Experimental Study on Removal of SO$_3$ from Flue Gas by Na$_2$CO$_3$

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Abstract. The alkaline absorbent spraying technology is an efficient method for accurately removing SO$_3$ in flue gas. By studying the characteristics of the technology, the reaction mechanism, the migration rule of SO$_3$, and the experimental platform by using the real flue gas as the source of the alkaline absorbent jet removal of flue gas SO$_3$. The results of the study show that the efficiency of the alkaline absorbent to remove SO$_3$ is related to n(Na$_2$CO$_3$): n(SO$_3$), flue gas temperature, residence time and other factors; under the test conditions, the flue gas temperature is 320°C, n(Na$_2$CO$_3$): n(SO$_3$) is 1:4, the concentration of Na$_2$CO$_3$ solution after gasification is 52.6 mg/m$^3$, and the concentration of soot is 4680 mg/m$^3$ under standard conditions, which can ensure the removal efficiency of SO$_3$ is above 85%; The effect of the catalyst is small and can be ignored. The above results can provide a reference for the domestic coal-fired power plants to carry out the research and application of alkaline absorbent to remove flue gas SO$_3$ technology.

1. Introduction

Coal combustion will produce a lot of gaseous pollutants, and coal-fired power plants, as large coal consumers, are also large gaseous pollutants. Coal contains sulfur, and the flue gas from combustion contains a certain concentration of SO$_2$ or SO$_3$. When the excess air coefficient is greater than 1, about 0.5% to 2.0% of SO$_2$ will be further oxidized to form SO$_3$. In addition, the SCR (Selective Catalytic Reduction Technology) device will oxidize about 1.0% of SO$_2$ to SO$_3$ while removing NOX from the flue gas. Relevant data shows that the SO$_3$ concentration will increase about 1 times compared with before the SCR device is installed. SO$_3$ is the main cause of boiler tail flue corrosion, air preheater blockage, acid rain, and "blue plume". Therefore, it is necessary and significant to develop technology to remove SO$_3$ from flue gas[1-2].

At present, technologies for treating SO$_3$ in flue gas of coal-fired power plants at home and abroad are mainly divided into physical methods and chemical methods. The physical methods mainly include low and low temperature dust collectors, wet electric dust collectors, wet desulfurization towers, etc.; the chemical methods mainly include the technology of mixing limestone/dolomite in the furnace, SCR catalyst modification and alkali-based absorbent spraying method. Among them, although the low and low temperature dust collectors, wet electric dust collectors, and wet desulfurization towers can remove SO$_3$ in flue gas, they cannot eliminate the harm of SO$_3$ to upstream denitration devices, air preheaters and other equipment. The technology of mixing limestone/dolomite in the furnace is to reduce the generation of SO$_3$ during the pulverized coal combustion process, which is highly efficient and...
economical, but it affects the combustion process and reduces the boiler efficiency. It is generally used in high-sulfur coal units.

The technology of removing SO3 in the flue gas by the alkaline absorbent spraying method is to spray alkaline absorbent into the flue, react with SO3 to generate sulfate, and remove it through the dust removal equipment. Using this method can accurately and efficiently remove SO3 in flue gas. At present, there are many achievements abroad, few domestic studies, and few application examples[3-4].

This article will establish a test platform for the development of SO3 removal technology based on bypass flue gas, and analyze the effect of common alkaline absorbents on the SO3 removal of flue gas through platform testing to develop a technical route for the removal of SO3 for alkaline absorbents in China. Selection and selection of alkaline absorbents provide reference[5-7].

2. Alkaline absorbent spray removal SO3 test platform
A small amount of alkaline absorbent is sprayed into the flue gas at 280-380 °C in the form of a solution, and a "flashing" phenomenon occurs, and alkaline particles are quickly formed. Therefore, no matter whether the alkaline absorbent enters the flue gas in the form of solid powder or solution, it is a gas-solid two-phase reaction with SO3, and it is a non-catalytic gas-solid reaction.

2.1. Reaction mechanism
Generally, the particles formed by "flash evaporation" of alkaline absorbents have a small pore volume before reaction and can be regarded as a dense solid. The gas-solid reaction of non-porous dense particles is generally suitable for the shrinkage nucleation reaction model.

The reaction process of the alkaline absorbent particles and SO3 can be simplified into three steps: 1. Outer diffusion: SO3 diffuses from the main gas stream to the outer surface of the alkaline absorbent particles. 2. Internal diffusion: SO3 diffuses through the pores of the product layer to the surface of the unreacted layer. 3. Interface reaction: SO3 reacts with the alkaline absorbent on the surface of the unreacted layer.

Studies have shown that the temperature increase has a smaller contribution to the diffusion rate, while the concentration gradient has a greater effect on the diffusion rate. However, due to the low concentration of SO3 in the boiler flue gas and a small temperature gradient, the mass diffusion rate is limited. To improve the removal efficiency, the external diffusion resistance should be reduced, such as increasing the number concentration of the absorbent in the flue gas, Improve dispersion uniformity, etc. After the alkaline absorbent is dissolved and atomized, it can form evenly distributed fine particles after drying at high temperature, which can effectively improve the removal efficiency of SO3.

2.2. Migration rule of SO3
From generation to emission of SO3 in flue gas from coal-fired power plants, as flue gas conditions change, it will undergo a series of complex physical and chemical processes. It is of great significance to guide the prevention and removal of SO3 to understand the changing rules among the changes. Figure 2 shows the SO3 migration law of a coal-fired power plant.

SO3 is almost in the form of gaseous SO3 above 400 °C. At this time, SO3 has little effect on the operation of the unit. After the temperature drops below 400°C, SO3 will generate corrosive substances such as NH3HSO4 and sulfuric acid mist, which will have a great impact on the unit. The real flue gas after the economizer is used as the gas source to study the effect of alkaline absorbent on the removal of SO3 and the effect on the downstream flue is more comprehensive and reasonable.

2.3. The test platform for the removal of SO3 by alkaline absorbent using real flue gas
The test platform for the removal of SO3 by alkaline absorbent injection is built on a 330 MW unit. Using the real flue gas from the economizer as the gas source, the removal of alkaline absorbent after each stage of flue gas emission can be carried out more comprehensively. Research on SO3 capability. In order to improve the removal efficiency of SO3, the test platform was mixed with alkaline absorbent by spraying and spraying alkaline absorbent solution. It mainly includes dust removal system, heat
exchange system, dosing system, denitration system and flue, valves and related power and monitoring equipment. In addition, by adding functions such as dust removal, heat exchange, and SCR denitrification, the operating conditions of the platform can be flexibly controlled. The exhaust gas of the test platform is pressurized by a pressurized induced draft fan and then goes to electric dust removal, and is evacuated after being treated by the boiler tail gas treatment equipment.

3. The experiment of removing SO\(_3\) by spraying alkaline absorbent

3.1. Selection of alkaline absorbent

The change of the morphology during the reaction of the base absorbent with SO\(_3\) has a great influence on the SO\(_3\) absorption performance. The more common products of NaOH, Mg(OH)\(_2\), Ca(OH)\(_2\) and SO\(_3\) are denser after reaction. During the reaction between Na\(_2\)CO\(_3\) and SO\(_3\), CO\(_2\) gas is continuously generated, which keeps the particulate matter in a porous structure, which helps the diffusion of SO\(_3\) to the surface of the unreacted absorbent; the porous structure increases the specific surface area, which improves the efficiency of SO\(_3\) removal and can Make the reaction more complete. In this study, Na\(_2\)CO\(_3\) was used as the alkaline absorbent to study the factors affecting the efficiency of alkaline absorbent on the removal of SO\(_3\) under real flue gas.

3.2. Experimental method

By adjusting the parameters of each device on the platform to obtain the corresponding working conditions, and using the isopropyl alcohol absorption method to measure the SO\(_3\) concentration in the flue gas, the removal efficiency is calculated by calculating the SO\(_3\) concentration before and after injection. In order to study the SO\(_3\) removal efficiency under different working conditions, the influence of different control parameters on the SO\(_3\) removal efficiency was analyzed.

3.3. Research on influencing factors of SO\(_3\) removal efficiency

3.3.1. Effect of reactant molar ratio on SO\(_3\) removal efficiency.

Under a stable load, the opening of the baffle door is adjusted and the heat exchange system is processed to keep the smoke temperature and flow rate after the spray grid unchanged, and the molar ratio of Na\(_2\)CO\(_3\) to SO\(_3\) is changed by controlling the injection amount of Na\(_2\)CO\(_3\) solution. In this test, the concentration of Na\(_2\)CO\(_3\) solution after gasification is 52.6 mg/m\(^3\), and the average concentration of imported SO\(_3\) is about 33 mg/m\(^3\) (which has been converted to standard conditions, the same below), and the smoke after the injection point is maintained by adjusting the parameters of the heat exchange system The gas temperature is maintained at about 320\(^\circ\) C. When n(Na\(_2\)CO\(_3\)) : n(SO\(_3\)) is low, the removal efficiency of SO\(_3\) is low. When the ratio increased to 3:1, the efficiency increased significantly to 82%, and after increased to 3:1, the efficiency increased significantly to 91%, but as the ratio continued to increase, the trend line became slower. The residence time may be short, and some absorbents do not participate in the reaction.

3.3.2. Effect of residence time on SO\(_3\) removal efficiency.

Behind the jet grille, a thick straight flue is provided. The inner diameter of the flue is increased, and the flow velocity is reduced, so as to obtain enough measurement hole positions with a longer residence time interval in a relatively short flue. In this test, the concentration of Na\(_2\)CO\(_3\) solution after gasification is 52.6 mg/m\(^3\), the average concentration of imported SO\(_3\) is about 31 mg/m\(^3\), the average load of the unit is 303 MW, the average temperature of the flue gas is 322\(^\circ\) C, in n(Na\(_2\)CO\(_3\)): n When (SO\(_3\)) is 1:4, as the residence time becomes longer, the improvement in removal efficiency is more obvious. This is because more absorbents participate in the reaction, the overall economy and benefits, and the residence time is best controlled within 2-3 seconds.
3.3.3. *Effect of flue gas temperature on SO\(_3\) removal efficiency.* The heat exchange system of the test platform controls the smoke temperature at the exit of the jet grille by replacing the hot and cold heat exchange medium and changing the medium flow rate. In this test, the concentration of Na2CO3 solution after gasification was 52.6 mg/m\(^3\), the average concentration of imported SO3 was about 35 mg/m\(^3\), the average load of the unit was 301 MW, and n(Na2CO3): n(SO3) was 1:4. Under a smoke temperature of 300-400 °C, the removal efficiency does not change much. It may be that from above 300°C, the absorption rate of SO3 is less affected by the reaction at the gas-solid interface.

3.3.4. *Effect of soot content on SO\(_3\) removal efficiency.* The dust removal system of the test platform can change the outlet dust concentration by changing the strength of the electric field. In this test, the concentration of Na2CO3 solution after gasification is 52.6 mg/m\(^3\), the average concentration of imported SO3 is about 34 mg/m\(^3\), the average load of the unit is 298 MW, and n(Na2CO3): n(SO3) is 1:4. Next, by changing the output of the dust removal system, four smoke concentrations of 251 mg/m\(^3\), 1547 mg/m\(^3\), 4680 mg/m\(^3\), and 11042 mg/m\(^3\) were obtained. As the dust content in the flue gas increases, the removal efficiency reaches the highest value around 4680mg/m\(^3\). The reason for the analysis may be that when the dust content in the flue gas is low, after the alkali-based absorbent is adsorbed on the flue dust, a larger specific surface area is obtained, and a certain removal efficiency is improved. When the dust content in the flue gas continues to increase, some of the porous structure of the dust and the alkaline absorbent solid particles compete in space, making it difficult for SO3 to combine with the alkaline absorbent, thereby reducing the removal efficiency. The best soot concentration is around 4680 mg/m\(^3\).

4. *Influence of alkaline absorbent injection on denitration catalyst*  
In order to study the influence of the alkaline absorbent on the removal of SO3 on the denitration catalyst, a long-term operation test of the alkaline absorbent on the removal of SO3 was carried out. The test duration was 1 month and the average load rate was 228MW, of which the load below 132 MW accounted for 11%. During the test, the concentration of Na2CO3 solution was 52.6 mg/m\(^3\), and the lye absorbent was sprayed according to n(Na2CO3): n(SO3) as 1:4. The performance of the catalyst before and after the test is taken, and according to the test report, the activity of the second time is 36.4 and 36.2 respectively. It can be seen that the impact of spraying alkaline absorbent on the catalyst is less, and is within the acceptable range.

5. *Conclusion*  
Alkaline absorbent injection technology is an effective means to efficiently remove SO3 from the flue gas of coal-fired power plants. Based on the analysis of the gas-solid reaction mechanism and the migration rule of SO3, an experimental platform for the removal of SO3 by alkaline absorbent was designed and constructed. The factors affecting the efficiency of the removal of SO3 by Na2CO3 solution under real flue gas were studied. On this basis, the better operating conditions for the removal of SO3 by spraying Na2CO3 solution are obtained: smoke temperature 320°C, n(Na2CO3): n(SO3) is 1:4, the concentration of Na2CO3 solution after gasification is 52.6mg/m\(^3\) \(2\). The soot concentration is 4680mg/m\(^3\); and through experimental research, it is concluded that the alkaline absorbent injection has little effect on the SCR catalyst. The research results provide a theoretical basis for the power plant flue gas SO3 removal, which can be used as a reference for power plants and related research units.

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