Investigation on condensable particulate matter emission characteristics in wet ammonia-based desulfurization system

Rongting Huang 1, Hao Wu 2,* , Linjun Yang 1,*

1 Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, Southeast University, Nanjing 210096, China
2 School of Energy and Mechanical Engineering, Nanjing Normal University, Nanjing 210023, China

ARTICLE INFO

Article history:
Received 10 September 2019
Received in revised form 15 January 2020
Accepted 22 January 2020
Available online 5 February 2020

Keywords:
Ammonia-based WFGD
Aerosol emission
Condensable particulate matter (CPM)
Ultrafine particles
Emission control

ABSTRACT

Particulate matter emissions from ammonia-based wet flue gas desulfurization (Ammonia-WFGD) systems are composed of a filterable particulate matter and a condensable particulate matter (CPM) portion. However, the CPM part has been ignored for a long time, which results in an underestimation of the aerosol problems caused by Ammonia-WFGD systems. In our research, the characteristics of the CPM that emits from an Ammonia-WFGD system are investigated experimentally for the first time, with the US Environmental Protection Agency Method 202 employed as the primary measurement. The influences of some essential desulfurizing parameters are evaluated based on the experimental data. The results show that CPM contributes about 68.8% to the total particulate matter emission. CPM consists mainly of ammonium sulfates/sulfites, with the organic part accounting for less than 4%. CPM is mostly in the submicron fraction, about 71.1% of which originates from the \( \text{NH}_3 - \text{H}_2\text{O} - \text{SO}_2 \) reactions. The appropriate adjustments for the parameters of the flue gas and the desulfurizing solution can inhibit CPM formation to different extents. This indicates that the parameter optimizations are promising in solving CPM emission problems in Ammonia-WFGD systems, in which the pH adjustment alone can abate CPM emission by around 49%. The opposite variations of the parameters need attention because they can cause tremendous CPM emission increase.

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Introduction

Particulate matter (PM) emission from stationary sources is severe in China, which does harm to the weather, the atmospheric visibility and the human respiratory system (Andreae et al., 2005; Pöschl, 2006; Shen et al., 2015; Watts et al., 2015). In recent years, huge reformations regarding flue gas purifying system have been conducted in coal-fired power plants in China, which contribute greatly to the aerosol emission control and the air quality improvement (Yao et al., 2010; Wang et al., 2015; Yang et al., 2019). However, these control methods and the corresponding regulations aim mainly at filterable particulate matter (FPM), with condensable...
particulate matter (CPM) being ignored (Corio and Sherwell, 2000; Pei, 2015). FPM and CPM constitute total particulate matter (TPM). It has been reported that CPM contributes significantly to the total aerosol emission from stationary sources, which means that the current PM emission problems are largely underestimated (Yang et al., 2014; Feng et al., 2018; Morino et al., 2018). Besides, FPM emissions are considerably reduced with the developed FPM control technologies while CPM can hardly be removed. As a result, CPM accounts for higher proportions in TPM emissions (Yao et al., 2010; Qi et al., 2017). The control of CPM emission is urgent that draws much attention (Tsukada et al., 2008; Pei, 2015).

CPM is defined by the US Environmental Protection Agency (US EPA), which refers to gaseous materials that shift from gas phase to liquid or solid phase through condensation or reactions after being emitted from stack conditions to the ambient environment. Such a phase transformation is caused by temperature dropping and dilution. All CPM belongs to PM$_{2.5}$ (particulate matter with aerodynamic diameters $\leq$ 2.5 $\mu$m) and thus is more hazardous than normal aerosols due to its large specific surface area and long suspension time (Schwarze et al., 2006; Russell and Brunekeef, 2009). Many researches have been done about CPM emission from power plants and boilers (Tsukada et al., 2008; Pei, 2015; Cano et al., 2017; Qi et al., 2017). But seldom have they combined it with desulfurization devices.

Wet flue gas desulfurization (WFGD) systems are widely used for removing SO$_2$ from flue gas in stationary sources. This device is so powerful that many researches have been done based on it in expectation of removing more pollutants than just SO$_2$. For example, studies have been devoted to the simultaneous desulfurization and denitrification, and the integrated desulfurization and decarbonization (Bai and Yeh, 1997; Resnik et al., 2004; Yang et al., 2011; Zhao et al., 2011; Wang et al., 2018). However, in regard to the aerosol pollutants, researchers found that a WFGD system could generate more aerosols than it removed, causing serious aerosol emission problems (Yang et al., 2010; Shi et al., 2017). The ammonia-based wet flue gas desulfurization (Ammonia-WFGD) is famous for its high efficiency and low investment in removing SO$_2$ from industrial flue gas. But the excessive discharge of aerosols restricts its promotion and development, especially when particulate pollution is of great concern (Khakharia, 2013; Mertens, 2013). Some previous researches have been done regarding aerosol emission from Ammonia-WFGD systems (Huang et al., 2016b, 2017; Pan et al., 2015). Our previous studies pointed out that the NH$_3$–H$_2$O–SO$_2$ reactions were the main source of aerosol generation in an Ammonia-WFGD system, which were greatly influenced by the temperature and the reactants variation (Huang et al., 2016b, 2017). However, these researches fail to enroll CPM in measurements. One reason is the lack of recognition of the importance of CPM, as well as corresponding laws and regulations. Another reason is that CPM measurement is particularly challenging.

Currently, there are two main methods of CPM measurement. One is the EPA Method 202 which was promulgated in 1991 and revised in 2004 and 2010 (https://www.epa.gov/sites/production/files/2017-08/documents/method_202.pdf). Method 202 uses dry impingers and filters to collect CPM. The other method is the Conditional Test Method (CTM) 039 measurement of PM$_{2.5}$ and PM$_{10}$ (particulate matter with aerodynamic diameters $\leq$ 10 $\mu$m) emissions by dilution sampling (https://www3.epa.gov/ttn/tnv/ctm/ctm-039.pdf), which allows CPM to form in a manner that simulates the dilution and cooling processes of pollutants after being emitted into the atmosphere. The two measuring methods are both acceptable but have different emphases. Method 202 sticks to the CPM definition and measures what is defined as CPM. While the CTM 039 reflects what occurs in the atmosphere once the CPM precursors exit the stack (Cano et al., 2017).

In previous researches about the aerosol emission from Ammonia-WFGD systems, the most relevant measurements are done with an electrical low pressure impactor (ELPI) (Huang et al., 2016a, 2016b, 2017). ELPI is a fast-response instrument that provides transient tests for PM$_{10}$ concentrations and size distributions through the corona charge technology and cascade impactor classification (Keskinen et al., 1992; Maričić et al., 2000). It is widely used regarding aerosol researches (Marjamäki et al., 2000; Glover and Chan, 2004; He et al., 2015). Before entering the ELPI instrument, the raw flue gas is diluted and cooled with filtered dry air, which allows CPM to form in a diluted and low-temperature environment that is similar to the residence chamber in the CTM 039 method (Brachert et al., 2014). Theoretically, CPM could be included in ELPI measurement. But few researches verify that. (Maričić et al., 2000). Besides, ELPI gets the results based on assumptions that may be far from reality. Therefore, ELPI measurement cannot replace sampling methods. In contrast, CPM sampling measures the real PM emission with gravimetric methods that are more reliable.

CPM is difficult to remove due to its small sizes. Pei’s research (2015) showed that high-efficiency dust removal devices could hardly reduce the CPM emission. The test results of Li et al. (2017a) for an ultra-low-emission coal-fired power plant showed that the wet electrostatic precipitator (WESP) could reduce the FPM emission by nearly 60%, but could only reduce 22.2% CPM. Zheng et al. (2018) stated that the removal rate of CPM was 65.37% after WESP, much lower than that of FPM (94.93%). Fortunately, previous researches showed that FGD operations had significant effects on PM emissions (Huang et al., 2016b, 2017; Pan et al., 2015). Therefore, it might be a better solution if CPM emission could be controlled through desulfurizing parameter optimization.

To explore the possibility of reducing CPM emission through parameter optimizations, researches were done on the basis of an Ammonia-WFGD system to investigate the CPM emission characteristics and their feedbacks to parameter adjustments. The research work helped better understand the categories and the sources of PM emission from an Ammonia-WFGD system and provide basic data for CPM emission control. Since the flue gas might not enter directly into the atmosphere after desulfurization, Method
202 was selected to measure CPM in experiments. Besides, a new version ELPI instrument was also employed to show CPM emission characteristics more than just mass concentrations.

1. Materials and methods

1.1. Ammonia-WFGD system

The schematic diagram of the pilot-scale Ammonia-WFGD system is shown in Fig. 1. This system consists of a flue gas providing unit, a solution recirculation unit, and a desulfurization tower. The flue gas providing unit includes a roots blower, a gas flowmeter, an SO2 gas cylinder with a mass flow controller, a static mixer, and a high-power heater. A steady flow of room air is mixed with SO2 in the static mixer, which is afterwards heated to the desired temperatures to generate the simulated flue gas. The solution recirculation unit includes a desulfurizing solution tank, an oxidation blower, a heater, an agitator, two pumps, and a flow meter to control the solution flow. As the primary component of the WFGD system, the desulfurizing scrubber is installed with three levels of sprayers to convert the desulfurizing solution into droplets and a set of demisters at the outlet to intercept droplets. In the scrubber, the simulated flue gas and the sprayed solution droplets fully contact, during which processes SO2 is removed while new aerosols are generated. Outside the scrubber placed an isolated desulfurizing solution tank so as to simplify the adjustment of solution characteristics. The desulfurizing solution was taken from an industrial Ammonia-WFGD device. Aqueous ammonia is added continuously to keep a constant pH during the system running. The agitator ensures the solution mixing well. The SO2 concentrations before and after the WFGD are tested with a flue gas pollutants analyzer (ecom-J2KN, ecom GmbH, Germany).

In an ordinary experiment, the flue gas volume flow is set 80 Nm³/hr (Nm³: cubic meter at normal condition 273.15 K and 101.325 kPa), the flue gas temperature 100°C, the solution temperature 50°C, the solution pH 5.5, the solution mass concentration 15%, the liquid to gas ratio 12 L/Nm³, and the SO2 concentration 2857 mg/Nm³. These parameter settings are used as the standard operating conditions for this experimental system.

1.2. Aerosol measuring, sampling and analyzing

The US EPA Method 5 and Method 202 (with dry impingers) were combined to sample FPM and CPM after WFGD. The schematic diagram and the photograph of the sampling train are shown in Fig. 2a and b, respectively. The CPM sampling assemblies (A-2000, Environmental Supply Company, USA) include the condenser, the water dropout impinger, the modified Greenburg-Smith impinger, and the CPM filter. The other components, such as the FPM sampling probe and the auto-sampler, are purchased from Laoshan Mountain Electronic Instrument Factory. The emitted flue gas was withdrawn isokinetically with a sampling nozzle from the outlet of the Ammonia-WFGD system, which was heated to 125°C through a heating probe. The FPM was collected on a glass fiber filter maintained at the same temperature. After being dried at 105°C for 2 hr and resting in a dry container at room temperature for another 2 hr, the FPM filter was weighted with an analytical balance (AP125D, SHIMADZU, Japan) and so was the FPM mass determined. Following the FPM filter, a condenser cooled the flue gas to below 30°C, in which process CPM formed. The CPM was captured in the condenser, in the dry impingers, and on the CPM filter. Ultrapure water, acetone, and hexane were used to rinse the CPM collection part and the connecting tubes in between to get the water rinses and the organic rinses respectively. The CPM filter was extracted with ultrapure water and hexane and so we have the water extracts and organic extracts. The water rinses and
the water extracts were combined, dried, and weighted to get the inorganic mass in CPM samples. The organic mass in CPM samples could be obtained with the same procedure. The sum of the organic mass and the inorganic mass was the total CPM emission. Preliminary experiments were conducted to determine the appropriate sampling parameters. At least 4 parallel samples were taken for each experimental condition.

The chemical components of the samples were investigated with an inductively coupled plasma optical
emission spectrometer (ICP-OES) (Optima 8000, PerkinElmer, USA), an ion chromatography (IC) (ICS-2100, Dionex, USA), and an ultraviolet (UV) spectrophotometer (UV-1800, Mapada Instruments, China). The ICP-OES could measure metal elements such as Na\(^+\), K\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\).

The ammonia contents were determined with a UV spectrophotometer according to the Nessler’s reagent spectrophotometry. The IC measured the anion species such as SO\(_4^{2-}\), NO\(_3^-\), Cl\(^-\), and F\(^-\).

The morphology of the CPM collected in impingers and tubes was difficult to observe. Thus, a PM sampler (Dekati PM\(_{10}\) impactor, Dekati Ltd, Finland) was used to sample FPM and CPM, the assemblies of which are shown in Fig. 3. For FPM, flue gas was withdrawn isokinetically through the first sampling nozzle and a heating probe. The PM\(_{10}\) impactor was connected after the probe to sample FPM. Both the flue gas and the impactor were heated to 125°C to ensure the removal of uncombined water. For CPM sampling, flue gas was withdrawn through another sampling train (via sampling nozzle 2). A heated FPM filter was employed to remove FPM from the hot flue gas. A condenser cooled the flue gas to <30°C to initiate CPM formation. The water dropout impinger could avoid too much water entering the PM\(_{10}\) impactor and, meanwhile, spare time for CPM growth and stabilization. After these two parts, CPM became mature and stable, the morphology of which was representative. CPM was then collected by the PM\(_{10}\) impactor installed after the water dropout impinger. The morphology of the collected FPM and CPM was analyzed with a field emission scanning electron microscope (Ultra plus, Zeiss, Germany).

An electrical low pressure impactor plus (ELPI\(^+\), Dekati Ltd., Finland) was also employed to measure CPM size distribution (Fig. 4). More information on ELPI\(^+\) could be found in Järvinen’s research (Järvinen et al., 2014). It was connected after the water dropout impinger in Method 202, replacing the modified Greenburg-Smith impinger and the following instruments in Fig. 2a. CPM would be formed in the condenser with the temperature dropping. The water dropout impinger removed the condensed moisture and allowed CPM to grow and stabilize. After that, CPM could be measured with ELPI\(^+\).

2. Results and discussion

2.1. CPM emission characteristics

The Ammonia-WFGD system was run according to the standard operating conditions described in Section 1.1. The emitted aerosol concentrations were measured with both ELPI\(^+\) and Method 202. Fig. 5a shows the testing results from the sampling method, in which the TPM emission was about 139.7 mg/Nm\(^3\) with the FPM and the CPM accounting for 31.2% and 68.8%, respectively. The contribution of CPM was nearly twice that of FPM to the total aerosol emission from the system. Therefore, the CPM emission characteristics and its influencing factors were worthy of investigations for the purpose of reducing aerosol emission. The CPM size distribution was measured with ELPI\(^+\) and displayed in Fig. 5b. As can be seen, all CPM belongs to PM\(_{2.5}\) fraction, including mainly submicron particles. The cumulative distribution showed that over 95% of CPM was smaller than 0.2 μm. Previous research stated that large amounts of ultra-fine aerosols could be generated through NH\(_3\)–H\(_2\)O–SO\(_2\) reactions in Ammonia-WFGD processes, especially at low temperatures (Huang et al., 2016b). These reactions could be the possible sources of CPM formation.
The morphologies of the FPM and the CPM are shown in Fig. 6. The particulate matters in the FPM were much larger than those in the CPM, which were of different shapes and sizes (Fig. 6a). The particles in the CPM were submicron and mostly spherical which adhered to each other (Fig. 6b). The morphologies revealed the size and exterior characteristics of the FPM and the CPM, which agreed with the ELPI$^+$ testing results. The background in Fig. 6 was dark and greasy because the Apiezon grease L was applied to the surface of the aluminum foil to reduce the rebound of collected particles during sampling.

The CPM sampled at the standard conditions were divided into the organic part and the inorganic part. The weighing analysis showed that CPM contained mainly inorganic components, accounting for more than 96%. Similar high proportions of the inorganic fraction in CPM had been reported by previous researches (Corio and Sherwell, 2000; Yang et al., 2014; Pei, 2015). In order to confirm this result, the weighing analysis was also applied to the desulfurizing solution with the same procedure. The results showed that the organic components accounted for less than 16% of the total weight. Therefore, the low organic proportion in CPM was reasonable due to the fact that organic substances in the solution could hardly vaporize at desulfurization temperatures (below 100°C). The organic fraction in CPM was not important due to its little contribution to the total weight. Consequently, the focus was on the inorganic fraction in this paper, leaving the organic part analyzed only with the weighing method.

Chemical analysis was conducted on CPM samples. Fig. 7 showed quantitatively the cation and anion species contained in the CPM aqueous sample. The presence of Ca and Mg in the result was probably due to that some aerosols generated...
in the WFGD scrubber were too tiny to be collected by the FPM filter. Those containing Ca and Mg would penetrate the FPM filter and be collected as CPM. The CPM contained primarily $SO_4^{2-}$ and $NH_4^+$ which accounted for about 71% and 22% in weight ratio. This inferred that the CPM consisted mainly of ammonium sulfates or ammonium sulfites that were generated from the $NH_3-H_2O-SO_2$ reactions and the condensation processes. To further explore the CPM sources, control experiments were conducted in the absence of $SO_2$ in the flue gas at the standard conditions. The results in Fig. 8 showed that the CPM emission was about 27.8 mg/Nm³ without $SO_2$ in the flue gas, approximately 71.1% lower than the normal emission in the presence of $SO_2$. This suggested that about 71.1% of the CPM came from the $NH_3-H_2O-SO_2$ reactions, making it the main source of CPM emission. Consequently, the key to reducing the CPM emission from an Ammonia-WFGD system was to inhibit the $NH_3-H_2O-SO_2$ reactions.

The $NH_3-H_2O-SO_2$ reactions were generally controlled by the ammonia concentration, the $SO_2$ concentration, the water vapor concentration, and the reaction temperature. For EPA Method 202, the temperature was required to be lower than 30°C during CPM sampling, which was unchangeable. The water vapor was saturated due to the huge temperature reduction. The $SO_2$ concentration was related to the initial $SO_2$ concentration in the flue gas and the desulfurization efficiency of the WFGD system. The initial $SO_2$ concentration could not be chosen manually and usually varied in different systems. The desulfurizing efficiency had been investigated in many researches but the output $SO_2$ concentration was limited by laws and regulations, which was not flexible. The ammonia concentration, namely the ammonia emission, was the one that was ignored but worthy of investigation for the purpose of reducing CPM emission. It has been discussed in previous researches that the ammonia emission from Ammonia-WFGD was sensitive to the flue gas temperature, the solution temperature, the solution concentration, and the solution pH (Huang et al., 2016b, 2017, 2020). Therefore, these parameters were chosen as influencing factors to explore the CPM emission variations.

It should be noted that the two aerosol formation mechanisms were not isolated. $NH_3-H_2O-SO_2$ reactions occurred in the desulfurizing scrubber and thus the generated aerosols could be collected in FPM, such as adhering to larger particles. Some of the entrained droplets became very tiny after dehydration at high temperatures and could probably penetrate the FPM filter and be captured as the CPM.

2.2. Influences of desulfurizing parameters on CPM emission

2.2.1. Flue gas temperature

The flue gas temperature before WFGD was adjusted to 60, 100, and 140°C, while the other parameters remained the same as in the standard conditions. At each temperature was the CPM emission measured, with the results displayed in Fig. 9. As can be seen, the CPM emission increased from 61.6 to 208.0 mg/Nm³ when the flue gas temperature rose from 60 to 140°C. The CPM increase was faster when the temperature exceeded 100°C than that in the lower temperature range. The variation of the CPM emission was similar to that of normal aerosols reported in previous researches (Huang et al., 2016b). The main reason for the CPM increase was about the $NH_3-H_2O-SO_2$ reactions, which occurred both in the WFGD scrubber and in the CPM sampling train. High flue gas temperature inhibited the reactions in the scrubber (Huang et al., 2017), leaving more $NH_3$ and $SO_2$ passing through the FPM filter and entering CPM collecting part. The unreacted $NH_3$ and $SO_2$ thus acted as reactants for the reactions in the CPM sampling train and boosted the CPM formation. The inhibitory action on the $NH_3-H_2O-SO_2$ reactions in the scrubber increased with temperatures rising (Huang et al., 2017), which trend agreed with the CPM variation. Additionally, higher temperatures raised the actual flue gas velocity in the scrubber, promoting the droplet entrainment by flue gas and hence the aerosol generation (Pan et al., 2019). Some of the generated aerosols with tiny sizes penetrated the FPM filter interception and contribute to CPM emission.

2.2.2. Desulfurizing solution temperature

The temperatures of the desulfurizing solution also affected the CPM emission despite that the CPM was formed at a
controlled temperature during the sampling process. Based on a normal WFGD experiment, the solution temperature was adjusted to 30, 50, and 70 °C, respectively. The CPM emission was tested in each condition with the results shown in Fig. 10. As can be seen, the CPM emission was approximately 73.1 mg/Nm³ at 30 °C, which increased to 234.0 mg/Nm³ when the solution temperature rose to 70 °C. The possible explanation was that, in the scrubber where solution droplets and flue gas coexist, the partial pressure of ammonia in the gas phase was positively correlated to the solution temperature according to Henry’s law (Shi et al., 1999; Li et al., 2017b). Therefore, in the state of equilibrium, more gaseous ammonia would be released to the flue gas at higher solution temperatures. The gaseous ammonia didn’t tend to be consumed in the scrubber because the higher solution temperature also increased the environmental temperature in the scrubber, which was not favorable for NH₃–H₂O–SO₂ reactions, thus saving more unreacted NH₃ and SO₂ for CPM formation. Note that the CPM raised slowly when the solution temperature increased from 30 to 50 °C while the increase was tremendous when the temperature rose from 50 to 70 °C. Such a phenomenon agreed with previous researches which stated that the inhibition of the NH₃–H₂O–SO₂ reactions started at around 50 °C and became dramatic at temperatures higher than 65 °C (Huang et al., 2017). Therefore, it is suggested that the solution temperature should be kept low to diminish CPM formation from reactions.

2.2.3. Desulfurizing solution concentration
The WFGD solution concentration was also important in affecting CPM emissions. Experimental investigations were done with different initial desulfurizing solution concentrations. The maintaining of the solution concentrations was realized by controlling the discharge of recycling solution and the adding of fresh water. CPM samples were taken when the solution concentrations stabilized at certain values. From the testing results in Fig. 11, the CPM emission increased steadily with the solution concentration rising, being 68.2, 96.2, and 142.3 mg/Nm³ for the concentrations of 10%, 15%, and 20%, respectively. The ammonia content in the solution increased with the solution concentration, which consisted of mainly NH₃–H₂O and NH₄⁺. Due to the constant pH of the desulfurization solution, the concentrations of NH₃–H₂O and NH₄⁺ would both rise with solution concentrations while keeping a constant ratio between them. The increase of NH₃–H₂O in the liquid phase enhanced the mass transfer of ammonia from the liquid phase to the gas phase and, at the same time, raised the partial pressure of ammonia in the flue gas (Li et al., 2017a; Huang et al., 2020). Consequently, more ammonia escaped from solution to flue gas and exist as gaseous NH₃. Some of the gaseous NH₃ reacted to form aerosols in the scrubber and the other became parts of CPM after penetrating FPM filters. Besides, the reaction-generated aerosols in the scrubber had very tiny sizes, which might not be 100% collected by FPM filters. It is possible that some of them got through the FPM filter and contributed to CPM formation.

2.2.4. Desulfurizing solution pH
The Ammonia–WFGD system was operated at the standard conditions with the desulfurizing solution pH varying between 4.5 and 6.5. The desulfurizing efficiencies were monitored because they were usually influenced more by the pH changes than the other parameters. Fig. 12 presented the CPM emission concentrations and the SO₂ removal efficiencies at each pH condition. The solution pH increase caused the rise of both SO₂ removal efficiencies and CPM emissions. On one hand, the pH variation was realized by changing the injection rate of aqueous ammonia into the solution. The higher pH meant more ammonia injection at one time, which led to more ammonia content in the solution and enhanced the dissolution and the chemical absorption of SO₂. The SO₂ removal efficiency was hence promoted (Dou et al., 2009). On the other hand, ammonia mainly existed as NH₃–H₂O and NH₄⁺ in the liquid phase with the relationship shown with the following equation (Darde et al., 2012; Chu et al., 2016).

\[
\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-
\]  

(1)

As the equation showed, more ammonia content in the solution yielded more NH₃–H₂O and NH₄⁺. Meanwhile, the higher pH meant the excess concentration of OH⁻ in the
solution, resulting in a higher ratio of \( \text{NH}_3 \cdot \text{H}_2\text{O} \) to \( \text{NH}_4^+ \) (Huang et al., 2020). Consequently, the \( \text{NH}_3 \cdot \text{H}_2\text{O} \) concentration ascended in the solution, leading to more gaseous \( \text{NH}_3 \) in the flue gas and thus more CPM formation according to the discussions in Section 2.2.3.

The research results showed that the CPM emission could possibly be controlled by lowering the solution pH, but the desulfurizing efficiency should also be watched. The CPM control effects regarding pH adjustment could be determined by the combined consideration of the \( \text{SO}_2 \) removal efficiency and the CPM reduction. No pH adjustments were suggested in the case of severe \( \text{SO}_2 \) emission restrictions. In the requirement of the \( \text{SO}_2 \) removal efficiencies of more than 95%, the solution pH should be no less than 5.0. The solution pH could be around 4.5 if the desulfurization efficiencies of 90% were satisfying, where the reduction of CPM emission was around 48.9% according to the measurements.

### 2.3. Summary of parameter influences

From the discussion of the experimental results, it is clear that all the above parameters have influences on the CPM emission to different extents. To evaluate quantitively the inhibitory actions they have on the CPM emission, the utmost CPM reduction rate for one parameter \( R_{\text{max}} \) is defined as follows:

\[
R_{\text{max}} = \left( E_{\text{max}} - E_{\text{min}} \right) / E_{\text{std}} \times 100\% \tag{2}
\]

where \( R_{\text{max}} \) (%) is the utmost CPM reduction rate that is caused by some parameter; \( E_{\text{std}} \) (mg/Nm\(^3\)) is the CPM emission at the standard conditions; \( E_{\text{min}} \) (mg/Nm\(^3\)) is the lowest CPM emission when the optimization of one parameter reaches its limit.

Each parameter has an upper limit and a lower limit, one of which leads to the utmost CPM reduction and the other ends with a tremendous CPM emission soar. And the limits of each parameter can be determined if applied in an industrial device. For example, in an industrial Ammonia-WFGD system, the flue gas temperatures before the scrubber are usually within 60–140°C. The temperatures of 60 and 140°C can be seen as the lower and the upper limit of flue gas temperature. Combined with our experimental results, the temperature of 60°C results in the utmost CPM reduction rate and, meanwhile, 140°C causes the utmost CPM emission increase. Likewise, the CPM reduction rate reaches the maximum when the solution temperature becomes 30°C. The desulfurization solution concentrations are different in various industries but seldom lower than 10%. Therefore, 10% can be seen as the lower limit of the concentration. In regard to the solution pH, the value should be higher than 4.5 to ensure the desulfurizing efficiencies of over 90%. The calculation results of the utmost CPM reduction rates due to each parameter are shown in Fig. 13. In order to have a thorough evaluation of each parameter, the CPM emission increase caused by their opposite shifts is also calculated and shown in Fig. 13. As can be seen, the positive values of \( R_{\text{max}} \) represent the utmost inhibitory actions each parameter has on CPM emission, while the negative ones indicate the promotion effects when these parameters shift oppositely to the same extent. According to the comparison of the positive values, the solution pH has the best control effect on CPM emission with the reduction rate being nearly 49%. Correspondingly, the promotion of the CPM emission caused by solution pH increase also ranks first among these parameters, being around –174%. The solution pH has the dominant influences on the CPM emission among the discussed parameters. The CPM reduction rate is 36% and –116% for the flue gas temperature variations. For the solution concentration, the reduction and the promotion of CPM emission are both low, being 29% and –48%, respectively. The CPM emission may be least sensitive to the solution concentration from an overall perspective. The CPM reduction rate for the solution temperature is 24%, being the lowest among the four parameters. But its promotion to the CPM emission is as high as –143%, only second to the solution pH. Optimizing the solution temperature may not reduce CPM emission significantly, but increasing it would cause a great emission boost.

In summary, the desulfurizing parameters have great influences on CPM emission. The parameter optimizations are promising in reducing CPM emission by preventing its formation, in which the pH optimization alone can abate nearly half of the emission. They can be used as auxiliary methods when external purifying devices are employed.

![Fig. 12: CPM emission and desulfurization efficiencies influenced by solution pH variations. Error bar: n ≥ 4.](image-url)

![Fig. 13: Utmost CPM reduction rates caused by desulfurizing parameters.](image-url)
to deal with CPM emission problems. Furthermore, it is dispensable to waste space or money on new CPM-purifying devices in case that the parameter optimizations alone could meet the CPM reduction requirements. In addition, the parameters should be paid attention to all the time because the inappropriate variations of them shall boost CPM emission.

3. Conclusions

The aerosol emissions from an Ammonia-WFGD system are complicated, in which the condensable PM accounts for a considerable proportion. In order to study the CPM emission characteristics, EPA Method 202 was applied to measure the CPM mass concentration, the ELPI⁺ was used to show the size distributions, and the Dekati PM10 impactor was employed to sample CPM for morphology analysis. Some essential parameters were selected to explore how they influenced the CPM emission. The testing results were analyzed to investigate the possibilities of eliminating CPM emission by desulfurizing parameter optimizations. On the basis of the results and discussions, conclusions are drawn and listed below.

(1) The Ammonia-WFGD system can emit large quantities of aerosols, in which CPM weighs higher than FPM, accounting for about 68.8% in terms of the mass concentration.

(2) More than 96% of the CPM is inorganic, which is consistent with the high proportions of SO₄²⁻ (71%) and NH₄⁺ (22%) in CPM.

(3) The CPM emitted from the Ammonia-WFGD system contains mostly submicron particles, about 71.1% of which are generated from NH₄H₂O–SO₃ reactions.

(4) CPM emission can be reduced to different extents by the decrease of the WFGD parameters such as the flue gas temperature, the desulfurizing solution temperature, the solution concentration, and the solution pH.

(5) The parameter optimizations are promising in reducing CPM emission, in which the pH variation alone can result in nearly 49% CPM reduction.

(6) The opposite variations of the parameters can boost significantly CPM emission. Therefore, any parameter adjustment should be treated cautiously, especially when it is used as an auxiliary method in solving CPM emission problems.

Acknowledgments

This work was supported by the National Key Research and Development Program of China (No. 2016YFC0203703), the National Natural Science Foundation of China (Nos. 51576039, 51806107 and 21276049), the Scientific Research Foundation of Graduate School of Southeast University (No. YBJJ1610), and the Research Innovation Program for College Graduates of Jiangsu Province (No. KYLX16_0283).

References


