Study on the condensable particulate matter removal characteristics of air pollution control devices in a Chinese ultra-low emission coal-fired generating unit

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Abstract. Condensable particulate matter (CPM) belongs to PM$_{2.5}$. In addition, it is one of PM$_{2.5}$ main contributors. But CPM emissions are often overlooked in coal-fired power plants. As a result, this paper studies the removal characteristics of (CPM) from air pollution control devices (APCDs) in a Chinese ultra-low emission coal-fired generating unit. The quality and content of flue gas particles, including CPM and filterable particulate matter (FPM), were measured at four points: the selective catalytic reduction (SCR) input, air preheater (APH) inlet, electric precipitator (ESP) outlet, and wet flue gas desulphurization (WFGD) outlet. The removal characteristics of each APCD were studied. Within the scope of this study, it is found that: ① CPM emission concentration accounts for 94.9% of total particle emission concentration, and is higher than the ultra-low particulate matter outflow guidelines for coal-fired power plants in China; ② WFGD has the highest CPM inorganic component removal ratio of 97.02%, and ESP has the highest CPM organic component removal ratio of 58.46%, among APCDs; ③ SO$_4^{2-}$, NH$_4^+$, F$^-$, and Cl$^-$ are the most abundant water-soluble ions in CPM.

1. Introduction

Power plant flue gas toxins are an vital environmental protection subject. The particulate matter released into the environment from coal-fired control plants is called total particulate matter (TPM), which incorporates FPM and CPM. With respect to the quality relationship between CPM and FPM, most researchers accept that the CPM content has possessed a major position in TPM [1]. In spite of the fact that CPM has pulled in a part of consideration, the research on CPM is still incomplete. CPM could be a gas phase in the flue environment, but it is changed into liquid phase or solid phase within the climatic environment [2]. Investigate appears that CPM is the foremost imperative component of PM$_{2.5}$ radiated by coal-fired power plants [3]. PM$_{2.5}$ will gather overwhelming metals and organic matter, which is greatly destructive to the environment and human wellbeing. In most nations, CPM isn't tested, so the level of particulate matter emanation will be genuinely belittled.

CPM is partitioned into organic and inorganic components, but their mass ratios are different in different studies. In some research, inorganic components account for the majority. For example, it is studied by CORIO LA and SHERWELL J [4] that inorganic components accounted for 77% of the
CPM mass. In another part of the study, it is believed that organic components in ultra-low-emission power plants account for the majority. For example, research by Li J et al. [5-6] have shown that CPM organic components account for 54.4%-81% of all CPM mass. Water soluble ions play a critical part in CPM inorganic components. Water soluble anions mainly primarily incorporate SO$_4^{2-}$, NO$_3^-$, Cl$^-$, NH$_4^+$, and F$^-$, and their other gaseous precursors are SO$_3$, NOx, HCl, NH$_3$, and HF [5-6]. The water-soluble metal ions basically incorporate K$^+$, Na$^+$, and Ca$^{2+}$ because these elements are highly volatile. Some researchers have also studied the mass concentration changes of CPM and FPM in one or some APCDs to study the effect of common APCDs to remove CPM and FPM. However, most of them only study the effect of one or a few devices on the removal of CPM and FPM, and do not cover the removal effect of all APCDs on CPM and FPM. For example, QI Z et al. [7] focused on the impact of low-temperature electric precipitator on the emission characteristics and removal ratio of particulate matter. Therefore, this paper takes a Chinese ultra-low-emission coal-fired unit as an example to study the removal ratio of APCDs on particulate matter, which includes FPM, CPM, CPM organic components, CPM inorganic components, and CPM water-soluble ions, and analyse the reasons.

2. Materials and Methods

2.1. Unit overview
We test particulate matter in a 600 MW ultra-low emission coal-fired unit, and the power generation load during the test is 75%. APCDs incorporate SCR, APH, ESP and WFGD in turn. Among them, the SCR denitrification device is equipped with three layers of catalysts, and the flue gas first passes through two layers of honeycomb catalysts and then a layer of plate catalysts; the electrostatic precipitator has 2 chambers and 5 electric fields; the desulfurization device is a limestone-gypsum wet desulfurization. The sampling points are SCR inlet, APH inlet, ESP outlet and WFGD outlet.

2.2. CPM sampling method
FPM and CPM are examined at the same time, in which EPA strategy 202A [2] is embraced. Figure 1 appears the test procedure and equipment. FPM is catching from pipe gas by quartz filter membrane, which is warmed to over 120°C. After that, Only CPM is left. Isokinetic testing is utilized. After sampling, purge with nitrogen to avoid the influence of SO$_2$ and other gases on the results. Preserve the quartz filter membrane, which retains the FPM. Use deionized water and acetone solution to rinse the condenser tube, buffer bottle and relevant connectors successively to obtain the organic and inorganic components in CPM respectively. FPM is obtained through the quartz filter membrane. The filter membrane and flushing fluid are sent to the laboratory for analysis to obtain the mass concentration of each substance. In this study, three tests were performed for each inspecting area, and three sets of tests were gotten. The ultimate result is the normal of the three.
3. Results and Discussion

3.1. Concentration changes of FPM and CPM along the flue gas system

Figure 2 shows the concentration of FPM and CPM at the four measuring points. It can be observed that the removal radio of FPM and CPM is different for each environmental protection equipment. The total removal radio of FPM and CPM are 99.99% and 90.71%, respectively. The removal radio of APCDs for CPM is lower than that of FPM, and the CPM emission concentration accounts for 94.9% of TPM. The FPM emission concentration is 1.75 mg/Nm$^3$. The CPM emission concentration is 32.7 mg/Nm$^3$, which is much higher than 5 mg/Nm$^3$. 5 mg/Nm$^3$ is the ultra-low emission standard in Chinese coal-fired power plants. This will lead to the disappreciation of the particulate emissions level.

For FPM, the removal radio of SCR, ESP and WFGD are 47.27%, 99.99% and 23.24%, respectively. For CPM, the removal radio of SCR, ESP and WFGD were 2.16%, 19.02% and 88.27%, respectively. For FPM, the equipment with the highest removal radio is ESP. In this paper, the removal radio of ESP was 99.99%. ESP was originally developed to remove FPM. And in China, the removal rate of ESP for FPM is basically above 99%. For CPM, the equipment with the highest removal radio is WFGD, which may be related to the composition of CPM. We will analyze the components of CPM in Section 2.2 and Section 2.3.
3.2. Concentration variation of organic and inorganic components in CPM along the flue gas system

Figure 3 shows the mass concentrations in CPM at four measuring points. The ratio of organic and inorganic components changes dynamically. At the SCR inlet, APH inlet and ESP outlet, the mass concentration of inorganic components accounts for the majority. But at the outlet of WFGD (where particulate matter is discharged to the outside), the mass concentration of organic components accounts for the majority. This is consistent with the conclusions in the literature [5-6] that the organic components of CPM emitted by ultra-low-emission coal-fired power plants account for the majority. Moreover, for the organic components of CPM, the removal radio of SCR, ESP, and WFGD are 47.87%, 58.46% and 23.46%, respectively. For CPM inorganic components, the removal efficiencies of SCR, ESP and WFGD are 11.23%, 7.10% and 97.02%, respectively.

For CPM organic components, ESP has the highest removal radio among all APCDs. There are two main reasons for this. The first reason is that in ESP, FPM can adsorb organic components of CPM, and then organic components are removed by ESP along with FPM. The second reason is that the high voltage of ESP can destroy some organic components [7].

Among all APCDs, WFGD has the largest removal radio for inorganic components. The gaseous precursors SO$_3$, HCl and HF of inorganic components SO$_4^{2-}$, Cl$^-$ and F$^-$, are acidic, and they account for a large proportion of the inorganic components [4] (Figure 4). The slurry sprayed by WFGD is alkaline and can react with acidic gaseous precursors. Therefore, the inorganic components in CPM can be removed well in WFGD. Figure 2 shows that for CPM, the equipment with the highest removal radio is WFGD. This is because the CPM produced by the boiler contains more inorganic components (Figure 3), and the impact of removing inorganic components by WFGD is nice.

SCR can increase the organic components and slightly reduce the inorganic components. Studies have shown that in the process of SCR denitration, volatile organic compounds will be generated [8], so the CPM organic components increase. As for the alter within the quality of the inorganic components, it is primarily related to the water-soluble ions SO$_4^{2-}$ and NH$_4^+$. In SCR, 0.5%-1.5% of SO$_2$ will be catalyzed to produce SO$_3$, which is the gaseous precursor of the inorganic component SO$_4^{2-}$ of CPM. Moreover, if the NH$_3$ is sprayed excessively, the escaped NH$_3$ will become the gaseous precursor of the inorganic component NH$_4^+$. SO$_2$ reacts with fugitive ammonia to produce NH$_4$HSO$_4$ and (NH$_4$)$_2$SO$_4$. The melting point of NH$_4$HSO$_4$ is 147°C, the melting point of (NH$_4$)$_2$SO$_4$ is 235-280°C, and the operating temperature of SCR is 350-400°C. In the CPM sampling device, the temperature in the FPM section is 120°C, and the temperature in the CPM section is lower than 30°C. Therefore, during the sampling process, NH$_4$HSO$_4$ and (NH$_4$)$_2$SO$_4$ will not appear in the CPM section. That is, although both SO$_3$ and NH$_3$ are gaseous precursors of inorganic components in CPM, their products NH$_4$HSO$_4$ and (NH$_4$)$_2$SO$_4$ do not belong to CPM. Although the gaseous precursors SO$_3$ and NH$_3$ of CPM inorganic components are generated and increased in SCR, they reacted to generate non-
CPM NH₄HSO₄ and (NH₄)₂SO₄. Therefore, the test results of CPM inorganic components are slightly reduced. This can also be verified in the analysis of water-soluble ion concentration in section 2.3.

3.3. **Distribution characteristics of inorganic water-soluble ions in CPM along flue gas system**

![Pie charts showing the distribution of inorganic water-soluble ions in CPM along different points in the flue gas system.](image)

Figure 4. Proportion of each inorganic water-soluble ion distribution.

The concentration of inorganic water-soluble ions in CPM is always changing with the advance of the vent gas process. Figure 4 appears the dispersion of inorganic water-soluble particles in CPM. It can be observed that at the SCR inlet, APH inlet and ESP outlet, the three largest inorganic water-soluble ions are Cl⁻, F⁻ and SO₄²⁻ in sequence; while at the WFGD outlet, the four largest ions in sequence are SO₄²⁻ and NH₄⁺, F⁻, and Cl⁻. This is also in line with the emission situation of literature research [5-6]. Figure 5 shows the mass concentrations of these four ions at four measuring points.

It can be seen from Figure 5 that at the SCR inlet, APH inlet and ESP outlet, the mass concentrations of Cl⁻ and F⁻ are higher than SO₄²⁻ and NH₄⁺. But at the total outlet, that is, the WFGD outlet, the situation is reversed. This shows that in this study, the proportion of each ion changes dynamically with the progress of the flue gas. The gaseous precursors of SO₄²⁻, F⁻ and Cl⁻ in CPM are SO₃, HF and HCl, respectively. The source of NH₄⁺ is the escaped ammonia in SCR, that is, NH₃ that has not reacted with NOₓ.
Figure 5. Mass concentrations of the four water-soluble ions with the highest.

The reason why Cl\textsuperscript{-} and F\textsuperscript{-} are removed in a large amount in WFGD and in a small amount in SCR and ESP is that the slurry sprayed by WFGD is alkaline and can undergo acid-base neutralization reaction with gaseous precursors HF and HCl. The reason why NH\textsubscript{4}\textsuperscript{+} and SO\textsubscript{4}\textsuperscript{2-} are largely removed in APH and ESP is that the temperature in APH and ESP decreases, which causes the gaseous precursors NH\textsubscript{3} and SO\textsubscript{3} of NH\textsubscript{4}\textsuperscript{+} and SO\textsubscript{4}\textsuperscript{2-} to react to form NH\textsubscript{4}HSO\textsubscript{4}. If it runs in this way for a long time, it may cause APH blockage and lower ESP dust removal ratio, which requires attention. The reason for the increase of NH\textsubscript{4}\textsuperscript{+} in SCR is that when ammonia is sprayed in SCR, part of the ammonia does not react with NO\textsubscript{X} to form fugitive ammonia.

4. Conclusions
In this paper, the CPM removal characteristics of APCDs from a coal-fired generating unit in China are studied. The flue gas particles including CPM and FPM were sampled at the four positions. Furthermore, their quality and composition were analysed. The study found:

1) Within the scope of this study, the CPM emission concentration accounts for 94.9% of the TPM. In addition, the CPM emission concentration is much higher than the FPM emission concentration, and it is additionally higher than the ultra-low outflow guidelines of coal-fired power plants in China. This demonstrates the importance and necessity of CPM research. In addition, the organic component accounts for most of the total quality of CPM.

2) Among the APCDs involved in this article, WFGD has the highest CPM inorganic component removal radio of 97.02%, and ESP has the highest CPM organic component removal radio of 58.46%. This is because in ESP, CPM organic components are removed by ESP along with FPM, and high voltage can destroy some organic components. WFGD can remove SO\textsubscript{3}, HCl and HF through acid-base reaction, which are the gaseous precursor of the CPM inorganic components SO\textsubscript{4}\textsuperscript{2-}, Cl\textsuperscript{-} and F\textsuperscript{-}, respectively.

3) Inside the scope of this consider, the CPM inorganic water-soluble particles with the most noteworthy mass concentration are: SO\textsubscript{4}\textsuperscript{2-}, NH\textsubscript{4}\textsuperscript{+}, F\textsuperscript{-}, and Cl\textsuperscript{-}.

In future work, other than customary APCDs, environmental protection equipment should be studied and added to achieve the goal of controlling CPM, particularly the organic component. The control of CPM inorganic components can be accomplished by controlling several ions with relatively high content, such as SO\textsubscript{4}\textsuperscript{2-}, NH\textsubscript{4}\textsuperscript{+}, F\textsuperscript{-}, and Cl\textsuperscript{-}.

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