removal rate of SO3 and the import concentration of SO3 is shown Table 4. As depicted in Table 4, the higher import concentration of SO₃ is, the higher removal rate of SO₃ can be obtained. The analysis result suggests that SO₃ exists in the form of

the sub-micron acid mist after wet flue gas desulfurization equipment. Then the high voltage electric field increases the probability of sub-micron particles charged, which improves the capture efficiency.

 Table 4. Test results of collaborative removal of SO₃ by wet electrostatic precipitators

Generator	Installed capacity MW	Load rate %	Import concentration of SO ₃ mg/m ³	Export concentration of SO ₃ mg/m ³	Removal rate %
Α	330	100	0.76	0.38	50.00
В	660	100	1.45	0.43	70.35
С	330	100	1.66	0.43	74.10
D	330	100	2.44	0.42	82.79
Е	600	100	2.82	0.47	83.33

4 Conclusion

This paper analyzes the effect of cooperative removal of SO₃ by ultra-low emission technology in some tested coal-fired power plants by using CCM. The results show that the cooperative removal of SO₃ is effective by ultra-low emission technology in coal-fired power plants. The SO₃ emission concentration is effectively decreased, but there is a difference of removal effect between different equipments. The front-end equipments play a major role in removing SO₃. The removal rate of SO₃ is above 80% by low-low temperature electrostatic precipitators. Through the absorption of smoke, most removal rate of SO₃ is above 80 % by electrostatic-fabric integrated precipitators. Using wet flue gas desulfurization equipment can removal SO₃ synergeticly, but the effect is limited. By wet electrostatic precipitators, the cooperative removal effect of SO₃ varies with the import concentration of SO3, but the SO3 emission concentration can be controlled to a lower level.

Acknowledgments

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References

- L. Chen, Y. Zhao, Y. Bao, etal, J. Power ENG, 86-92 (2014).
- 2. Y. Shao, J. Xu, ne Elect. Pow. Tech., **37**,49-52 (2016).
- 3. Erickson. 2002 Conference on SCR and SNCR for NOX Control.Pittsburgh, USA, 133-136 (2002).
- 4. A. Cowdrick, Southeastern Electric Exchange 1986 Annual Conference of the Engineering and Operations Division and the Real Estate Section, Kissimmee. USA, 211-213 (1986).
- 5. D Fleig. Ind. Eng. Chem. Res., **50**, 8505-8514 (2011).
- 6. J. Cui, Z. Guo, Elect. Power, 48, 7-11 (2015).
- 7. C. Dene C, Ca EPRI, 1-84 (2004).
- 8. B. Xiang, Energy & Fuels, (2017).

- 9. D. Fleig, Energy & Fuels, **26**, 5537-5549 (2012).
- 10. 10.R. K, J. Air Waste Manage Assoc NLM, 54, 750-762,(2004).
- 11. S. Deeming A, Synthesis, 46, 27-31 (2014).
- 12. Y. Bo, J. Xue, Z. Li, CSEE, (2013).
- 13. Z. Zhou, D. Zhang, C. Zhai, etal, CSES, (2011).
- 14. Y. Zhang, ZJU, (2013).
- 15. SEPA, AQSIQ, GB13223—2011, (2011).
- 16. SHEPA, Shanghai Quality and Technical Supervision, DB31/933—2015, (2015).
- 17. EPA, EPA Method 8, (1990).
- 18. JIS, .JIS K0103-2005, (2005).
- 19. EPA, Determination of Sulfuric Acid Vapor or Mist and Sulfur Dioxide Emissions form Stationary Sources.
- 20. ASTM. Method of ASTM 3226-73T, (1988).
- 21. NDRC, DL/T998-2006, (2006).
- 22. AQSIQ, SAC, GB/T 21508-2008, (2008).
- 23. ISO, ISO 4221-1980, (1980).
- 24. ISO, ISO 7934-1989, (1989).
- 25. BS, BS 6069-4.1:1990, (1990).
- 26. Y. Ding, Springer Singapore, (2016).
- 27. R. J. Jaworowski, J. Air Poll. Cont., **29**, 43-46 (1979).
- Y. Li, B. Wu, X. Xu, J. Envir. Sci. 17, 126-130 (1997).
- 29. J. Thibault, F. Steward, D. Ruthven, Can J Chem Eng, **60**, 796-801 (1982).
- Z. Wang, Q. Huan, C. Qi, etal, Energy Procedia, 14, 1911-1917 (2012).
- 31. D. Pan, H. Wu, R. Huang, etal, JSEU (EE), 46, 311-316 (2016).
- D. Hu, H. Wang, T. Guo, etal, Sci. Tech. and Engi., 15, 92-99(2015).
- Y. Chen, X. Chen, J. Xiong, Construction&Design for Project, 41-42 (2004).
- R. Blythe, H. Thorn, U. S. EPA /DOE /EPRI Combined Power Plant Air Polluion Control Symposium, (2005).
- 35. G. Tberlet, Hartenstein H, Licata A, The Power Gen, (1999).