

Research Progress on Control and Removal Technology of SO₃ of Coal-fired Power Plants

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Abstract. SO₃ is one of pollutants in flue gas of coal power plants. It mainly derived from coal combustion in boiler and selective catalytic reduction denitrification system. The content of SO₃ in flue gas were influenced by the combustion mode, sulfur content in fuel, composition of denitrification catalyst and fly ash. SO₃ and water vapour generated H₂SO₄ droplets. Sulfate secondary particles in atmosphere could cause haze, acid rain and other disastrous weather. High concentration of SO₃ could cause blockage and corrosion and affect the safe operation of the units. The generation mechanism of SO₃ was discussed. The latest research progress on control and removal technology of SO₃ was summarized. The study in this paper provides a reference for pollutant treatment in coal-fired power plants.

1 Introduction

sulphur trioxide (SO₃) is one of pollutants in flue gas of coal power plants. The concentration of SO₃ was lower over the past years, so SO₃ emissions was not received sufficient attention. With the widespread application of SCR denitrification equipment and ultra-low emission modification, the amount of SO₃ generated has increased significantly. The adverse effects of SO₃ emissions on the power plants and environment were obvious. The control and removal technology of SO₃ was widely concerned.

According to reports [1], 22 states in the United States have proposed emission limits of SO₃ for coal-fired power plant of which 14 states emission limits is less than 6 mg/m³. In Germany, the concentration emission standards of the mixture of SO₂ and SO₃ are 50mg/m³. In Japan, SO₃/H₂SO₄ is included in particulate control. For domestic coal-fired power plants, the SO₃ emission concentration has not be defined. The synergistic removal of atmospheric pollutants was supported to control the emission of pollutants such as sulfur trioxide, mercury and arsenic[2].

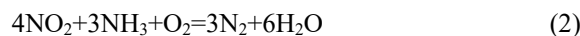
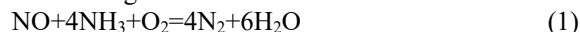
The generation and removal technology of SO₃ in coal-fired power plants was carried out. The mechanism and harm of SO₃ were analyzed. The control and removal technology of SO₃ were summarized. The applicability of technical methods was compared and discussed.

2 Generation mechanism of SO₃

Combustible sulfur in coal organic sulfur, including organic sulfur, elemental sulfur and ferrous sulfide, converted to SO₂ during combustion progress. The SO₂

gas continued to be oxidized to SO₃ at high temperature [3]. The amount of SO₃ produced was greatly affected by the sulfur content in coal. Under complete combustion conditions, the amount of SO₃ increased with the increase of sulfur content in coal. The main role of SO₃ in the formation process was the gas phase reaction between SO₂ and O₂, accounting for about 60% of the total SO₃. The metal oxides such as V₂O₅, Fe₂O₃, SiO₂ and Al₂O₃ in suspended fly ash and the pipe wall played catalytic effect on the conversion of SO₂ to SO₃. When the flue gas passed through the economizer convection heating surface, the concentration of SO₃ in the flue gas was further increased.

At present, the selective catalytic reduction (SCR) denitrification was used widely. V₂O₅ was the most important active ingredient in vanadium and titanium catalysts, which also promoted the conversion of SO₂ to SO₃ during denitrification process simultaneously [4,5]. The following reaction existed in the SCR reactor.



During the above reactions, the denitrification reaction was very rapid which was controlled by diffusion. Oxidation reaction of SO₂ was a slow reaction and was controlled by chemical kinetics. The structural form and wall thickness of the catalyst affected the generation of SO₃. In the SCR reactor, about 0.5%-1.5% of the total amount of SO₂ was oxidized to SO₃. Therefore, the denitrification efficiency and the conversion rate of SO₂/SO₃ were important indicators for SCR denitrification system.

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The SO₂/SO₃ conversion rate of the initial catalyst was generally less than 1%. However, with the prolonged use of the catalyst, the catalytic activity decreased gradually, and specific surface area of catalytic decreased gradually. Catalyst was contaminated by elemental deposition on the surface of catalyst such as K, As, P in the flue gas. Deactivation of the catalyst reduced the denitrification efficiency, but the oxidation rate of SO₂ increased instead.

SO₃ and water vapour in flue gas reacted to H₂SO₄ droplets. The H₂SO₄ droplets were discharged from the chimney into the atmosphere, increasing the opacity of the flue gas. In general, blue feathers occurred when the concentration of H₂SO₄ in the flue gas reached to 10-20 ppm. Submicron H₂SO₄ acid mist was discharged into the atmosphere to form secondary particle sulfate. Sulfate is one of the important sources of PM_{2.5} in the atmosphere, causing haze and acid rain, which is a serious hazard to human health.

When the temperature of the flue gas was lower than the dew point temperature of the sulfuric acid vapor, the sulfuric acid vapor condensed to form sulfuric acid droplets. Sulfuric acid vapor or droplets adhered to metal surfaces of the flue and air preheaters, causing low temperature corrosion and ash blocking.

The acid dew point was closely related to the sulfuric acid vapour concentration. The acid dew point of the flue gas increased significantly with the increase of SO₃ concentration in the flue gas. If the flue gas acid dew point increased, the boiler exhaust temperature needed to be increased accordingly. Generally, the temperature of the flue gas at the outlet of the air preheater is about 10 °C-15°C higher than the acid dew point of the flue gas. The increase of exhaust gas temperature led to an increase in boiler exhaust loss, so the overall efficiency of the unit was reduced.

In recent years, air preheater blockage of the ultra-low emission coal-fired units was becoming more and more serious. After the flue gas passed through the SCR denitrification device, the concentration of SO₃ in the flue gas increased. SO₃, water vapour and escape NH₃ of the flue gas reacted to form ammonium bisulfate. The melting point of ammonium bisulfate is 147 °C. The operating temperature of the air preheater is generally 120 °C-420 °C. In the middle and low temperature section of the air preheater, ammonium bisulfate was strong adhesion. The ammonium bisulfate and the fly ash in the flue gas adhered to the wall of the air preheater, which caused corrosion and blockage of the air preheater. The resistance of the air preheater raised and the thermal efficiency decreased. In the SCR denitrification reactor, permanent deactivation of the catalyst could occur if the catalyst was covered by ammonium bisulfate for a long time[6].

3 Control and removal technology of SO₃

3.1 Control technology of SO₃ in the boiler

The generation of SO₃ in the boiler was mainly controlled by fuel, combustion process and inhibitor. Burning or blending low-sulfur coal could reduce the sulfur content in the fuel to reduce the proportion of SO₃ generated during combustion. However, the replacement of coal must require the adaptability of equipment such as boiler, pulverized coal systems and dust removal. Replacement of coal could cause wear on the flue and equipment in the flue.

During combustion progress, the oxygen concentration and combustion temperature in the flame increased as the air excess factor increased. The amount of SO₃ generated was also increased correspondingly. Therefore, reducing the air excess coefficient was advantageous for suppressing the generation of SO₃ under the condition of satisfying complete combustion. Low excess air coefficient combustion or rich-light combustion method used to suppress NO_x formation could help to reduce SO₃ formation in the boiler. The amount of SO₃ generated by the ash deposition on the pipe wall could be reduced by blowing.

Some alkaline substances were sprayed into the boiler to react with SO₃ [7]. The conversion rate of SO₃ in the boiler was reduced by 40-80%, which effectively reduced the concentration of SO₃ at the boiler outlet. Alkaline substances used commonly were mainly calcium or magnesium-based additives such as calcium hydroxide, calcium carbonate and magnesium hydroxide. SO₃ removal efficiency was related to the chemical properties of the additive and its surface physical characteristics. The removal efficiency of SO₃ was also affected by some factors such as the location of the addition and the operating conditions of the boiler. As the increasing of temperature, the amount of additives, and the contact time, the adsorption capacity of the additive for SO₃ was increased. Long-term operational data from the Mansfield and Gavin power plants in the United States indicated that the removal rate of SO₃ reached more than 90% at the molar ratio of 7:1 of Mg/SO₃.

3.2 Optimization of denitrification catalyst

The denitrification activity and the lower SO₂ oxidation rate of the catalyst was maintained by adjusting the active component content of the catalyst or adding an auxiliary agent. V₂O₅ had strong activity on denitrification and SO₂ oxidation. As the V₂O₅ mass fraction increased, the SO₂ oxidation activity raised faster than the denitrification reaction. Therefore, the mass fraction of V₂O₅ in the catalyst was generally controlled to be 0.8% to 1.2%. In the catalyst formulation, specific metal oxides, such as Y₂O₃, GeO₂, NiO, BaO, MoO₃, etc., were doped to improve the surface characteristics of the catalyst[8]. Oxidation reaction of SO₂ was suppressed by weakening the adsorption capacity of SO₂ on the catalyst surface. Catalysts for high denitrification activity and low SO₂ oxidation rate were developed based on the different sites of denitrification and SO₂ oxidation.

In addition, the wall thickness of the catalyst affected the oxidation rate of SO_2/SO_3 [9]. In the case of other conditions remain unchanged, the smaller the wall thickness of the catalyst, the lower the oxidation rate of SO_2/SO_3 . But the corresponding mechanical strength and wear resistance were reduced. In the preparation process of the catalyst, when the pore structure of the catalyst was improved, the penetration of SO_2 into the catalyst could be effectively controlled. It was beneficial to reduce the oxidation rate of SO_2/SO_3 .

Therefore, under the premise of ensuring denitrification efficiency, the conversion rate of SO_2/SO_3 during the reaction process was suppressed by optimizing the catalyst formulation. The emission of SO_3 was reduced by increasing the specific surface area and reducing the wall thickness of the catalyst. However, it was necessary to consider the mechanical strength of the catalyst and the requirements for fly ash abrasion resistance.

3.3 Removal technology of SO_3

The content of SO_3 in the flue gas could be effectively reduced by spraying an alkaline absorbent in the flue. The removal effect of SO_3 was related to the type, physicochemical properties of the absorbent, the mixing uniformity of the adsorbent and the flue gas. The reaction temperature and residence time were related to the injection position of the adsorbent affects. The type and characteristics of adsorbents were important parameters of this technology.

The absorbents currently studied were mainly alkaline substances such as calcium, magnesium and sodium. Magnesium hydroxide, calcium hydroxide, sodium hydrogen sulfate, limestone powder were practically used. The absorbent were sprayed in the form of a powder or a slurry. Studies on four kinds of absorbents such as calcium-based and magnesium-based showed that [10], the absorbent effect of SO_3 was $\text{Mg}(\text{OH})_2 > \text{Ca}(\text{OH})_2 > \text{MgO} > \text{CaO}$. The results of the removal of SO_3 by two kinds of $\text{Ca}(\text{OH})_2$ and CaCO_3 absorbents showed that the former was better removal effect than the latter [11]. As the residence time of the absorbent was extended, the removal effect of SO_3 was increased.

The injection position of the absorbent was mainly between the economizer and the SCR or between the SCR and the air preheater [12]. When the absorbent was injected between the economizer and the SCR, the negative effect of SO_3 on the catalyst and denitrification efficiency was reduced. When the adsorbent was injected into the flue between the SCR and the air preheater, the blockage of air preheater caused by ammonium hydrogen sulfate and ash bonding could be effectively alleviated. The adsorbent could also be injected before or after the electrostatic precipitator to remove SO_3 and reduce the total amount of SO_3 emissions.

3.4 Synergistic removal technology

The SO_3 in the flue gas was synergistically removed through ultra-low emission equipment such as low-temperature electrostatic precipitators, wet desulfurization tower and wet electrostatic precipitators.

The temperature of the flue gas was lowered below the acid dew point in the low temperature electrostatic precipitator. The sulfuric acid droplets formed by the condensation of SO_3 were adsorbed on the surface of the particulates and removed together with the particulates. The synergistic removal efficiency of low-temperature electrostatic precipitators was differences in current research results. Studies showed that the removal rate of SO_3 by low-temperature electrostatic precipitators was up to 95% [13], and some reports that the final SO_3 removal efficiency was about 73.78% [14]. The above differences should be due to different operating parameters of the unit and equipment.

The removal efficiency of SO_2 by wet desulfurization was very high, but the research results of removal efficiency of SO_3 were not consistent. It was affected by various factors such as capacity of machine assembly, load rate, coal quality and desulfurization tower type.

The flue gas temperature dropped rapidly in the absorption tower. The unabsorbed SO_3 in the flue gas was converted into submicron sulfuric acid aerosol particles that were difficult to trap. The low dust concentration in the flue gas was not enough to adsorb sulfuric acid mist, so the removal efficiency of SO_3 by the wet desulfurization tower was low. Based on the measured data [15], the removal efficiency of SO_3 acid mist in flue gas by single tower and double tower wet desulfurization devices were between 30%~40% and 50%~65%, respectively.

The wet electrostatic precipitator is a high-efficiency dust removal terminal equipment, which is arranged behind the wet desulfurization system. Wet electrostatic precipitator has high capture rate for $\text{PM}_{2.5}$, acid mist, aerosol and submicron particles in flue gas. The removal efficiency of SO_3 acid mist in flue gas by wet electrostatic precipitator was between 30% and 76% [16,17]. The effect of wet electrostatic precipitator on removal efficiency of SO_3 was not affected by installed capacity and load rate of the units. The measured results of the unit installed low-temperature electrostatic precipitator, wet desulfurization tower and wet electrostatic precipitator showed that [15], the total removal rate of SO_3 by synergistic removal technology was as high as 93.98% on 100% working condition.

Based on the above analysis, various control and removal technology of SO_3 had adaptability and limitations respectively. The amount of SO_3 generated could be reduced from the source by selecting a low-sulphur fuel and optimizing the combustion process. However, the adaptability of boilers, pulverized coal systems, denitrification systems, and electrostatic precipitator must be considered. The amount of SO_3 generated in the SCR system could be reduced by optimizing the SCR catalyst formulation and structure. However, catalyst activity and denitrification efficiency must be guaranteed. Alkaline absorbent spray into the flue was an effective method for removing SO_3 , but the operating cost was increased correspondingly. The final

SO₃ emission concentration could be synergistically controlled by ultra-low emission equipment located at the end of the flue. But the problems of blockage or corrosion of SCR catalyst and air preheater caused by SO₃ could not be solved.

4 Conclusions

The generation and emission of SO₃ in coal-fired power plants cause problems such as ash, blockage and corrosion of the equipment, which affects the safe operation of the unit and causes environmental pollution. The control and removal technology SO₃ in flue gas are received extensive attention.

The control of SO₃ generated during the combustion in the boiler was mainly achieved by reducing the sulfur content of the fuel, optimizing the combustion process, and injecting additives into the boiler. The conversion rate of SO₂/SO₃ in the SCR denitrification reactor was reduced by optimizing the formulation and structure of the denitrification catalyst.

The alkaline absorbent was sprayed at different positions in the flue to remove SO₃, so that the SCR denitrification catalyst, the air preheater and the flue were protected. The total amount of SO₃ emissions was controlled through the synergistic removal technology of pollutant control facilities such as low-temperature electrostatic precipitator, wet desulfurization tower and wet electrostatic precipitator. According to different coal-fired generating units and environmental protection equipment, control and removal technology of SO₃ should be combined to effectively reduce SO₃ concentration in flue gas.

References

1. Zhang You. Research and application of SO₃ measurement in flue gas, Zhejiang University (2013)
2. Hu Dong, Wang Hai gang, Guo Tingting, Sun Baomin. Research and Development of Mitigating Technology of SO₃ in Flue Gas from Coal Power Plants, Science Technology and Engineering, 15(2015)
3. Ahn J, Okerlund R, Fry A, et al. Sulfur trioxide formation during oxy-coal combustion, International Journal of Greenhouse Gas Control 5(2011)
4. Zhu Congbing, Jin Baosheng, Zhong Zhaoping, et al. Selection of carrier for V₂O₅-WO₃/TiO₂ catalyst, Proceeding of the CSEE, 28(2008)
5. Forzatti P. Present status and perspectives in de-NO_x SCR catalysis, Applied Catalysis A: General, 222(2001)
6. Ye Zhuang, Jason Kaumb, Richard Liggett, et al. Impacts of acid gases on mercury oxidation across SCR catalyst, Fuel Processing Technology, 88(2007).
7. Wang Hongliang, Xue Jianming, Xu Yueyang, et al. Formation and control of SO₃ from coal-fired power plant, Electric Power Technology and Environmental Protection, 30(2014)
8. KWON D W, PARK K H, HONG S C. Enhancement of SCR activity and SO₂ resistance on VO_x/TiO₂ catalyst by addition of molybdenum, Chemical Engineering Journal, 284(2016).
9. Schwammle T, Bertsche F, Hartung A, et al. Influence of geometrical parameters of honeycomb commercial SCR-DeNO_x-catalysts on de-NO_x-activity, mercury oxidation and SO₂/SO₃ - conversion, Chemical Engineering Journal, 222(2013)
10. Chen Xiaolu, Zhao Qingxin, Bao Yiqun, et al. Experimental research on SO₃ removal, Journal of Chinese Society of Power Engineering, 34(2014)
11. Chen P. Research of SO₃ removal from flue-gas by calcium-based absorbents, Shandong University, (2011)
12. Moretti A L, Triscori R J, R Itzenthaler D P. A system approach to SO₃ mitigation. Combined Power Plant, Air Pollutant Control Mega Symposium. (2006)
13. Li Jianguo, Li Zhuhai, Li Weidong, et al. Research on Flue Gas Co-benefit Control Technical Route in Coal-fired Power Plants, China Environmental Protection Industry, 5(2015)
14. Liao Zengan, Research and Development of Low Temperature Electrostatic Precipitation Technology for Utilization of Waste Heat in Coal-fired Power Plants, Liaoning Urban and Rural Environmental Science & Technology, 33(2013)
15. Chen Pengfang, Zhu Gengfu, Zhang Junxiang. Research on SO₃ removal efficiency by flue gas co-benefit control technique of coal-fired power plants based on field tests, Environmental Pollution and Control, 39(2017)
16. Shen Zhigang, Liu Qizhen, Tao Leixing. et al. Removal characteristics of particulate matters in flue gas by wet electrostatic precipitator, Chinese Journal of Environmental Engineering, 5(2016)
17. Luo Fei, Hu Bin, Wu Hao, Yang Linjun. et al. Experimental study on removal properties of PM_{2.5} and sulfuric acid mist by wet electrostatic precipitator, Journal of southeast university, 47(2017)