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Influence of flue gas desulfurization (FGD) installations on emission characteristics of $PM_{2.5}$ from coal-fired power plants equipped with selective catalytic reduction (SCR)[☆]

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ABSTRACT

Flue gas desulfurization (FGD) and selective catalytic reduction (SCR) technologies have been widely used to control the emissions of sulphur dioxide (SO_2) and nitrogen oxides (NO_X) from coal-fired power plants (CFPPs). Field measurements of emission characteristics of four conventional CFPPs indicated a significant increase in particulate ionic species, increasing $PM_{2.5}$ emission with FGD and SCR installations. The mean concentrations of $PM_{2.5}$ from all CFPPs tested were 3.79 ± 1.37 mg/m^3 and 5.02 ± 1.73 mg/m^3 at the FGD inlet and outlet, respectively, and the corresponding contributions of ionic species were 19.1 ± 7.7% and 38.2 ± 7.8%, respectively. The FGD was found to enhance the conversion of NH_3 slip from the SCR to NH_4^+ in the $PM_{2.5}$, together with the conversion of SO_2 to SO_4^{2-}, and increased the primary NH_4^+ and SO_4^{2-} aerosol emissions by approximately 18.9 and 4.2 times, respectively. This adverse effect should be considered when updating the emission inventory of CFPPs and should draw the attention of policy-makers for future air pollution control.

1. Introduction

China accounted for 50.2% of the total world coal consumption, with 44.8% of coal consumed nationwide being used for electricity generation at the end of 2015 (National Bureau of Statistics of China, 2016; British Petroleum, 2016; US Energy Information Administration, 2016). Consequently, coal-fired power plants (CFPPs) are considered a major source of primary fine particulate matter ($PM_{2.5}$) and precursors of secondary $PM_{2.5}$ (sulphur dioxide (SO_2) and nitrogen oxides (NO_X)). In recent years, the eastern part of China has suffered from severe pollution related to $PM_{2.5}$. Notably, sulphate-nitrate-ammonium (SNA) aerosol account for nearly one third of the $PM_{2.5}$ during the haze episodes in megacities such as Beijing and Shanghai (Huang et al., 2014). The gas-to-particle conversion, i.e., formation of new particles from SO_2, NO_X and ammonia (NH_3, mainly from agricultural field and animal grazing) emissions is considered to be the major cause of SNA aerosol.

To meet the very strict emission standards for air pollutants, the vast majority of CFPPs have been equipped with flue gas desulfurization (FGD) and denitrification installations to reduce the emissions of SO_2 and NO_X, respectively. The limestone-based wet FGD and ammonia-based selective catalytic reduction (SCR) are now the most commonly used technologies for SO_2 and NO_X removal, respectively. Until 2015, the installed capacity of CFPPs equipped with FGD and SCR accounted for 92.8% and 95.0% of the total installed capacity (895 GW), respectively, exceeding the total installed capacity of CFPPs operating in the United States, European Union, Japan and India together (817 GW) (Liu et al., 2016a; EndCoal, 2016).

It is expected that a substantial reduction in SO_2 and NO_X emissions and, therefore, air quality improvement will be achieved after widespread application of these flue gas cleaning systems. However, the FGD and SCR installations may cause adverse effects as additional primary particulate matter emissions increase (Electric Power Research Institute, 2012; Lonsdale et al., 2012;

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Srivastava et al., 2004). Several studies have shown that entrainment of gypsum (a product of the FGD) slurry could increase primary $PM_{2.5}$ emissions and change particle size and composition concurrently (Córdoba, 2015; Meij and Te Winkel, 2004; Wang et al., 2008). Additionally, NH_4^+ was expected to be emitted into the atmosphere along with gypsum slurry entrainment, since excessive NH_3 (as a reducing agent) slipped from the SCR is partly absorbed by the recirculation slurry in an FGD, where ammonium (NH_4^+) is formed from NH_3 and accumulates to relatively high concentrations.

To date, little attention has been paid to the influence of the NH_3 slip through the FGD process and the emission characteristic of primary $PM_{2.5}$ from CFPPs, although NH_3 emission from fossil fuel combustion has been found to have significant impacts on air quality (Pan et al., 2016c). The purpose of this study is to investigate how the FGD affects primary $PM_{2.5}$ emissions from CFPPs equipped with SCR. We conducted real-time measurements of particle size distribution from four conventional CFPPs in China. The size-resolved chemical composition of $PM_{2.5}$ and gaseous ammonia concentrations of the flue gas were also measured.

2. Methodology

Four conventional pulverized coal-fired power plants (PP1-PP4; with generation capacity of 300 MW for PP1 and PP3, 200 MW for PP2 and 600 MW for PP4) were selected for $PM_{2.5}$ emission characterization in this study. Each boiler employed low NO_X combustion technology and an ammonia-based SCR system for NO_X removal, followed by electrostatic precipitators (ESPs) and a limestone-based FGD scrubber in sequence. In PP1, conventional ESPs were located after the SCR units and operated at a temperature of about 130 °C. Except for PP1, each boiler employed low temperature ESPs that operated at 90 °C to reduce the fly ash resistivity to achieve higher collection efficiency (Wang et al., 2015).

The sampling procedures for $PM_{2.5}$ based on the dilution sampling method were detailed in our previous study (Li et al., 2015). The flue gas sample was introduced in a jet along the axis of the dilutor and then mixed with the dilution air. The flow rate of dilution air was kept constant under a condition of 2 bars over pressure and the temperature was maintained equal to the flue gas temperature. This enables the prevention of undesired condensation or nucleation of volatile components due to a temperature drop. A similar secondary ejector dilutor draws a constant volume flow rate from the primary stage. The sample air was further diluted with filtered ambient temperature air to a high enough dilution ratio to quench nucleation and condensation, providing an overall dilution ratio of about 64. We used an electrical low-pressure impactor (ELPI, Dekati Ltd., Finland) to measure, in situ, the size distribution of the $PM_{2.5}$ (from 0.03 to 2.5 μm in diameter, divided into ten size fractions) for PP1 and PP2. Additionally, a new electrical low-pressure impactor (ELPI+, Dekati Ltd., Finland, which measured the sizes from 0.006 to 2.5 μm in diameter, divided into 14 size fractions) was employed for PP3 and PP4. For each FGD scrubber, the flue gas was measured at the inlet and outlet simultaneously.

The size-segregated particulate matter was collected on aluminium foil attached to the collection substrates with Apiezon L grease for gravimetric measurement and on a Teflon filter for chemical analysis. The sampling time for $PM_{2.5}$ was 90 min at each site to obtain enough samples for chemical analysis. At the wet FGD outlet, flue gas was also sampled for NH_3 content by a cellulose filter impregnated with citric acid following a quartz filter to remove particles with a sampling time of 15 min.

Due to deficient PM sample collected in each stage of ELPI/ELPI + for soluble-ions analysis, we combined the samples from several adjacent stages into three different bulk samples using in accordance with the size fractions of <0.1 μm, 0.1–1.0 μm and 1.0–2.5 μm. Teflon filters were extracted in an ultrasonic bath for 30 min with 15 mL ultrapure water in a capped plastic tube. The ultrasonic bath water was mixed with ice bags to prevent overheating. The major anions (Cl^-, F^-, NO_3^- and SO_4^{2-}) and cations (K^+, Ca^{2+}, Na^+, Mg^{2+} and NH_4^+) of each extraction were determined by ion chromatography (Dionex ICS-2000, Thermo Fisher Scientific Inc., USA). The cellulose filters were also extracted by ultrapure water and analysed for NH_4^+ concentration by ion chromatography.

3. Results

3.1. Size distributions of $PM_{2.5}$ at inlet and outlet of the FGD

The distribution of the number concentration of $PM_{2.5}$ at the inlet of the FGD showed at least two distinct modes (Fig. 1): (i) a submicron mode with peak diameter around or less than 0.1 μm; and (ii) a supermicron mode with peak diameter larger than 1.0 μm. A number of previous studies have also found similar results so that it is generally called a bimodal distribution (Fraboulet et al., 2007; Li et al., 2009; Lind et al., 1996; Mohr et al., 1996; Niemelä et al., 2009; Ylätalo and Hautanen, 1998). Compared to PP1, PP2-PP4 did not show such a clear supermicron mode at the FGD inlet. This is probably due to the equipment of low temperature electrostatic precipitators, which are considered to be more effective at removing the supermicron mode particles than the conventional ESPs. As ELPI + measurement size range be extended down to 7 nm, it was found that the peak particle size in PP4 (~0.02 μm) was much smaller than the other power plants (~0.1 μm). The observation of the ultrafine mode (with peak diameter around 20 nm) particles after the ESPs indicated the formation of NH_4^+ salts (NH_4HSO_4 or $(NH_4)_2SO_4$) from slipped NH_3 in the ESPs, because there was in principle enough NH_3 and SO_3 in the flue gas (Li et al., 2015).

The size distribution markedly changed when flue gas had passed through the FGD scrubbers (Fig. 1). The number concentration greatly increased, with a clear peak in diameter varying from 0.03 μm to 0.1 μm. By FGD, the number concentration of particles at peak size increased by a factor of 1.99, 3.57, 1.19 and 1.43 for these four CFPPs, respectively. The average number concentration of $PM_{2.5}$ for all power plants at the FGD inlet was 9.77×10^5 $\#/cm^3$ with a range of 1.09×10^5 $\#/cm^3$ to 6.49×10^6 $\#/cm^3$. At the FGD outlet, the average number concentration was almost doubled to 1.94×10^6 $\#/cm^3$ with a range of 1.09×10^5 $\#/cm^3$ to 6.49×10^6 $\#/cm^3$.

For all CFPPs tested, the effect of the FGD on the size-segregated mass concentration was similar (Fig. 2), with a clear increase in PM_1 ($PM_{0.1}$+$PM_{0.1+1}$) but a decrease in $PM_{1\text{-}2.5}$. It seems that liquid sprays in the FGD scrubbers can promote the removal of coarser particles (diameter > 1 μm), but are relatively inefficient in removing finer particles. This result was consistent with the change in particle number distribution (Fig. 1). The mass concentration of $PM_{0.1}$ showed the largest increase for all CFPPs tested by an average factor of 2.6 (range 1.6–4.3) while $PM_{0.1\text{-}1}$ increased by 2.2 times (range 1.6–3.5). In contrast, $PM_{1\text{-}2.5}$ decreased by about 34.1% (between 9.8% and 55.9%). In summary, $PM_{2.5}$ increased by about 56.3% (between 4.7% and 119.0%) after the FGD process.

3.2. Ionic composition of $PM_{2.5}$ at the inlet and outlet of the FGD

The total concentration of ions in $PM_{2.5}$ ranged from 0.10 to 1.27 mg/m^3 at the inlet of the FGD and increased to 0.38–2.80 mg/m^3 at the outlet. The percentage of ionic species in $PM_{2.5}$ also increased from 14.9% (±2.6%, standard deviation) to 32.7 (±9.5%) during the FGD process. The total concentration of ions in all three