

# The Effects of Flue Gas SO<sub>3</sub> on the Operation of Coal-Fired Units and Countermeasures

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**Abstract:** There exists a certain amount of SO<sub>3</sub> in flue gas discharged from coal-fired power plants. The implementation and “ultra-low emission” retrofitting of SCR in China greatly increased the concentration of SO<sub>3</sub> in flue gas, which will lead to fouling, erosion and plugging of the SCR reactor and the air preheater downstream. With the lowered dew point of the flue gas, the ammonia slipped from the SCR reactor together with the SO<sub>3</sub> in flue gas will leads to dust accumulation in the Electric Precipitator or in the Bag-house Filter, too. In this study, the main effects and its mechanism of SO<sub>3</sub> on the safety, stability and efficiency of units were analyzed, and measures to control SO<sub>3</sub> were proposed.

**Keywords:** Coal-Fired Flue Gas, SO<sub>3</sub>, Operation of Units, Control of SO<sub>3</sub>

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## 1. Introduction

In the operation process of coal-fired power plants, a small amount of SO<sub>3</sub> exists in most flue gases, which depends on sulfur content in the charge coal, ranging from about 1 μL/L to 30-40 μL/L. As environmental protection standards become increasingly strict, boilers of coal-fired power plant have been equipped with selective catalytic reduction (SCR) flue gas denitrification, dedusting (electrostatic precipitator or bag-house filter) and wet flue gas desulfurization (WFGD) facilities to remove routine pollutants such as NO<sub>x</sub>, dust and SO<sub>2</sub> generated in the process of coal combustion. However, the catalyst of a SCR denitrification system can oxidize some of the SO<sub>2</sub> in flue gas into SO<sub>3</sub>, thereby SO<sub>3</sub> concentration in flue gas increases. The emission of SO<sub>3</sub> can cause plume opacity which leads to some environmental problems. On the other hand, the SO<sub>3</sub> in flue gas can make acid dew point rise, thereby leading to corrosion, fouling, and plugging problems of air preheater and other devices. From the view point of environmental protection, safety, stability and performance, the SO<sub>3</sub> in flue gas of coal-fired power plants should be paid more attention.

## 2. Production of SO<sub>3</sub> in Coal-Fired Flue Gas

The SO<sub>3</sub> in coal-fired flue gas is mainly produced in two processes. Firstly, it is generated during the process of coal combustion, that is, combustible sulfur in coal changes into SO<sub>2</sub>, and then part of SO<sub>2</sub> is further oxidized to form SO<sub>3</sub>; secondly, during the process of economizer and SCR denitrification, part of SO<sub>2</sub> in flue gas was catalyzed and oxidized into SO<sub>3</sub> by fly ash in flue gas and SCR catalyst.

### 2.1. Generation of SO<sub>3</sub> in the Process of Coal Combustion

Most sulfur in coal changes into SO<sub>2</sub> during the process of coal combustion, and about 0.5%-2% of SO<sub>2</sub> is further oxidized into SO<sub>3</sub>. The quantity of SO<sub>3</sub> during the process of coal combustion is influenced by the type of boilers, combustion conditions, sulfur content in fire coal, and excess air coefficient. Among them, sulfur content in fire coal is the main factor influencing SO<sub>3</sub> concentration in flue gas. As shown in Figure 1, SO<sub>3</sub> concentration in flue gas correlates positively with sulfur content in fire coal, while the increase of combustion temperature and oxygen concentration can also

enhance the production rate of SO<sub>3</sub> [1].

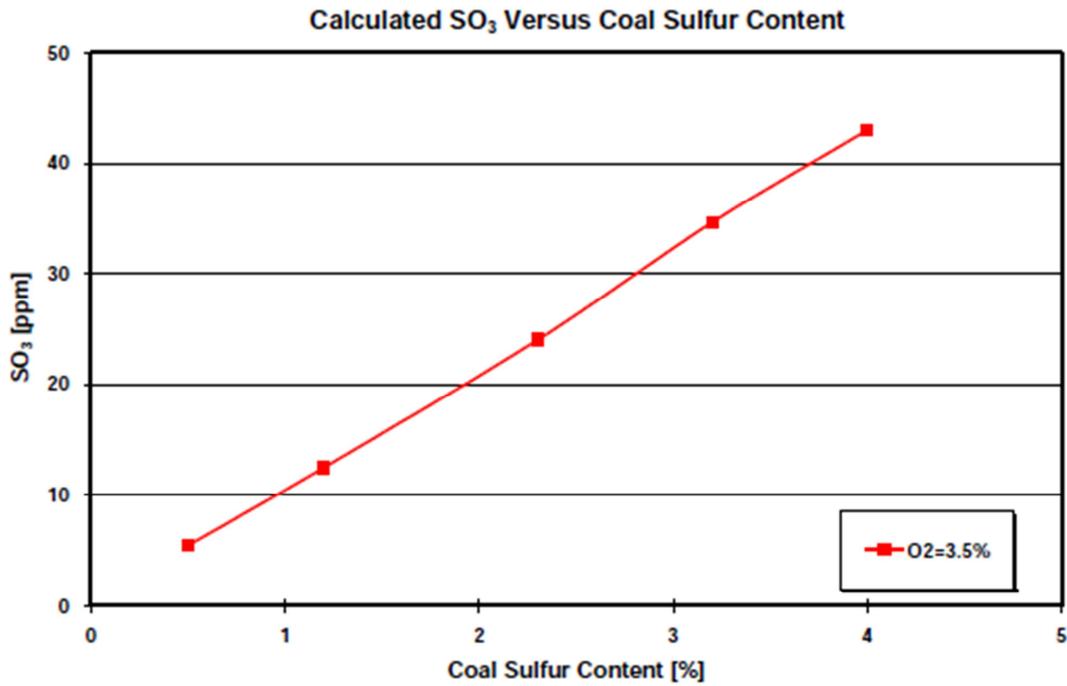


Figure 1. Changes of SO<sub>3</sub> concentration in flue gas with sulfur content in fire coal.

### 2.2. Production of SO<sub>3</sub> in the Process of Catalyzing

In economizer (427-593°C), under the catalyzing action of iron oxides in fly ash and metal in the heating surface of pipes, SO<sub>2</sub> reacts with O<sub>2</sub> and forms SO<sub>3</sub>, which depends on SO<sub>2</sub> concentration, fly ash concentration and composition, the area of convection heating surface, the temperature distribution of flue gas and the wall of pipes, excess air coefficient, flue gas humidity, etc [2]. According to the results of a test conducted in a spot, SO<sub>3</sub> concentration in flue gas could be reduced by furnace purging, further proving that soot formation on the wall of a pipe can catalyze the oxidation of SO<sub>2</sub>.

process of SCR flue gas denitrification in boilers of coal fired power plants, and V<sub>2</sub>O<sub>5</sub> can catalyze the oxidation of SO<sub>2</sub> [3, 4]. That is, it can catalyze part of SO<sub>2</sub> into SO<sub>3</sub> during the process of removing NO<sub>x</sub> from fuel gas. In a SCR denitrification system, about 0.5%-3% of SO<sub>2</sub> is oxidized into SO<sub>3</sub>, which depends on the type of catalysts and operation conditions.

With the increase of V<sub>2</sub>O<sub>5</sub> content in catalysts, the oxidation rate of SO<sub>2</sub> rises; along with the increase of reaction temperature, the oxidation rate of SO<sub>2</sub> also rises gradually [4]. Seen from Figure 2, as the temperature of flue gas decreases by 10°C, the oxidation rate of SO<sub>2</sub> reduces by about 0.15% [5].

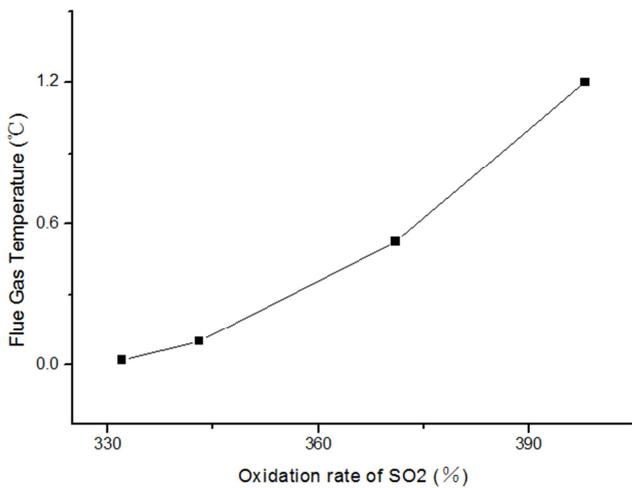


Figure 2. Variations in the oxidation rate of SO<sub>2</sub> with the increase of flue gas temperature.

Catalysts V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> have been widely applied for the

## 3. Effects of SO<sub>3</sub> on the Operation of Units

### 3.1. Influences on the Acid Dew Point of Flue Gas

SO<sub>3</sub> has great effects on the acid dew point of flue gas [6]. As shown in Figure 3, the acid dew point of flue gas ranges from 95 to 150°C. When the temperature of flue gas is lower than its acid dew point, SO<sub>3</sub> is easy to react with H<sub>2</sub>O in flue gas to generate gaseous H<sub>2</sub>SO<sub>4</sub>, and part of gaseous H<sub>2</sub>SO<sub>4</sub> is then condenses into liquid H<sub>2</sub>SO<sub>4</sub>. The condensation rate depends on temperature and SO<sub>3</sub> concentration. After SCR is installed, as SO<sub>3</sub> concentration increases, its acid dew point can rise by 5-10°C. Generally speaking, temperature at the entrance of flue gas to an air preheater is higher than the acid dew point of flue gas as a margin for a little air permeates into the air preheater, which keeps the equipments or pipes downstream are not affected. But with the operation of SCR,

the margin of temperature will be offset, and with the increase of operation time, the air permeates into the air preheater will increase, which rises the risk of corroding on the parts down stream of the flue gas.

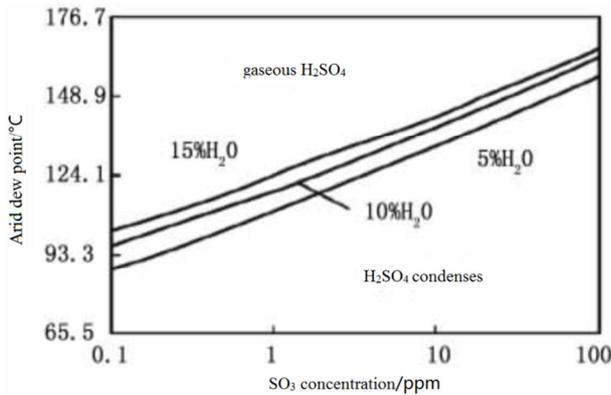


Figure 3. Relationship between the acid dew point and the SO<sub>3</sub> concentration of flue gas.

### 3.2. Effects on SCR

When temperature ranges from 275 to 350 °C [7], SO<sub>3</sub> can react with NH<sub>3</sub> and generates ammonium bisulfate or ammonium sulfate in SCR reactor, which mainly depends on SO<sub>3</sub> concentration, and the lower temperature is called minimum operating temperature (MOT) of SCR. As a unit operates at low load, which means a decrease of temperature in SCR reactor, the produced ammonium bisulfate (ABS) will deposit in pores of a catalyst to reduce its surface area and cover the active sites, thereby making the catalyst inactive. To inhibit the formation of ammonium bisulfate, temperature must be higher than MOT when SCR functions. If SCR operates at temperature lower than MOT, it will lead to catalyst blocking.

When deposition is not serious, the process is reversible, and making operation temperature exceed dew point can promote the evaporation of ammonium bisulfate and recover the activity of catalyst [8] (Figure 4). However, to remove ammonium bisulfate from catalyst effectively, it is necessary to recover the catalyst at high temperatures (375-400°C [9]). For domestic units, conditions of the recovery temperature for removing ammonium bisulfate are limited from many aspects. In addition, the duration of the recovery period depends on the operation time of SCR at below MOT, SO<sub>3</sub> concentration, and operation temperature in the recovery period. If operation temperature is lower than its dew point for a long time, a large amount of fly ash will accumulate in catalyst. As a unit operates at low load, the resistance of catalyst will increase rapidly, thereby resulting in catalyst blocking (Figure 5), which will affect the safety of the unit operation. To avoid catalyst blocking, load should be higher than the minimum load that can be accepted by SCR when a unit operates. To ensure a safe temperature at low load operation, it is necessary to install economizer bypass, which will decrease the thermal efficiency of the unit.

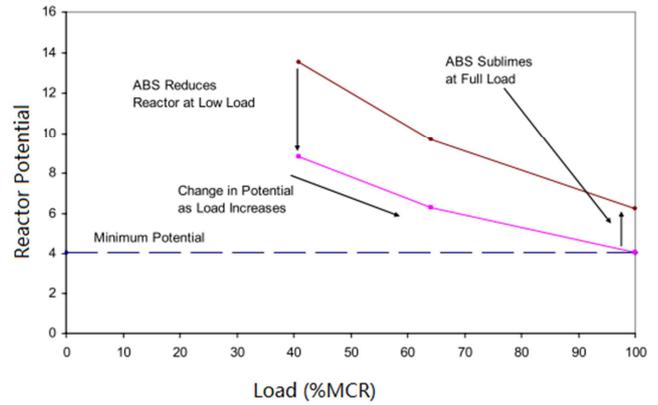


Figure 4. Effects of unit operation load on the formation of ammonium bisulfate.



Figure 5. Fouling and plugging of catalyst.

### 3.3. Influences on Air Preheaters

After SCR, system the flue gas enters air preheater. At the cold end of the air preheater with low flue gas temperature, SO<sub>3</sub> can transform into gaseous H<sub>2</sub>SO<sub>4</sub> easily, which will speed up the reaction with ammonia escaped from SCR. Figure 6 shows the changes of NH<sub>3</sub> concentration with the increase of SO<sub>3</sub> concentration. Generally speaking, when temperature is equal to or lower than 205°C, SO<sub>3</sub> transforms into ammonium bisulfate.

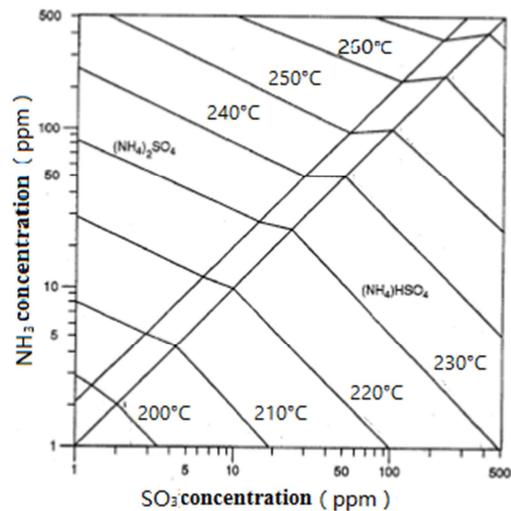


Figure 6. Relations of SO<sub>3</sub> and NH<sub>3</sub> concentration with existing form.

The capacity of ammonium bisulfate to catch fly ash is very strong, and it will combine with fly ash particles in fly ash to form sticky sediment depositing on the surface of an air preheater, which will increase the resistance of an air preheater and the power consumption of an induced draft fan. If the deposition is serious, the units will need to be shut down because the air preheater needs to be cleaned.

According to the statistical results of unit operation obtained by China Guodian Corporation, the pressure loss of an air preheater in 30% of 300 MW units and 34% of 600 MW units is higher than 2 kPa, and it is higher than 1.2 kPa in most units (Figure 7).

If the fouling and plugging of an air preheater in a 600 MW unit increases the side resistance of flue gas by 1.5 kPa, and the side pressure resistance of primary and secondary air rises by 0.5 kPa, the annual loss of three big fans of a unit reaches about 3.10 million yuan (electric charge is 0.35 yuan/kW·h) when the volume of flue gas is 2 000 000 Nm<sup>3</sup> /h and utilization time is 5 000 h. The blockage of an air preheater can make air volume and efficiency decrease and reduce the maximum load of a system. If operation time at full load is 600 h each year, the loss of electric charge caused by electricity generation is about 1 050 million yuan. Seriously fouling and plugging of an air preheater can also lead to surging and unexpected shut down of the fans [10]. The fouling and plugging of an air preheater is shown in Figure 8.

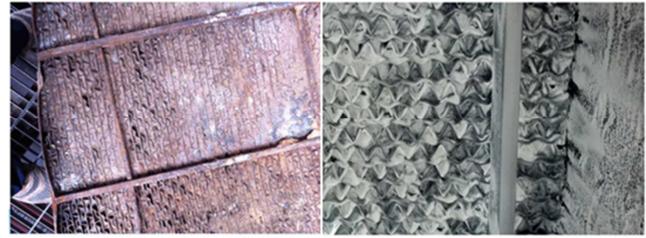


Figure 8. Fouling and plugging of air preheater.

At the heat exchange components of air preheater cold end, where the flue gas temperature is in range of 146-207°C, ammonium bisulfate is moderately acidic and very sticky. It adheres to the heat exchange components inside of an air preheater to corrode its wall. If SO<sub>3</sub> concentration is high, excessive SO<sub>3</sub> will concentrate into acid mist at the cold end of an air preheater. With the acid condensation, scaling in an air preheater becomes more serious, and the formed sediment is wet or sticky, which can aggravate the erosion of heat exchange components. According to actual operation experience, corrosion and blockage caused by SO<sub>3</sub> can make the resistance of an air preheater increase, even affect the safe operation of the unit.



Figure 9. Corrosion of air preheater.

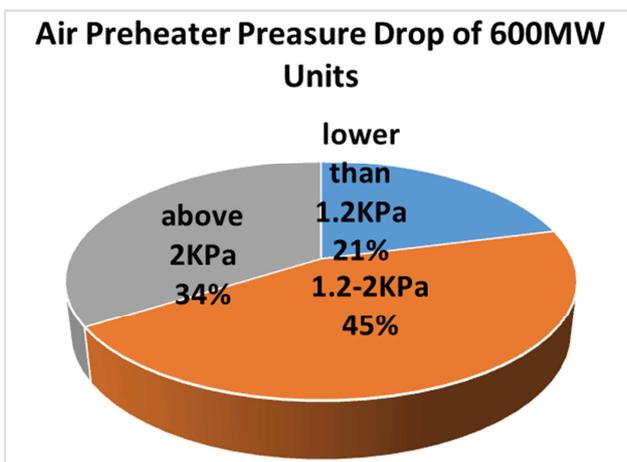
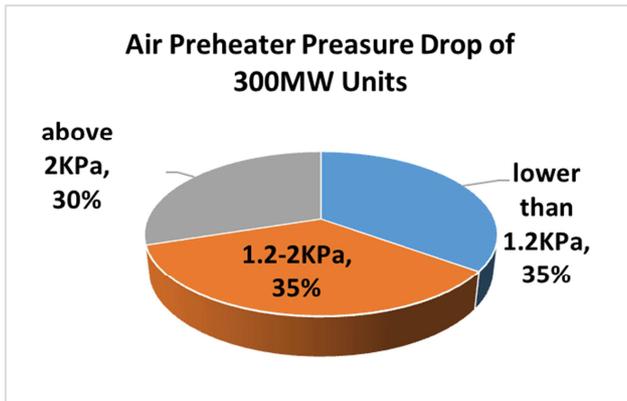


Figure 7. Distribution of differential pressure drop of air preheater in units of China Guodian Corporation.



Figure 10. Dust Accumulates in Electric Precipitator.

### 3.4. Effects on Dust Collectors

As temperature is lower than acid dew point where the dust collector operates, SO<sub>3</sub> exists in the form of sulfuric acid mist. The total surface area of dust in flue gas is very large, which provides a good condition for the condensation and adhering of sulfuric acid mist. For Bag-house Filter, if SO<sub>3</sub>

concentration is too high, the filter cake becomes more sticky with the deposition of  $\text{SO}_3$ , which is difficult to remove. For electric precipitator, when  $\text{SO}_3$  concentration is low, the condensation of  $\text{SO}_3$  can decrease the specific resistance of dust greatly [11], thereby avoiding the occurrence of back corona and enhancing dedusting efficiency; as  $\text{SO}_3$  concentration is high, dust will accumulate around barbed wires. [12]



Figure 11. Dust Accumulates on Filters.

#### 4. Countermeasures

Control of  $\text{SO}_3$  in flue gas should not only meet the demand of pollutant discharge for environmental protection but also provide guarantee for the safety, efficient and stable operation of units. In possible conditions,  $\text{SO}_3$  concentration in upper flue gas should be reduced as much as possible, thereby decreasing the effect on the operation of downstream equipment. Under normal circumstances, when it is difficult to burn fully low-sulfur coal, a method of blending low-sulfur coal should be involved to decrease the production of  $\text{SO}_3$ . In high-sulfur coal regions, a method of spraying alkaline sorbents in furnace or after could be adopted, and it can be divided into dry and wet spraying according to the form of the sprayed sorbents. For dry spraying, sorbents such as  $\text{CaO}$  [13],  $\text{MgO}$ ,  $\text{Na}_2\text{CO}_3$  and trona [14] are chosen, eg. the Marietta Power Plant in the United States; for wet spraying, sorbents such as  $\text{NaHSO}_3$  (SBS),  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$  are selected, eg. the Gavin Power Plant and the Codan Company [15, 16] in the United States.

The spraying position and type of sorbent determine the action range. For instance, if the  $\text{Mg}(\text{OH})_2$  sorbent is sprayed on the top of a furnace,  $\text{SO}_3$  concentration at the entrance of SCR will decline, and slagging inside of a furnace can be relieved, but the increase of  $\text{SO}_3$  concentration in SCR can not be controlled. Spraying  $\text{MgO}$  dry powder or  $\text{NaHSO}_3$  solution at the entrance of SCR can reduce the deposition of ammonium bisulfate in an air preheater to avoid the blockage of the air preheater, decrease acid dew point and temperature of flue gas at the entrance of an air preheater, improve the thermal efficiency of boilers, and alleviate the erosion of heating surface at the tail.

In order to maintain the stable running of units, sorbents

should be sprayed on the top of furnace and in front of SCR and an air preheater. To remove  $\text{SO}_3$ , sorbents should be mixed well with flue gas, but most units face a great challenge in respect of design due to the limitation of space and pipes. The removing ways of  $\text{SO}_3$  and selection of sorbents should be determined according to the operation situation of a unit. To expand the operation temperature window of SCR and enhance the load adaptability of SCR in a unit,  $\text{SO}_3$  can be removed in front of SCR entrance. In order to improve the operation condition of air preheater,  $\text{SO}_3$  can be removed in front of the air preheater. Calcium-based sorbents can increase the specific resistance of fly ash, so it should not be used in a power plant where the electric precipitator operates inefficiently.

#### 5. Conclusions

There is a small amount of  $\text{SO}_3$  in flue gas of coal-fired power plants. With the implementation and “ultra-low emission” retrofitting of SCR in China,  $\text{SO}_3$  concentration in flue gas increases greatly, and causes many problems. The erosion and plugging in the SCR catalyst or in the air preheater will become more serious. From the economic view,  $\text{SO}_3$  in flue gas can greatly increase the energy consumption of the system running. High concentration of  $\text{SO}_3$  will also cause dust accumulation in the Electric Precipitator or in the Bag-house Filter.

Control of  $\text{SO}_3$  in flue gas should not only meet the demand of environmental protection but also provide guarantee for the safe, efficient and stable operation of the units. Spraying alkaline sorbents can remove  $\text{SO}_3$  from flue gas effectively. According to the actual situation of a power plant, suitable spraying positions and sorbents should be chosen to reduce the erosion, fouling and plugging of equipment, decrease the temperature of flue gas at the entrance of an air preheater and the power consumption of a wind turbine, and enhance the thermal efficiency of the unit.

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