

# TRANSFORMATION AND REMOVAL OF AMMONIUM SULFATE AEROSOLS AND AMMONIA SLIP FROM SELECTIVE CATALYTIC REDUCTION IN WET FLUE GAS DESULFURIZATION SYSTEM

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**Abstract.** Selective catalytic reduction (SCR) denitration may increase the emission of  $\text{NH}_4^+$  and  $\text{NH}_3$ . The removal and transformation characteristics of ammonium sulfate aerosols and ammonia slip during the wet flue gas desulfurization (WFGD) process, as well as the effect of desulfurization parameters, were investigated in an experimental system equipped with a simulated SCR flue gas generation system and a limestone-based WFGD system. The results indicate that the ammonium sulfate aerosols and ammonia slip in the flue gas from SCR can be partly removed by slurry scrubbing, while the entrainment and evaporation of desulfurization slurry with accumulated  $\text{NH}_4^+$  will generate new ammonium-containing particles and gaseous ammonia. The ammonium-containing particles formed by desulfurization are not only derived from the entrainment of slurry droplets, but also from the re-condensation of gaseous ammonia generated by slurry evaporation. Therefore, even if the concentration of  $\text{NH}_4^+$  in the desulfurization slurry is quite low, a high level of  $\text{NH}_4^+$  was still contained in the fine particles at the outlet of the scrubber. When the accumulated  $\text{NH}_4^+$  in the desulfurization slurry was high enough, the WFGD system promoted the conversion of  $\text{NH}_3$  to  $\text{NH}_4^+$  and increased the additional emission of primary  $\text{NH}_4^+$  aerosols. With the decline of the liquid/gas ratio and flue gas temperature, the removal efficiency of ammonia sulfate aerosols increased, and the  $\text{NH}_4^+$  emitted from entrainment and evaporation of the desulfurization slurry decreased. In addition, the volatile ammonia concentration after the WFGD system was reduced with the decrease of the  $\text{NH}_4^+$  concentration and pH values of the slurry.

**Keywords:** Selective catalytic reduction (SCR), Wet flue gas desulfurization (WFGD), Ammonium sulfate, Ammonia slip, Emission characteristics.

**Introduction.** The emission of fine particulate matter (PM<sub>2.5</sub>) and PM<sub>2.5</sub> precursors ( $\text{SO}_2$  and  $\text{NO}_x$ ) from coal-fired power plants (CFPPs) is one of the most critical environmental issues in China, and has received extensive attention (Yao et al., 2010; Pui et al., 2014; Zhang et al., 2015a; Wu et al., 2017). To reduce the emissions of  $\text{SO}_2$  and  $\text{NO}_x$ , selective catalytic reduction (SCR) denitration and limestone-based wet flue gas desulfurization (WFGD) systems have been widely used in CFPPs, so that the flue gas is subjected to denitration and desulfurization before being finally discharged into the atmosphere (Zhu, 2006; Liu et al., 2016a). However, recent studies have found that these air pollution control devices (APCDs) may change the physical and chemical characteristics of PM<sub>2.5</sub> (Liu et al., 2016b; Xu et al., 2016; Pan et al., 2017). Because the optimum operating temperature of  $\text{V}_2\text{O}_5$ - $\text{WO}_3/\text{TiO}_2$  catalysts is in the range of 350–420°C, the SCR unit is usually placed before the electrostatic precipitator (ESP) and WFGD (Topsoe et al., 1995; Busca et al., 1998). The SCR system can promote the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  while

reducing NO<sub>x</sub> to N<sub>2</sub> (Kamata et al., 2001). SO<sub>3</sub> can react with unreacted NH<sub>3</sub> (ammonia slip) at the appropriate temperature to form ammonium sulfate or bisulfate aerosols (M.A.Khashimkhanova, et al 2020;). The formed ammonium sulfate aerosols and NH<sub>3</sub> slip are removed and transformed in the downstream ESP and WFGD, and change the PM<sub>2.5</sub> emission characteristics at the outlet of the WFGD system. Li et al. (2015) performed on-site measurements in two CFPPs and found that an increase in the removal efficiency of NO<sub>x</sub> from 55% to 79% led to a doubling of the PM<sub>2.5</sub> concentration in flue gas emitted out of the WFGD system and a significant increase of SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> in PM<sub>2.5</sub>. Cheng et al. (2019) proposed that the fine particle concentration significantly increases after WFGD as a result of SCR denitrification, and the ESP and WFGD system are not effective in removing ammonium sulfate aerosol generated by SCR. These reported works have only focused on the impact of SCR on PM<sub>2.5</sub> emission characteristics, while the transformation mechanisms of ammonium sulfate aerosols and ammonia slip from SCR in the subsequent APCDs have not been systematically studied. The WFGD system is usually the last treatment device before the flue gas is discharged into the atmosphere. Therefore, investigating the transformation characteristics of ammonium sulfate aerosols in the desulfurization process is very important for reducing PM<sub>2.5</sub> emissions. In addition, although NH<sub>4</sub><sup>+</sup> /NH<sub>3</sub> is not currently included in China or other countries' CFPPs emission control policies, more researchers have begun to pay attention to NH<sub>4</sub><sup>+</sup> /NH<sub>3</sub> emissions (Pan et al., 2016a; Li et al., 2017). Recently, it has been observed that NH<sub>4</sub><sup>+</sup> accounts for about 10% of the total mass of PM<sub>2.5</sub> during haze episodes in urban areas (Tian et al., 2016), and that fossil fuel combustion, including primary ammonium aerosols and ammonia slip emitted from CFPPs, contributes 90% of the atmospheric NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub> (Pan et al., 2016a). Ammonium aerosols contribute significantly to reduced atmospheric visibility due to their hygroscopicity (Chen and Tsai, 2000; Yang et al., 2007), and ammonia is the precursor to secondary ammonium aerosols (Griffith et al., 2015; Zhang et al., 2015b). Therefore, identifying the contribution of the SCR and WFGD to NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub> emission would be of great help to air pollution control. In this paper, the removal and transformation characteristics of ammonium sulfate aerosols and ammonia slip generated by a SCR system in the subsequent WFGD process were studied. In addition, the effects of the desulfurization parameters on the NH<sub>4</sub><sup>+</sup> /NH<sub>3</sub> emission were also explored. This study is of great significance for quantitative study of the impact of SCR on the emission characteristics of CFPPs, and may provide a basis for optimizing desulfurization systems to reduce the emission of ammonium aerosols and ammonia.

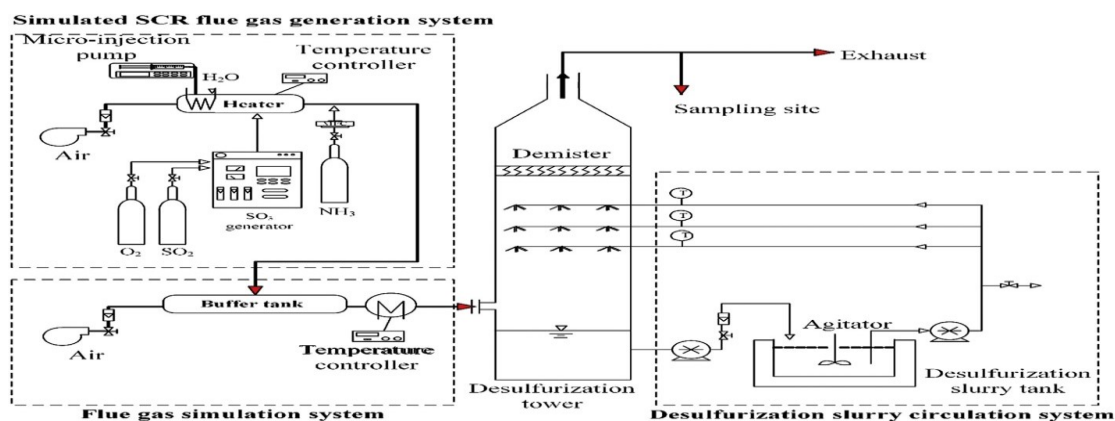
### 1. Materials and methods

#### 1.1. Experimental system

The schematic layout of the experimental system is shown in Fig. 1, and consists of a simulated SCR flue gas generating system and a simulated WFGD system. The simulated SCR flue gas generation system was used to generate the simulated SCR flue gas containing ammonium sulfate aerosol and ammonia slip. The simulated flue gas, with a flow rate of 3 m<sup>3</sup>/hr consisting of NH<sub>3</sub>, SO<sub>3</sub>, H<sub>2</sub>O and cleaned air, was mixed and heated in the buffer tank. The heating temperature was 350°C. SO<sub>3</sub> was formed by oxidation of SO<sub>2</sub> on a commercial V<sub>2</sub>O<sub>5</sub>-based catalyst at 550°C. The water vapor was injected to the system using a microinjection pump and heated pipeline. In the pipeline downstream of the buffer tank, the ammonia slip reacted with SO<sub>3</sub> and water vapor to generate ammonium sulfate aerosols, and then passed through a heated pipeline and entered the simulated WFGD system. The WFGD system included a simulated flue gas unit, a desulfurization scrubber and a desulfurization slurry circulation unit, with 80 m<sup>3</sup> /hr volume flux. The purified air and simulated SCR flue gas were uniformly mixed in the buffer tank and heated to 120°C before entering the spray scrubber. The concentration of ammonium sulfate

and  $\text{NH}_3$  slip in the flue gas at the inlet of the WFGD system was similar to that of actual CFPPs. The simulated flue gas and the desulfurized slurry were in countercurrent contact in the tower. The desulfurization tower had a three-level spray and a demister. The tower body was made of polycarbonate tubes that had excellent heat resistance. The desulfurization slurry was prepared from gypsum that was provided by a coal-fired power plant, and its soluble ion concentrations are shown in Table 1. The pH value of the desulfurization slurry was maintained at a constant value of  $5.6 \pm 0.1$ , and a heater was installed in the slurry tank to control the slurry temperature. The experiments were carried out at a liquid–gas ratio of  $12 \text{ L/m}^3$ , and a slurry concentration of 15%. The inlet flue gas temperature and desulfurization slurry temperature were 120 and  $45^\circ\text{C}$ , respectively.

1.2. Sampling and analysis methods As shown in Fig. 2, a measurement system containing a sampling gun, cyclone (S110, Dekati Ltd., Finland), diluter, particulate matter (PM) impactor (Dekati Ltd., Finland), two-stage absorption bottle and parallel dust sampler (3008, Testo Ltd., Germany) was designed for sampling (Cheng et al., 2019). The PM impactor and the absorption bottle set were used to collect ammonium-containing particles and gaseous ammonia, respectively. The sample gas was drawn from the center of the tube at a flow rate of  $10 \text{ L/min}$  and then entered into the cyclone to remove the particles  $>10 \mu\text{m}$ . Then, a diluter was used to avoid the condensation of water vapor caused by temperature drop (Yi et al., 2006). The PM impactor divided the particles with aerodynamic diameter less than  $10 \mu\text{m}$



**Fig. 1 – Schematic diagram of the experimental system. SCR: selective catalytic reduction.**

(PM<sub>10</sub>) into three groups (i.e.,  $<1.0$ ,  $1.0\text{--}2.5$ , and  $2.5\text{--}10.0 \mu\text{m}$ ). was formed by the desulfurization process; this is referred to After all particles were removed, the flue gas entered the . When the inlet flue gas carried ammonium sulfate absorption bottles. An ice-water bath ensured that the water aerosols ( $\text{NH}_4^+$ ), the PM sampled at the outlet of WFGD vapor in the flue gas was completely condensed.

The filters were divided into three groups according to the particle size distributions of  $<1$ ,  $1.0\text{--}2.5$  and  $2.5\text{--}10.0 \mu\text{m}$ , and each group was ultrasonically extracted with ultrapure water three times. The  $\text{NH}_4^+$  concentration was measured by an ultraviolet spectrophotometer (UV-1600, Mepod Ltd., China) using the Nessler reagent method. The remaining soluble anions ( $\text{Cl}^-$ ,  $\text{NO}^-$  and  $\text{SO}_4^{2-}$ ) and cations ( $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$ ) were analyzed using an ion chromatograph analyzer (ICS- 2100, Dionex Ltd., USA) and inductively coupled plasma optical emission spectrometer (Optima 8000, PerkinElmer Ltd., USA), respectively.

### 1.3. Experimental procedure.

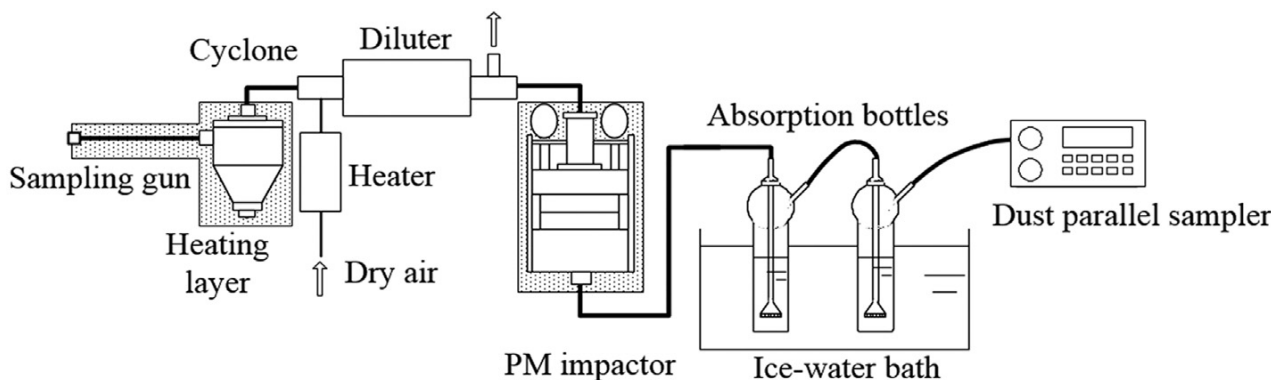
Tests were conducted with and without simulated SCR flue gas to study the removal characteristics of ammonium sulfate aerosols and ammonia slip during the WFGD process. When the simulated SCR flue gas generation system was shut down, ammonium-containing PM10 sampled at the scrubber outlet

Species	Concentration (mg/L)	Species	Concentration (mg/L)
	3252.9 ± 255.98		26.8 ± 1.56
SO <sub>4</sub> <sup>2-</sup>	4359.9 ± 221.33	K <sup>+</sup>	1562.2 ± 78.27
Cl <sup>-</sup>	59.1 ± 9.21	Ca <sup>2+</sup>	92.3 ± 10.24
NO <sup>-</sup>	122.3 ± 1.21	Na <sup>+</sup>	388.6 ± 25.67
NH <sub>4</sub>		Mg <sup>2+</sup>	

(NH<sub>4</sub><sup>+</sup>) was composed of the escaped ammonium sulfate aerosols (NH<sub>4</sub><sup>+</sup>) and newly formed ammonium-containing PM10 (NH<sub>4</sub><sup>+</sup>). Therefore, the escaped ammonium sulfate concentration (NH<sub>4</sub><sup>+</sup>) and the removal efficiency of ammonium sulfate aerosol (x) by the slurry scrubbing can be calculated as follows:

$$x = \frac{1}{4} \frac{NH_{4\text{ in}}^P - NH_{4\text{ esc}}^P}{NH_{4\text{ in}}^P} \times 100\%$$

The removal characteristics of ammonia slip were investigated using the same experimental method. To investigate the formation characteristics of ammonium-containing particles and gaseous ammonia during the desulfurization process, the simulated SCR flue gas generation system was shut down; the PM10 and net flue gas at the outlet of the WFGD system were sampled and analyzed. Because the NH<sub>4</sub><sup>+</sup> concentration and pH value of the desulfurization slurry are closely related to the formation of ammonium-containing particles and gaseous ammonia, the effects of desulfurization slurry characteristics were investigated. In addition, it has been suggested that incomplete adsorption of the ammonia slip by the WFGD process and reabsorption of the escaped ammonia slip by the entrained slurry droplets and condensed water are the main reasons for the increase of NH<sub>4</sub><sup>+</sup> concentration in the fine particles at the outlet of the WFGD system. Therefore, the effect of ammonia slip concentration at the inlet of WFGD system on the formation of ammonium and ammonia was also studied.



**Fig. 2 – Schematic diagram of sampling system. PM: particulate matter.**

Finally, the effects of desulfurization parameters including liquid/gas ratio, desulfurization slurry concentration and inlet flue gas temperature on ammonium-containing aerosol emissions were investigated. Parallel experiments were re-peated at least three times.

## 2. Results and discussion.

### 2.1. Removal characteristics of ammonium sulfate aerosols and ammonia slip by WFGD system.

Fig. 3 displays the size-segregated distribution of  $\text{NH}_4^+$  concentration in  $\text{PM}_{10}$  before and after the WFGD system. The experimental parameters were the same as in Section 1.1. Before desulfurization, the ammonium sulfate aerosols generated by the heterogeneous reactions of  $\text{NH}_3\text{-SO}_3\text{-H}_2\text{O}$  were mainly submicron particles; therefore, the  $\text{NH}_4^+$  concentration was highest in the size fraction of  $<1 \mu\text{m}$ , which was  $0.082 \text{ mg/m}^3$  and accounted for about 61.4% of the total  $\text{NH}_4^+$  in  $\text{PM}_{10}$ . After desulfurization, the  $\text{NH}_4^+$  concentration in  $\text{PM}_{10}$  increased from  $0.134$  to  $0.321 \text{ mg/m}^3$ , with the concentration of  $\text{NH}_4^+$  in the size fractions of  $<1$ ,  $1\text{-}2.5$  and  $2.5\text{-}10 \mu\text{m}$  increased by factors of 2.76, 1.89, and 1.78, respectively, indicating that new fine particles containing  $\text{NH}_4^+$  may be formed during the desulfurization process. In addition, since the slurry scrubbing has a low removal efficiency of fine particles (Pan et al., 2016b), uncaptured ammonium sulfate aerosol inevitably appears in the WFGD outlet flue gas. Therefore, the ammonium-containing  $\text{PM}_{10}$  at the outlet of the WFGD system was composed of the escaped ammonium sulfate aerosols and the new ammonium-containing particles formed by the desulfurization process.

According to the experimental and calculation methods shown in Section 1.3, the escaped and newly formed  $\text{NH}_4^+$  concentration in each size segment of  $\text{PM}_{10}$  and the removal efficiency of ammonium sulfate aerosols by desulfurization are shown in Fig. 4. It is clear that the majority of newly formed ammonium-containing particles emitted from the scrubber were in the submicrometer range. The removal efficiency of ammonium sulfate aerosol by spray scrubbing was only 21.4% for  $\text{PM}_{10}$  and increased with the increase of particle size. This is because the inertial force and diffusion force play vital roles in removing particles in the WFGD tower and are closely related to the size of the particles (Kim et al., 2001; Lim et al., 2006; Pan et al., 2016b). The particles  $<1 \mu\text{m}$  had the lowest removal efficiency because the particle within the range  $0.1\text{-}1 \mu\text{m}$  were less affected by inertial force and diffusion force and thus difficult to capture (Lim et al., 2006). The removal efficiency of particles larger than  $1 \mu\text{m}$  depended on the inertial force, and increased as the particle size increased (Kim et al., 2001). With the combined effects of aerosol escape and new formation, the  $\text{NH}_4^+$  emissions from the desulfurization system were mainly concentrated in the submicron size segment.

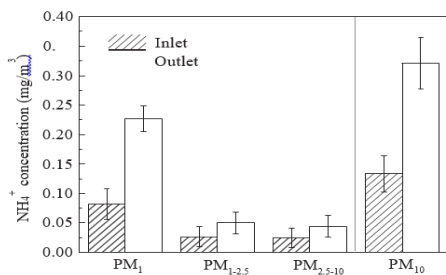


Fig. 3 - Size-segregated distribution of  $\text{NH}_4^+$  concentration in particulate matter (PM) before and after wet flue gas desulfurization (WFGD) system.  $\text{PM}_1$ ,  $\text{PM}_{1-2.5}$ ,  $\text{PM}_{2.5-10}$ , and  $\text{PM}_{10}$  refer to PM with aerodynamic diameters of  $<1$ ,  $1.0\text{-}2.5$ ,  $2.5\text{-}10.0$  and  $<10.0 \mu\text{m}$ , respectively.

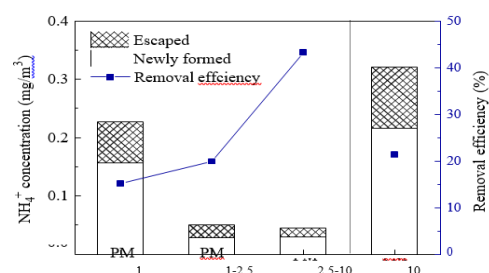


Fig. 4 - Size-segregated distribution of  $\text{NH}_4^+$  concentration in  $\text{PM}_{10}$  at outlet of WFGD system and the removal efficiency of ammonium sulfate aerosol.

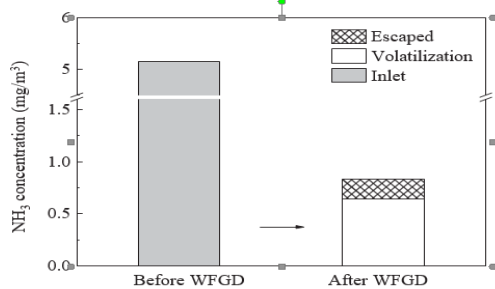
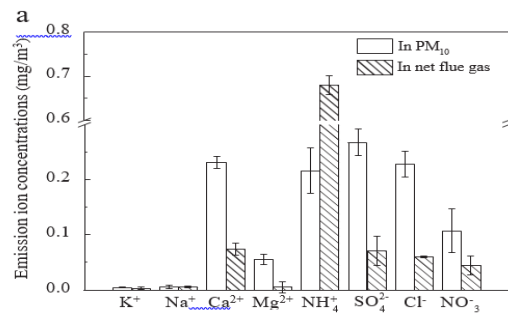
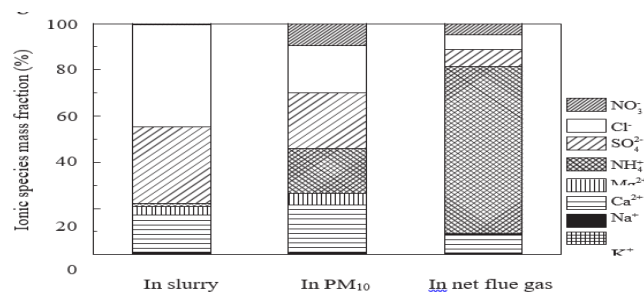


Fig. 5 – NH<sub>3</sub> concentration before and after WFGD system.



a



b

**Fig. 6 – (a) Soluble ion concentrations and (b) compositions in the desulfurization slurry, PM10 and net flue gas collected at the outlet of WFGD system.**

Fig. 5 displays the NH<sub>3</sub> concentration before and after the WFGD system. Ammonia slip can be effectively adsorbed by the desulfurization slurry in the scrubber with a removal efficiency of 96.4%, because of its high-water solubility. However, 0.64 mg/m<sup>3</sup> of gaseous ammonia at the outlet of WFGD system was generated by the desulfurization process. Although the pH value of the slurry was 5.6, there was still a small amount of 20 ammonium in the slurry in the form of NH<sub>3</sub>·H<sub>2</sub>O, which is a volatile substance (Ye et al., 2018). When the sprayed droplets encounter the hot flue gas, the NH<sub>3</sub>·H<sub>2</sub>O in slurry can be evaporated out of the scrubber as gaseous ammonia, resulting in an increase in the ammonia concentration at the WFGD outlet.

## 2.2. Formation characteristics of ammonium-containing particles and gaseous ammonia during the slurry scrubbing process.

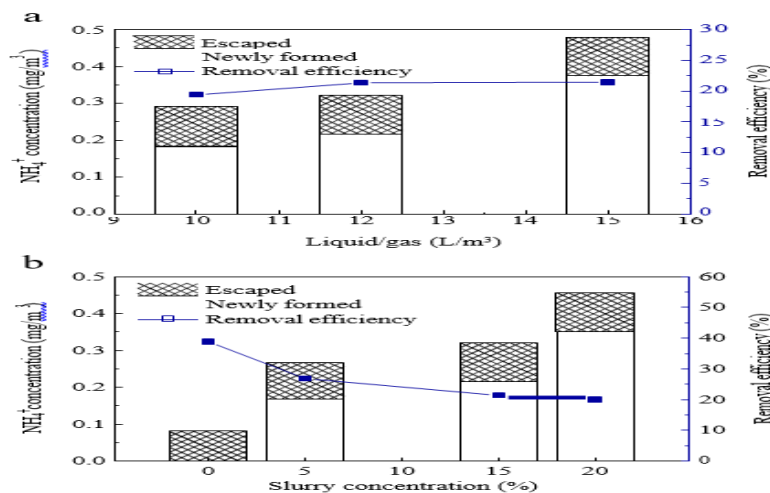
### 2.2.1. Ammonium and ammonia formation characteristics.

The soluble ion concentrations in PM<sub>10</sub> and net flue gas collected at the outlet of the WFGD system were measured, as shown in Fig. 6. The concentration of gaseous ammonia was converted to the corresponding NH<sub>4</sub><sup>+</sup> concentration. In the desulfurization net flue gas, the concentration of NH<sub>4</sub><sup>+</sup> was much higher than that of other ions, which proves that gaseous ammonia is indeed carried in the flue gas, and gaseous water in the flue gas can carry little soluble ions. The NH<sub>4</sub><sup>+</sup> concentration in net flue gas was 3.15 times higher than in PM<sub>10</sub>, although the total ion concentration in PM<sub>10</sub> was higher than in the net flue gas. The main ion composition of the desulfurization slurry consisted of Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>. The ionic components of PM<sub>10</sub> and the desulfurization slurry were similar but different in proportion. The proportion of NH<sub>4</sub><sup>+</sup> in the desulfurization slurry was only 1.2%, but it was as high as 19.4% in the entrained PM<sub>10</sub>. This may indicate that ammonium-containing particles at the outlet of the WFGD system not only come from the slurry entrainment, but also from the re-condensation of gaseous ammonia generated by slurry evaporation. A small amount of NH<sub>3</sub>·H<sub>2</sub>O in the desulfurization slurry could easily be

evaporated by hot flue gas as gaseous ammonia. Correspondingly, some of this volatile  $\text{NH}_3$  can be reabsorbed by condensate droplets or entrained in slurry droplets due to its high solubility. Therefore, even if the  $\text{NH}_4^+$  concentration in the desulfurization slurry was very low, a high content of  $\text{NH}_4^+$  was still contained in the fine particles at the outlet of the scrubber. It is worthwhile to note that the samples in this study were collected very close to the outlet of the scrubber, where the flue gas temperature was about  $56^\circ\text{C}$ . So, it can be inferred that as the flue gas temperature decreased in the downstream of WFGD, the saturated water vapor in flue gas tended to condense to droplets, causing more gaseous ammonia to be adsorbed, which enhanced the transformation of  $\text{NH}_3$  to  $\text{NH}_4^+$ . Moreover, in real desulfurization flue gas in CFPPs,  $\text{NH}_3$  can also form ammonium sulfate aerosols through heterogeneous reactions with  $\text{SO}_2/\text{SO}_3$  and water vapor (Pan et al., 2016c; Huang et al., 2016); therefore, the ratio of ammonium in particles to gaseous ammonia will be larger than in this study.

### 2.2.2. Effect of desulfurization slurry characteristics.

The  $\text{NH}_4^+$  accumulated in the desulfurization slurry mainly comes from the capture of ammonia slip and ammonium sulfate aerosols in flue gas, which is affected by the type of coal used and the ammonia injection into the SCR system. As shown in Fig. 7a, the concentration of ammonium and ammonia formed by desulfurization increased significantly as the  $\text{NH}_4^+$  concentration in slurry increased from 14.93 to 122.05 mg/L, while increasing slightly as the  $\text{NH}_4^+$  concentration in slurry increased from 122.05 to 405.55 mg/L. With a higher  $\text{NH}_4^+$  concentration in the desulfurization slurry, the vapor pressure of the slurry increased and the ammonia volatility rose, resulting in an increase in the ammonia concentration ammonium content in particles.



**Fig. 8 – Effect of (a) liquid/gas ratio and (b) desulfurization slurry concentration on the  $\text{NH}_4^+$  concentration in  $\text{PM}_{10}$  at outlet of the WFGD system and the removal efficiency of ammonium sulfate.**

The concentration of ammonia formed by slurry evaporation was almost constant when the pH value of the desulfurization slurry increased from 4.5 to 5.6, while increasing slightly as the pH value increased from 5.6 to 6.5. For the  $\text{NH}_4^+$  equilibrium (Reaction (3)) in the desulfurization slurry, the chemical equilibrium will move to the right in a stronger base environment, leading to more  $\text{NH}_3$  volatilization during slurry evaporation. In a conventional WFGD system, the pH value of the desulfurization slurry is between 5.5 and 6.5. In the special tower type, such as the two-tower double-circulation system, the pH value is approximately 4.5–

5.0 in the first-stage tower and 5.5–6.5 in the second-stage tower. Therefore, fluctuations in slurry pH within the normal range have little effect on  $\text{NH}_3/\text{NH}_4^+$  emissions.



### 2.2.3. Effect of ammonia slip concentration.

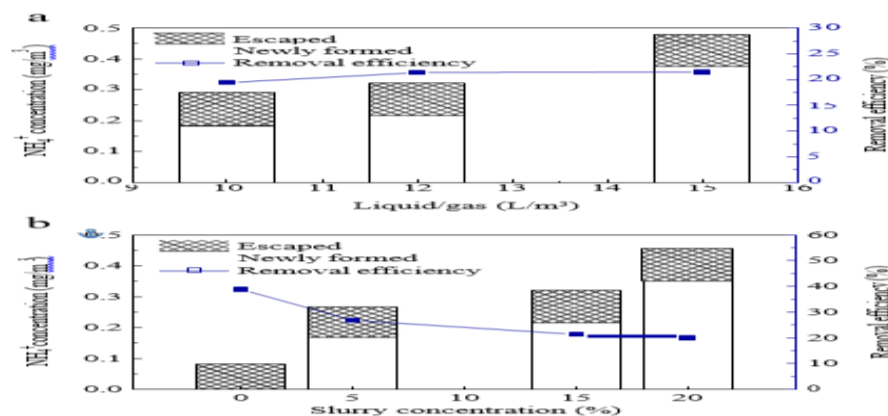
The effect of ammonia slip concentration on the formation of ammonium-containing particles and gaseous ammonia was studied, as shown in Fig. 7c. When the concentration of  $\text{NH}_3$  slip increased from 0 to 5 ppmV, the concentration of formed gaseous ammonia slightly increased, while the ammonium concentration in  $\text{PM}_{10}$  did not change, indicating that the escaped ammonia slip was not the main reason for the increased concentration of ammonium in  $\text{PM}_{10}$ . Ammonia slip can be effectively adsorbed by the desulfurization slurry in the scrubber due to its high-water solubility, so the concentration of escaped ammonia slip is very low and not sufficient to affect the formation of ammonium-containing particles. Therefore, the  $\text{NH}_4^+$  content accumulated in the desulfurization slurry is the major factor affecting the formation of ammonium-containing particles and ammonia during the slurry scrubbing process.

## 2.3. Effect of desulfurization parameters on ammonium aerosol emission.

### 2.3.1. Effect of the liquid/gas ratio.

Fig. 8a shows the effect of liquid/gas ratio on the  $\text{NH}_4^+$  concentration in  $\text{PM}_{10}$  after desulfurization, and the removal efficiency of ammonium sulfate aerosols. The liquid/gas ratio was controlled by adjusting the flow volume of the desulfurization slurry. The other parameters were the same as in Section 1.1. When the liquid/gas ratio increased from 10 to 15  $\text{L}/\text{m}^3$ , the concentration of  $\text{NH}_4^+$  in  $\text{PM}_{10}$  increased from 0.29 to 0.48  $\text{mg}/\text{m}^3$ , and the removal efficiency of ammonium sulfate aerosols increased slightly. The concentration of volatile gaseous ammonia increased with the increase of slurry volume. In addition, higher desulfurization slurry volume flow means higher nozzle pressure, which leads to the formation of more fine droplets. These fine droplets were more likely to be entrained out of the scrubber by the flue gas.

Therefore, the emitted  $\text{NH}_4^+$  concentration in  $\text{PM}_{10}$  shows a significant increase with the increase of the liquid/gas ratio. At the same time, with a higher liquid/gas ratio, more slurry droplets were sprayed into the scrubber, resulting in a greater probability of collision capture between particles and droplets, which increased the removal efficiency of ammonium sulfate aerosols.



**Fig. 8 – Effect of (a) liquid/gas ratio and (b) desulfurization slurry concentration on the  $\text{NH}_4^+$  concentration in  $\text{PM}_{10}$  at outlet of the WFGD system and the removal efficiency of ammonium sulfate.**



### ***2.3.2. Effect of desulfurization slurry concentration.***

Fig. 8b illustrates the effect of desulfurization slurry concentration on the emitted  $\text{NH}_4^+$  concentration and the removal efficiency of ammonium sulfate aerosol. The remaining parameters were the same as in Section 1.1. Increasing the slurry concentration from 0 (clean water scrubbing) to 20% resulted in an increase in the entrained  $\text{NH}_4^+$  concentration from 0.08 to 0.17  $\text{mg}/\text{m}^3$ . When scrubbed with clean water, the  $\text{NH}_4^+$  emitted from the desulfurization system was all escaped ammonium sulfate aerosols. With a higher slurry concentration in the desulfurization slurry, slurry containing more solid particles and soluble ions was entrained out of scrubber, resulting in an increase in the concentration of fine particles and  $\text{NH}_4^+$  after desulfurization. On the other hand, the removal efficiency of ammonium sulfate aerosols decreased with the increase of slurry concentration. With more solid content in the desulfurization slurry, the slurry would be harder to atomize by the nozzles, resulting in the generation of more large particles, which is detrimental to the capture of ammonium sulfate aerosols. Therefore, a reasonable reduction in the concentration of the desulfurization slurry is beneficial to reduce the concentration of fine particles in the desulfurization flue gas, and enhance the removal efficiency of the ammonium sulfate aerosol, thereby reducing the  $\text{NH}_4^+$  emissions from the WFGD system.

### ***2.3.2. Effect of desulfurization slurry concentration.***

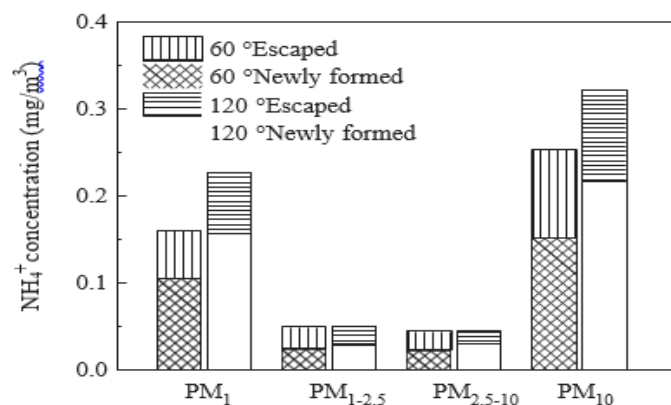
Fig. 8b illustrates the effect of desulfurization slurry concentration on the emitted  $\text{NH}_4^+$  concentration and the removal efficiency of ammonium sulfate aerosol. The remaining parameters were the same as in Section 1.1. Increasing the slurry concentration from 0 (clean water scrubbing) to 20% resulted in an increase in the entrained  $\text{NH}_4^+$  concentration from 0.08 to 0.17  $\text{mg}/\text{m}^3$ . When scrubbed with clean water, the  $\text{NH}_4^+$  emitted from the desulfurization system was all escaped ammonium sulfate aerosols. With a higher slurry concentration in the desulfurization slurry, slurry containing more solid particles and soluble ions was entrained out of scrubber, resulting in an increase in the concentration of fine particles and  $\text{NH}_4^+$  after desulfurization. On the other hand, the removal efficiency of ammonium sulfate aerosols decreased with the increase of slurry concentration. With more solid content in the desulfurization slurry, the slurry would be harder to atomize by the nozzles, resulting in the generation of more large particles, which is detrimental to the capture of ammonium sulfate aerosols. Therefore, a reasonable reduction in the concentration of the desulfurization slurry is beneficial to reduce the concentration of fine particles in the desulfurization flue gas, and enhance the removal efficiency of the ammonium sulfate aerosol, thereby reducing the  $\text{NH}_4^+$  emissions from the WFGD system.

### ***2.3.3. Effect of the inlet flue gas temperature.***

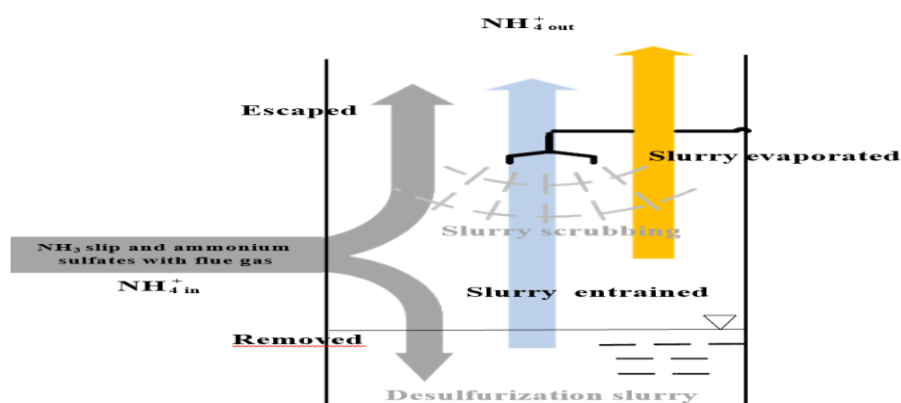
Because of the application of a low-temperature electrostatic precipitator, the flue gas temperature of the desulfurization scrubber inlet may be very low. The temperature of the inlet flue gas increased from 60 to 120°C, resulting in an increase in the concentration of  $\text{NH}_4^+$  in newly formed PM, while the efficiency of spray scrubbing on the capture of ammonium sulfate remained almost unchanged. Other parameters were the same as in Section 1.1, and the results are shown in Fig. 9. With a higher flue gas temperature, the evaporation and entrainment of the slurry droplets was enhanced, leading to more  $\text{NH}_4^+$ -containing particles emitted with the flue gas, especially in sub-micrometer particulate matter (PM1). However, the removal efficiency of the ammonium sulfate aerosol was less affected by the inlet flue gas temperature, because the flue gas temperature was much lower than the melting points of both  $\text{NH}_4\text{HSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  aerosols.

**2.4. Transformation and removal of ammonium and ammonia during the desulfurization process.**

Based on the above-mentioned results, the transformation mechanism of ammonium and ammonia during the desulfurization process can be shown in Fig. 10. In actual CFPPs, the  $\text{NH}_4^+$  in the desulfurization slurry is mainly derived from the SCR denitration process. When the hot flue gas and the sprayed desulfurization slurry droplets are in countercurrent contact, a portion of the ammonium sulfate aerosols and  $\text{NH}_3$  slip generated by SCR are captured by the falling slurry droplets, and correspondingly part of the droplets is carried out of the scrubber by the flue gas to form fine particles. As the desulfurization slurry circulates, the  $\text{NH}_4^+$  dissolved in the slurry continuously accumulates, resulting in an increase in the concentration of  $\text{NH}_4^+$  in the entrained droplets. In addition, a small amount of ammonium in the slurry can be vaporized by hot flue gas to form gaseous ammonia. As the flue gas temperature goes down, the saturated water vapor in flue gas tends to condense to droplets, and some of the volatile ammonia is adsorbed by the condensed water and the entrained slurry droplets, which is the main cause for the increase of  $\text{NH}_4^+$  concentration in the PM discharged by desulfurization.



**Fig. 9 – Effect of inlet flue gas temperature on the size distribution of  $\text{NH}_4^+$  concentration at outlet of WFGD system.**



**Fig. 10 – Removal and transformation of ammonium sulfate aerosols and ammonia slip.  $\text{NH}_4^+$  and  $\text{NH}_4^+$  refer to all ammonia species carried in and out of the scrubber by the flue gas, respectively.**

Therefore, from the internal transformation mechanism, the  $\text{NH}_4^+$  and  $\text{NH}_3$  in  $\text{PM}_{10}$  and flue gas at the WFGD outlet are partly derived from the entrainment and evaporation of ammonium accumulated in the desulfurization slurry.

In real-world applications, to achieve higher denitrification efficiency, some CFPPs inject an excess of the reducing agent  $\text{NH}_3$ , resulting in an increase in the  $\text{NH}_3$  slip content in the flue gas.  $\text{NH}_4^+$  can accumulate in the circulating slurry to a very high concentration owing to its high solubility. When the accumulated  $\text{NH}_4^+$  level in the desulfurization slurry is high enough, the  $\text{NH}_4^+$  concentration in PM at the scrubber outlet will be higher than at the inlet. The increased  $\text{NH}_4^+$  in PM is derived from the captured ammonia slip, indicating that the WFGD system as a whole promotes the conversion of  $\text{NH}_3$  to  $\text{NH}_4^+$ , which is consistent with the experimental phenomenon observed in this study. Overall, the WFGD system reduces the total emission of  $\text{NH}_4^+$  and  $\text{NH}_3$ , especially gaseous ammonia, but also promotes the conversion of  $\text{NH}_3$  to  $\text{NH}_4^+$  and may increase the primary  $\text{NH}_4^+$  aerosols emission.

In addition, increasing the desulfurization parameters such as liquid/gas ratio, slurry concentration and inlet flue gas temperature would reduce the removal efficiency of slurry scrubbing on ammonium sulfate aerosols and ammonia slip, and enhance the formation of ammonium-containing particles and volatile ammonia, thereby increasing the  $\text{NH}_3/\text{NH}_4^+$  emission from the WFGD system.

### **3. Conclusions.**

In this study, the transformation and removal of ammonium sulfate aerosols and ammonia slip from SCR in a WFGD system was investigated. Experiments were designed to study the removal of ammonium sulfate aerosols and ammonia slip, formation of ammonium-containing particles and volatile ammonia, and emission of  $\text{NH}_3/\text{NH}_4^+$  during the WFGD process, respectively. The effect of desulfurization parameters was also explored. The results indicate that ammonium sulfate aerosols and ammonia slip in flue gas can be partly removed by the slurry scrubbing, while the entrainment and evaporation of  $\text{NH}_4^+$ -containing desulfurization slurry will generate new ammonium-containing particles and volatile ammonia. The WFGD system can promote the conversion of ammonia slip from SCR to ammonium-containing particles and may increase the additional emission of primary  $\text{NH}_4^+$  aerosols. Therefore, in the actual operation process, in addition to strictly controlling the ammonia injection in the SCR system, attention to the accumulation of  $\text{NH}_4^+$  in the desulfurization slurry is also beneficial to  $\text{NH}_3/\text{NH}_4^+$  emission control. In addition, while ensuring that the desulfurization efficiency meets the emission requirements, properly reducing the liquid/gas ratio, slurry concentration and inlet flue gas temperature can help reduce the  $\text{NH}_3/\text{NH}_4^+$  emission from the WFGD system.  $\text{NH}_3/\text{NH}_4^+$  emission is an environmental problem that has not been addressed by current regulations. In the next stage, we will conduct research in actual power plants to further study the transformation and removal mechanism of ammonium sulfate aerosols and ammonia slip under complex flue gas conditions.

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