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Investigation on the removal of SO_3 in ammonia-based WFGD system

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HIGHLIGHTS

- The SO_3 removal efficiencies are higher in ammonia-based WFGD.
- Increasing SO_3 concentration in flue gas will increase aerosol emission.
- Increasing particle concentration in flue gas will enhance SO_3 removal.
- Aerosol morphologies stay unchanged while SO_3 concentration varying.
- The Brownian diffusion is more important in SO_3 removal process.

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ABSTRACT

The SO_3 removal properties were investigated in the wet flue gas desulfurization (WFGD) system. The relationship of the aerosol emission properties and the SO_3 concentration in the flue gas was explored experimentally based on the ammonia desulfurization system. The impacts of the operating parameters, such as the liquid-to-gas ratio (L/G), the flue gas temperature, the superficial velocity, and the particle concentration in the flue gas on the SO_3 removal efficiency were studied. The results showed that when the SO_3 concentration in the flue gas increased, the aerosol emission concentration was higher although the aerosol sizes became smaller within the measurement range of the electrical low pressure impactor (ELPI). When the SO_3 concentration was 12 mg/Nm^3 and 47 mg/Nm^3, respectively, the aerosols emitted from the WFGD system showed the similar morphologies. Under the same operating conditions, the SO_3 removal efficiencies in the ammonia-based WFGD system were higher than those in the limestone–gypsum WFGD system, both of which rose with the increase of SO_3 concentrations. In the ammonia-based WFGD, the SO_3 removal efficiency would be improved when the L/G and the particle concentration in the flue gas were raised and the flue gas temperature and the superficial velocity were reduced. Two SO_3 removal mechanisms were proposed in the ammonia-based WFGD processes. One was the collision trap mechanism and the other was the heterogeneous reaction mechanism. The sulfuric acid aerosols formed though the quenching process of hot flue gas were measured to be mainly submicron particles. For the removal of these particles, the Brownian diffusion was proved to be the predominant removal mechanism in the collision trap processes, rather than the inertial impaction.

1. Introduction

The problem of sulfuric acid emission during industrial processes, such as from coal-fired power plants, has been reported frequently in recent years. Large quantities of sulfur oxide are generated during coal combustion processes, most of which are SO_2, with SO_3 occupying a fairly small portion. Researches indicated that additional SO_3 could be formed through the oxidation of SO_2 in subsequent flue gas cleaning systems [1–3], especially the selective catalytic reduction (SCR) fume denitrification [4–7]. SO_3 in the flue gas will not only cause corrosion and blocking problems to the downstream equipment, to affect the operation safety of the whole cleaning system [8,9], but also form primary and secondary pollutants to impact on human health [3,10]. The control of the SO_3 emission in the flue gas is of particular interest in the atmospheric sciences with the SO_3 removal technologies in the wet flue gas desulfurization (WFGD) systems paid great concern [8,11].

At the beginning of the sulfuric acid aerosol formation processes, the SO_3 exists as the gaseous molecules suspended in the flue gas, and then combines with the moisture to create sulfuric acid vapor when the temperature decrease. When entering the WFGD scrubber, the flue gas quickly cools down to below its

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dew point, and large amounts of sulfuric acid aerosol droplets are therefore generated through the spontaneous condensation initiated by the homogeneous and the heterogeneous nucleation of the acid vapor [11,12]. The sizes of the formed acid aerosols are particularly small with the mean diameters below 3 μm [13], which cannot be removed efficiently in desulfurization scrubbers.

The undesired aerosol formation in the flue gas cleaning processes and the aerosol problems in the industrial applications have been described and explained in various publications [14–16]. Meanwhile, many studies have been devoted to this subject and have put forward some sulfuric acid aerosol formation theories as well as control methods. As has been reported, it will improve the SO_3 removal efficiency to inject into the flue gas some alkaline matters such as aqueous ammonia, $Ca(OH)_2$, CaO, $NaHCO_3$ and $Mg(OH)_2$ [17,18], to employ the low-low temperature electrostatic precipitator (ESP) [19–21], or to equip the wet electrostatic precipitator (WESP) after desulfurization system [22,23]. These technologies and devices have been evaluated and demonstrated theoretically in many researches, and even implemented in some industrial plants. However, they are currently not widely applied in industry, mainly due to the high investment and operation costs [24]. In contrast, it would show some economic advantages to enhance the SO_3 removal efficiency through the process optimization in WFGD systems [8].

The studies concerning SO_3 removal in WFGD system are mostly based on the limestone–gypsum WFGD system [25–27], and seldom using the ammonia-based WFGD system. Thus the studies of the SO_3 removal in wet ammonia FGD systems can provide experimental foundation and theoretical basis for the practical use in industrial application.

On the basis of the wet ammonia desulfurization technology, the experiments were conducted concerning the influences of the SO_3 concentration on the aerosol emission properties after the WFGD system. The factors influencing the SO_3 removal efficiency was investigated for the further optimization of the WFGD systems in order to eliminate the damage of the SO_3 emission. Due to the fact that the SO_3 in flue gas would be completely turned into sulfuric acid aerosols in the WFGD scrubber, the removal of the sulfuric acid mist and the sulfuric acid aerosols were both related to the SO_3 removal.

2. Experimental

2.1. Experimental set-up

As shown in Fig. 1, the coal fired flue gas purification experimental set-up consists of a full-automatic coal fired boiler, a buffer tank, a selective catalytic reduction (SCR) denitrification system, an electrostatic precipitator (ESP), a heat exchanger, and an ammonia-based WFGD system. The rated flue gas volume flux of the system is ~400 Nm^3/h, which can be changed to adjust the superficial velocity in the WFGD scrubber. In order to change the flue gas condition, SO_2, SO_3, and aerosols can be added into the flue gas through the buffer tank. The aerosols added into the flue gas were generated by the aerosol generator (Topas SAG-410, Germany), and the fly ash used was taken from an industrial ESP fly ash silo. Water was used as the heat transfer medium in the heat exchanger to adjust the flue gas temperature before WFGD. The desulfurization scrubber was built as a spray tower of 5.6 m in height, with three solution spray levels set inside and a high efficiency mist eliminator equipped at the outlet. In the experiments, the flue gas volume was set as the rated one. The temperature of the flue gas before WFGD was kept at 120 °C. The desulfurization solution was heated to 50 °C. The liquid-to-gas ratio (L/G) was 14 L/m^3. The SO_2 concentration before WFGD was maintained at 2651 mg/Nm^3. While the flue gas volume was kept constant, the variation of the L/G could be achieved by changing the spraying volume of the desulfurization solution. After purification, the flue gas was emitted into the atmospheric environment and the desulfurization solution went back to the crystallizer tank, in which the aqueous ammonia was added in order to adjust the pH value to 5.5 for cycling use. The desulfurization solution used in the experiments was taken from an industrial desulfurization device.

2.2. Testing and analytic methods

The electrical low pressure impactor (ELPI, Dekati Ltd.) was used for the real-time measurement of the aerosol concentrations and the corresponding size distributions. The SO_2 concentration was tested online with a flue gas analyzer (RBR ECOM-J2KN, Germany). The pollutant PM sampler (Dekati Ltd.) was used for the aerosol sampling. The morphology of the aerosol samples was observed under a field emission scanning electron microscope (FESEM). According to the national standard and industrial standard of China [28,29] and the controlled condensation method (CCM) [2], the full-automatic isokinetic dust sampler coupled with a spiral condenser was used for sulfuric acid mist sampling, in which the flue gas was firstly heated to 180 °C to avoid the sulfuric acid condensation, and then cooled down to completely condense the acid. The condensate was collected and analyzed with an ion chromatograph analyzer (ICS-2100, American) to determine the SO_4^{2-} concentrations. Combined with the sampling volume of the flue gas, the SO_3 concentration in flue gas can be determined.

3. Results and discussion

3.1. SO_3 removal performance in WFGD processes

The SO_3 concentrations were adjusted to 12 mg/Nm^3 and 47 mg/Nm^3, separately. The SO_3 removal efficiencies were examined while the systems of the ammonia-based WFGD and the limestone–gypsum WFGD were operated under the same condition as mentioned in Section 2.1. As shown in Fig. 2, the removal efficiency of the SO_3 in the ammonia-based WFGD and in the limestone–gypsum WFGD both improved with the increase of the SO_3 concentration in the flue gas. In addition, the SO_3 removal efficiencies in the ammonia-based WFGD are within the range between 50% and 65%, which were generally higher than those in the limestone–gypsum WFGD regardless of the SO_3 concentrations. Under the rated operating condition, the SO_3 removal efficiencies in the limestone–gypsum WFGD were between 30% and 43%.

In the heat and mass transfer processes that occurred simultaneously between the gas phase and the liquid phase in the WFGD scrubber, the flue gas quenched to create the supersaturation gas phases in which the sulfuric acid aerosols were formed. The acid aerosols were generated partially through the spontaneous condensation initiated by the homogeneous nucleation, and partially through the sulfuric acid vapor condensation on foreign particles such as fly ashes, desulfurization solution droplets, and acid aerosols. The ionization of sulfuric acid occurred in the droplets as indicated in the following equations:

$$H_2SO_4 = H^+ + HSO_4^- \tag{1}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \tag{2}$$

During the ammonia-based WFGD processes, the sulfuric acid aerosols would be eliminated either by the collision trap of the desulfurization droplets or by the heterogeneous reaction with the gaseous ammonia that escaped from the desulfurization