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 been 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, conversed 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.

\[
\text{NO} + 4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (1)
\]

\[
4\text{NO}_2 + 3\text{NH}_3 + \text{O}_2 \rightarrow 3\text{N}_2 + 6\text{H}_2\text{O} \quad (2)
\]

\[
2\text{SO}_3 + \text{O}_2 \rightarrow 2\text{SO}_4 \quad (3)
\]

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 SO$_2$/SO$_3$ 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 SO$_2$ increased instead.

SO$_3$ and water vapour in flue gas reacted to H$_2$SO$_4$ droplets. The H$_2$SO$_4$ 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 H$_2$SO$_4$ in the flue gas reached to 10-20 ppm. Submicron H$_2$SO$_4$ acid mist was discharged into the atmosphere to form secondary particle sulfate. Sulfate is one of the important sources of PM2.5 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 SO$_3$ 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 SO$_3$ in the flue gas increased. SO$_3$, water vapour and escape NH$_3$ 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 SO$_3$

3.1 Control technology of SO$_3$ in the boiler

The generation of SO$_3$ 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 SO$_3$ 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 SO$_3$ generated was also increased correspondingly. Therefore, reducing the air excess coefficient was advantageous for suppressing the generation of SO$_3$ under the condition of satisfying complete combustion. Low excess air coefficient combustion or rich-light combustion method used to suppress NOx formation could help to reduce SO$_3$ formation in the boiler. The amount of SO$_3$ 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 SO$_3$[7]. The conversion rate of SO$_3$ in the boiler was reduced by 40-80%, which effectively reduced the concentration of SO$_3$ at the boiler outlet. Alkaline substances used commonly were mainly calcium or magnesium-based additives such as calcium hydroxide, calcium carbonate and magnesium hydroxide. SO$_3$ removal efficiency was related to the chemical properties of the additive and its surface physical characteristics. The removal efficiency of SO$_3$ 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 SO$_3$ was increased. Long-term operational data from the Mansfield and Gavin power plants in the United States indicated that the removal rate of SO$_3$ reached more than 90% at the molar ratio of 7:1 of Mg/SO$_3$.

3.2 Optimization of denitrification catalyst

The denitrification activity and the lower SO$_3$ oxidation rate of the catalyst was maintained by adjusting the active component content of the catalyst or adding an auxiliary agent. V$_2$O$_5$ had strong activity on denitrification and SO$_3$ oxidation. As the V$_2$O$_5$ mass fraction increased, the SO$_3$ oxidation activity raised faster than the denitrification reaction. Therefore, the mass fraction of V$_2$O$_5$ in the catalyst was generally controlled to be 0.8% to 1.2%. In the catalyst formulation, specific metal oxides, such as Y$_2$O$_3$, GeO$_2$, NiO, BaO, MoO$_3$, etc., were doped to improve the surface characteristics of the catalyst[8]. Oxidation reaction of SO$_3$ was suppressed by weakening the adsorption capacity of SO$_3$ on the catalyst surface. Catalysts for high denitrification activity and low SO$_3$ oxidation rate were developed based on the different sites of denitrification and SO$_3$ 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 absorbent and the flue gas. The reaction temperature and residence time were related to the injection position of the absorbent 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 Mg(OH)$_2$>Ca(OH)$_2$>MgO>CaO. The results of the removal of SO$_3$ by two kinds of Ca(OH)$_2$ and CaCO$_3$ absorbers 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 absorbent 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 absorbent 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$_3$ 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 PM2.5, 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
SO\textsubscript{3} 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 SO\textsubscript{3} could not be solved.

4 Conclusions

The generation and emission of SO\textsubscript{3} 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 SO\textsubscript{3} in flue gas are received extensive attention.

The control of SO\textsubscript{3} 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 SO\textsubscript{3}/SO\textsubscript{3} 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 SO\textsubscript{3}, so that the SCR denitrification catalyst, the air preheater and the flue were protected. The total amount of SO\textsubscript{3} 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 SO\textsubscript{3} should be combined to effectively reduce SO\textsubscript{3} concentration in flue gas.

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