Characteristics of Chemical Composition and Particle Size Distribution from Real Coal-fired Circulating Fluidised Bed (CFB) Boiler

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ABSTRACT

The chemical component (element, ion, and carbonaceous aerosols) behaviour in particle size distributions (PSDs) was studied by determining the particulate matter (PM) emitted from the circulating fluidised-bed (CFB) combustion flue gas. Four CFB coal-fired boilers were employed in power plants. The actual particle mass percentages and PSDs were measured using an electrical low-pressure impactor (ELPI). Ion concentrations (SO_4^{2-} , Cl^- , NO_3^- , Na^+ , NH_4^+ , Mg^{2+} , K^+ and Ca^{2+}) were determined by ion chromatography (IC), elements (Al, Ca, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, S, Si, Ti and Zn) were determined by inductively coupled plasma-mass spectrometry (ICP-AES), and the carbonaceous content (OC1, OC2, OC3, OC4, EC1, EC2 and EC3) was measured by thermal optical analysis. Significant differences were observed in the four boilers for PSD. Chemical species in particulate matter mainly concentrated in sizes 0.1–2.5 μm in aerodynamic diameter. In this work, the mass percentage of Ca, Ca^{2+} , SO_4^{2-} , NH_4^+ and OC were significantly high in different particle size regions. The mass concentrations of elements, ions, and carbonaceous aerosols in various sizes displayed trimodal or bimodal distributions; however, the peaks of mass concentrations of chemical species in different particle sizes varied greatly. Furthermore, the size distribution of chemical species was influenced by the pollution control device employed, and the same chemical species showed a marked difference among coal-fired boiler equipped with different pollution control devices. In addition, it was observed that the ratio of OC to EC was related to dust-cleaning method.

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Keywords: Coal-fired Circulating Fluidised Bed (CFB), Particulate matter, Particle size distribution, Chemical components

1 INTRODUCTION

Atmospheric particulate matter (PM) is one of the principal pollutants of urban air in China. PM emissions from coal-fired boilers are an important source of atmospheric pollution (Xu *et al.*, 2017; Yue *et al.*, 2020). The size distribution of particulate matter (PM) is a significant PM attribute and has previously been investigated (Linak *et al.*, 2002; Zhang *et al.*, 2012). It is important not only to understand its effects on human health, visibility impairment, climate change, and transformation processes during atmospheric transport, but also to contribute to the source apportionment researches (Racherla and Adams, 2006; Yang *et al.*, 2007; Pan *et al.*, 2013; Bari and Kindzierski, 2016; Zhang *et al.*, 2016; Jia *et al.*, 2018). Emissions from boilers have aroused great concern, as they not only produce gaseous pollutants, for instance, CO, CO₂, NO_x and SO₂ (Dios *et al.*, 2013; Hussain and Luo, 2019), but also emit PM. Moreover, the characteristics of PM are different because of combustion processes transformation, such as different types of boilers, different coal burning conditions and pollution control devices (Yi *et al.*, 2008; Ma *et al.*, 2017;

Wu *et al.*, 2018; Wang *et al.*, 2019). As is well-known, coal is the major energy for boiler combustion, and it is usually used in different industrial applications such as electricity, industrial heat, and residential heating with characteristics of coal-fired emission sources (Li *et al.*, 2018). China accounts for approximately one-third of the world's coal combustion every year (Ma *et al.*, 2016). Therefore, PM emitted from coal-burning boilers has caused considerable concern over the regional air pollution effects.

Chemical components (elements, ions and carbonaceous aerosols) from coal-fired boilers are released into the atmosphere as particle emissions and toxic elements have been found to be enriched in ultrafine and fine particles (Yoo *et al.*, 2005). Relevant studies have focused on the elements from coal-fired boilers (Gao *et al.*, 2016; Huang *et al.*, 2017; Lanzerstorfer, 2018). Water-soluble ions, especially, SO_4^{2-} , Ca^{2+} and NH_4^+ are significant in PM (Saarnio *et al.*, 2014); however, water-soluble ion emissions are affected by the chemicals used in the desulphurisation and denitrification processes (Saarnio *et al.*, 2014; Wu *et al.*, 2018). Carbonaceous aerosols, including organic carbon (OC) and elemental carbon (EC), are ubiquitous species in the atmosphere. OC is derived from the complete combustion of coal and secondary transformation (Saud *et al.*, 2013; Cornette *et al.*, 2020), whereas EC is mainly produced by incomplete combustion of coal (Masiello, 2004; Peng *et al.*, 2018). The OC and EC from coal-fired coal has been reported (Ma *et al.*, 2016). The conclusions from this study suggest that grate boiler emissions had higher levels of OC and EC, with emission rates about 16 and 10 times higher than those of the pulverised combustion boilers and circulating fluidised bed (CFB), respectively. However, the chemical composition of coal (elements, ions, and carbonaceous aerosols) has rarely been reported for the size distribution of particulate matter (PM), and their chemical feature have rarely been reported; previous studies have mainly focused on the chemical and physical properties of coarse particle emissions.

In this study, we characterise the PM at the outlet of particulate emission control devices (PECDs) for four coal-fired power plants (CFPPs) with CFB boilers, a new technology with the ability to reduce pollutant emissions (Li *et al.*, 2013). We describe the emission characteristics of eleven particle size intervals with a size range of 0.013–10.5 μm . The focus of the study was on particles that are emitted to the atmosphere from CFPP after different pollution cleaning devices. Therefore, based on different pollution control devices and flue gas temperatures, the characteristics of the particle chemical composition (element, ion and carbonaceous aerosols) in different particle sizes were studied. The actual particle mass percent and PSDs were picked up from electrical low-pressure impactor (ELPI) measurements. Based on the analysis method, the particle chemical composition (element, ion and carbonaceous aerosols) was determined.

2 METHODS

2.1 Selection of Sampling Points

Particulate sampling points were selected at the rectangular flue after the flue gas desulphurisation system (FGD). Four CFPPs were equipped with CFB units, which is one of the most widely used industrial boilers in China. The CFB boilers are widely employed in China and represent advanced combustion technologies. Table 1 lists the boiler load, equipment for pollution treatment, flue gas temperature (T) and flue gas relative humidity (RH) for the four boiler units, which are mainly utilised for power generation and supply resident heating. To reduce environmental pollution from thermal power plants, the air pollution removal technology is similar to other technologies. In this work, dust removal techniques are introduced: bag filter, electrostatic precipitators (ESP) and electrostatic bags (ESB). Desulphurisation technologies are employed with semi-dry flue gas desulphurisation (SDFGD), dry flue gas desulphurisation (DFGD), and ammonia desulphurisation (AD).

Table 1. Units, temperature, and particle control devices.

Boiler code	Load (t)	RH (%)	T (°C)	Dust remover	Desulphurisation	Denitrification
CFB1	1210	9.7	74	bag filter	SDFGD	SCR
CFB2	150	6	130	ESP	DFGD	SNCR
CFB3	480	11	50	Electric bag	AD	SNCR
CFB4	470	10	42.2	Electric bag	DFGD	No control

Fig. 1. Schematic configuration of APCDs and sampling site.

Denitrification methods include selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). During the test, all the boilers and the air pollution control devices (APCDs) were operated under normal conditions; in addition, the fuel properties and combustion conditions were stable. Fig. 1 illustrates the schematic configuration of APCDs and sampling site.

2.2 Sampling Methods

The sampling system consisted of a pump, ELPI⁺, pre-heat tube, isokinetic sampler probe, pre-cut cyclone (cut-off diameter of 10.23 μm), and one-stage dilution system. Clean and dry pressurised air was used as the dilution gas at a dilution ratio of approximately 8 in this work. An ELPI (ELPI⁺, Dekati Ltd., 101 pm) was applied to measure the particle size distributions of PM, which were divided into eleven size fractions and ranged from 0.006 to 10.23 μm in diameter, while particles with an aerodynamic diameter larger than 10.23 μm were removed by the pre-impactor (Marjamki *et al.*, 2000). When flue gas emission flowed into a pre-heat tube, a diluter (Finland, Dekati Ltd.), cyclone separator, and ELPI⁺ in turn, particulate matter was collected in the quartz membrane and Teflon membrane with a diameter of 25 mm by the ELPI impactor. During the sampling process, the stack flue gas was heated by the thermal insulation material. Therefore, the sample system is a real-time size analyser that facilitates study of PM directly emitted to the atmospheric environment.

2.3 Analytical Methods

In this experiment, the Teflon filters and quartz membrane were weighed to obtain mass concentrations of PM using an analytical balance, accurate to 0.01 mg (XPE105, Switzerland Mettler Toledo). Water-soluble ions (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , F^- , Cl^- , NO_3^- , NO_2^- and SO_4^{2-}) and elements (Si, Al, V, Ti, Cr, Mn, Fe, Cu, Zn, As, Se, Cd, Sb, Ba, Ti and Pb) were collected using Teflon filters and a quartz membrane with a 25 mm diameter, respectively. Particulate filters were cut into thin strips and then immersed in an ultrasonic bath (GT-2120QTS, China) for 10 min in mixed acid solutions (8 mL HNO_3 , 2 mL HCl and 1 mL H_2O_2), and ions and elements were extracted in a microwave digestion system (CEM, USA) for 45 min. The solution from Teflon filters was then drawn into a syringe, filtered, and injected into an ion chromatograph system (DIONEX ICS-900, Thermo Fisher Scientific Inc., USA) at a flow rate of 1.2 mL min^{-1} . The solution from the quartz membrane was analysed by inductively coupled plasma-mass spectrometry and atomic emission spectroscopy (ICP-AES) (ICP7000 Series-AES, Thermo Fisher Scientific Inc., USA).

OC and EC were sampled on the quartz membrane and then measured with the DRI model 2001A Thermal/Optical Carbon analyser (Thermo Fisher Scientific Inc., USA), which is based on the IMPROVE_A thermal/optical reflectance (TOR) protocol (Chow *et al.*, 2001). In a helium atmosphere, while the quartz filter was warmed at 120°C, 250°C, 450°C and 550°C, it produced OC1, OC2, OC3 and OC4, respectively. With an increase in temperature, EC1, EC2 and EC3 were determined in a 2% oxygen/98% helium atmosphere at 580°C, 740°C and 840°C, respectively. The pyrolyzed carbon fraction (POC) was measured when the reflected laser light achieved its original

intensity after oxygen was added to the combustion atmosphere. Therefore, OC is defined as OC1 + OC2 + OC3 + OC4 + POC, and EC is defined as EC1 + EC2 + EC3 – POC.

2.4 Quality Control

Filters were conditioned at a constant T ($20 \pm 5^\circ\text{C}$) and RH ($40 \pm 2\%$) for two days before and after weighting. After sample collection, filters were placed in the filter boxes at once, and then stored in a refrigerator at 2°C until chemical analysis. Each filter was weighed at least three times before and after sampling, and the particle mass was determined by subtracting the average of the pre-sampling weights from the average of the post-sampling weights. The quartz filters were baked at 900°C for 4 h before sampling. The sampling impactor was washed with deionised water before sampling. Anion/cation calibration solutions were used for calibration of the ICs on the AIM for at least one month. The minimum detection limits (MDLs) were: $0.2 \mu\text{g m}^{-3}$ (Cl^-), $0.2 \mu\text{g m}^{-3}$ (F^-), $0.2 \mu\text{g m}^{-3}$ (NO_3^-), $0.2 \mu\text{g m}^{-3}$ (NO_2^-), $0.3 \mu\text{g m}^{-3}$ (SO_4^{2-}), $1.8 \mu\text{g m}^{-3}$ (NH_4^+), $2.3 \mu\text{g m}^{-3}$ (Ca^{2+}), $0.8 \mu\text{g m}^{-3}$ (Mg^{2+}), $0.5 \mu\text{g m}^{-3}$ (K^+) and $0.6 \mu\text{g m}^{-3}$ (Na^+). Calibration curves of the measured elements were obtained, and the correlation coefficient values were all above 0.99. The minimum detection limits (MDLs) were: Al (16.4 ppb), Ca (243 ppb), Cr (6.20 ppb), Cu (1.47 ppb), Fe (32 ppb), K (17.7 ppb), Mg (7.4 ppb), Na (51 ppb), Pb (5.5 ppb), S (47 ppb), Si (23.2 ppb), Ti (3.16 ppb), Zn (23.1 ppb), Ni (6.9 ppb). The detection limits for OC and EC were 0.40 and $0.05 \mu\text{g cm}^{-2}$, respectively. The flow calibration, gas tightness test, blank filter test, and standard sample calibration were all conducted for QA/QC.

3 RESULTS AND DISCUSSION

3.1 Characteristics of Chemical Components in Size-segregated Particles

3.1.1 Element

Particle size distributions of element mass percent are shown in Fig. 2, fourteen elements in $\text{PM}_{2.5}$ were listed and studied from four CFB coal-fired units. Among all the elements, Ca, Al, and S, were main component in $\text{PM}_{2.5}$. However, the average mass percent of Ca was obviously higher than that of the other elements and accounted for a range from 10% to 28% in the four CFBs. In the power plant, Ca not only stems from coal combustion, but is also closely linked to desulphurisation methods. Ca from the dissolution of limestone is the main constituent of slurry, and the entrainment of slurry contributes significantly to $\text{PM}_{2.5}$ emissions (Li *et al.*, 2017). In our experiment, desulphurisation process with SO_2 reacting with the limestone slurry can reduce SO_2 emissions from the flue gas. Therefore, a large amount of water-based calcium was taken into the flue gas. The size distribution of element abundance in flue gas for coal combustion (Fig. 2) showed that the elements were distributed across almost all particle size classes with the peaks in different size fraction regions. Al, Cr, Fe and K peaked at $0.37\text{--}0.61 \mu\text{m}$, Na peaked at $0.37\text{--}0.95 \mu\text{m}$ and $6.89\text{--}10.23 \mu\text{m}$. S primarily focused in ultrafine particles with a size range of $0.13\text{--}0.61 \mu\text{m}$, the mass percentages of Cu, Pb and Ni were so low that they were found evenly in all size ranges. The mass percentage of Ca was remarkably high in all size ranges, and it seemed to be separated evenly between the fine and coarse fractions, as were Fe and S. But our results were different from the one reported by Gao *et al.* (2007) who measured elemental size distribution of PM_{10} at outlet of dust cleaning equipment in coal fired boiler and found that the size distribution of Ca, S and Fe is obvious bimodal with the peak at $0.1 \mu\text{m}$ and $2.5 \mu\text{m}$. Al and Si were the most prevalent components of coal combustion (Ninomiya *et al.*, 2004), both had the same particle size distribution trend and peaked at size ranges of $0.37\text{--}0.61 \mu\text{m}$ and $1.52\text{--}4.10 \mu\text{m}$.

3.1.2 Water-soluble ions

For ionic profiles, the size distribution of ionic mass percentage is given in Fig. 3, the determination results showed that SO_4^{2-} , Na^+ , NH_4^+ and Ca^{2+} were significant anions from $\text{PM}_{2.5}$ emissions in CFBs. Furthermore, in this work, the average mass percent of K^+ only accounted for 2.1% of the $\text{PM}_{2.5}$, lower than 11.1% as reported by Wang *et al.*, who selected and tested coal-fired boiler without air pollution control devices. The result indicated that dust-removing equipment may influenced K^+ remove performance. Ca^{2+} was at a relatively high level and it was

Fig. 2. Percentage of elements mass in each particle-size bin (the error bar represents the standard deviation of different elements).

confirmed that the entrainment of recirculated slurry contributes significantly to the $\text{PM}_{2.5}$ emissions because Ca^{2+} from limestone dissolution is the main slurry ingredient, and limestone may be mixed with some impurities, such as Mg^{2+} (Saarnio *et al.*, 2014). In this work, SO_4^{2-} was higher than NH_4^+ in terms of mass concentration, and both of them were found to be enriched in PM emitted from CFPP. The SCR/ SNCR installation may have led to an increase in NH_3 content in the flue gas, and some NH_3 was converted into NH_4^+ during the desulphurisation process before being emitted into the atmosphere. So it increased the NH_4^+ emission. The increase SO_4^{2-} concentration was due to SO_2 to SO_4^{2-} conversion occurred in the desulphurisation process prior to atmospheric emission. Simultaneously, the SCR/SNCR coupled with the desulphurisation system also tended to promote the conversion of NO_x to NO_3^- , leading increased NO_3^- emissions as well. Cl^- was relatively high, and was primarily released as HCl from feed coal fires (Senior *et al.*, 2000). The water-soluble ions in the eleven size fractions are shown in Fig. 3. In general, the abundances of most water-soluble ions were distributed in all particle size classes with peaks appearing in sizes less than $1\ \mu\text{m}$. The mass percentage of Mg^{2+} was very low in all size ranges and was quite even in all size ranges. SO_4^{2-} and NH_4^+ presented similar trends at less than $2.5\ \mu\text{m}$ with the peak at $0.37\text{--}0.61\ \mu\text{m}$, whereas SO_4^{2-} showed another peak at $2.44\text{--}4.10\ \mu\text{m}$. Cl^- and NO_3^- had similar size distributions, with peaks of $0.13\text{--}0.24$, $2.44\text{--}4.10$ and $6.89\text{--}10.23$. Na^+ presented two peaks at a range of $0.37\text{--}0.61$ and $1.52\text{--}1.44$. Ca^{2+} was mainly concentrated in sizes of $0.006\text{--}0.08$ and $0.61\text{--}0.95$.

Fig. 3. Percentage of ionic mass in each particle-size bin (the error bar represents the standard deviation of different ions).

3.1.3 OC, EC, and carbon fraction characteristics

Carbonaceous species included OC and EC. It was found that the abundance of EC was lower than that of OC in the size range of five units, similar to the results reported by Ma *et al.* (2016). Carbonaceous aerosols are subdivided into different fractions, which are usually employed as tracers of coal-burning sources (Han *et al.*, 2010). The carbon fractions (OC1, OC2, OC3, OC4, EC1, EC2 and EC3) can be recognized by the decomposition temperatures. As shown in Fig. 4, the size distribution of mass percentage of OC and EC in CFB displayed a double-peak distribution consisting of sub-micrometre modes with peaks at $PM_{0.13-0.24}$ and a coarse peak at $PM_{2.44-4.10}$. The mass percentage of OC1 from the CFB stack revealed a parallel size distribution with OC and EC, and the size displayed two peaks near 0.37 and 6.89 μm . The content of OC2 and OC3 in $PM_{0.13-0.24}$ was higher than that in other particle sizes. The mass percentage of OC4 revealed a trimodal distribution with peaks near 0.24, 0.95 and 4.10 μm , respectively. The abundance of EC1 and EC2 in $PM_{0.13-0.24}$ is at the highest level among size distribution.

3.1.4 Variation of particle size distributions (PSDs) across different pollution control devices

$PM_{2.5}$ contributed to 70% of the PM_{10} mass, which is higher than average mass percent (34%) of PM_{10} at WFGD outlet reported by Wu *et al.*, it may be thought that a desulfurization technology can influence PM (Álvarez-Ayuso *et al.*, 2006). The mass percentages of ionic species from smokestack flue gas for the four tested CFB power plants are presented in Fig. 5. It is noted that there is a

Fig. 4. Percentage of OC, EC, OC and EC fragments in different particle-size bins (the error bar represents the standard deviation of different carbons).

difference in the size distribution of ionic species in different CFBs. In this work, the content of NH_4^+ in different particulate diameters was significant enrichment and showed unimodal distribution in CFB3. The contents of Na^+ and K^+ made small differences, except for $\text{PM}_{0.95-1.52}$ and $\text{PM}_{4.10-10}$ in the four CFBs. The content of Cl^- had two or three peaks in different CFBs, such as CFB1 with $\text{PM}_{0.13-0.24}$ and $\text{PM}_{6.89-10.23}$, CFB3 with $\text{PM}_{0.37-0.61}$ and $\text{PM}_{2.44-4.10}$, and CFB4 with $\text{PM}_{0.37-0.61}$, $\text{PM}_{2.44-4.10}$ and $\text{PM}_{6.89-10.23}$. The content of SO_4^{2-} displayed a single peak in $\text{PM}_{0.37-0.61}$ in CFB3; However, all ions of $\text{PM}_{0.13-0.61}$ had a high abundance in CFB4. In CFB1, the SO_4^{2-} of $\text{PM}_{0.95-1.52}$ and $\text{PM}_{6.89-10.23}$ was obviously increased. In CFB1 and CFB4, NO_3^- showed trends similar to those of SO_4^{2-} . It emitted more NH_4^+ in CFB3 because of the plant equipped ESP coupled with AD and SNCR (Sereika *et al.*, 2017). AD removed SO_2 , replacing DFGD in CFB1, CFB2, and CFB4; however, AD process can release more new NH_4^+ to the atmosphere, and DFGD system can produce more Ca^{2+} or Ca. In addition, SCR/SNCR has been used to remove nitrogen oxides and it also forms new NH_4^+ (Ramachandran *et al.*, 2000; Arfaoui *et al.*, 2009). Ninomiya *et al.* (2004) showed that coal particle size can affect PM emission and its chemical species in different size fractions. Additionally, SO_4^{2-} had a good correlation with NH_4^+ (0.65) in CFB3 equipped with ammonia absorption methods for fume desulphurisation, so the main components in the particle samples might be $(\text{NH}_4)_2\text{SO}_4$. Ca^{2+} and SO_4^{2-} correlated well in different-sized particles (CFB1, CFB2 and CFB4 with 0.59, 0.78 and 0.69, respectively). From this result, it may be presumed that CaSO_4 is the main ingredient in the particle samples, and these compounds were formed in the particle phase principally during

Fig. 5. Ion distributions with different particle-sizes bins from four CFBs (%).

the flue gas desulphurisation process. It was regarded that APCDs can affected the abundance of chemical species in coal-fired boiler. (Meij and Winkel, 2004; Yi *et al.*, 2008).

The OC and EC mass percentages in different size fractions (0.006–10.23 μm) for the four units (measured with ELPI) are illustrated in Fig. 6. OC was observed to vary in the same particle size range from different CFB boilers. There are at least two obvious peaks that were observed for mass distribution of OC and EC in different sizes from four CFB units. The mass distribution of OC and EC from CFB2 equipped with ESP were different from those in other boilers. OC and EC revealed analogical size distribution from CFB1 equipped with bag dust cleaning, with the size showing one peak approaching 0.13 μm . However, the mass percentages of OC and EC from the four CFB stacks made a large difference in size distribution. The mass distribution of OC and EC from the CFB2 was more complex than those in the other CFBs. In CFB2, four conspicuous peaks for mass distribution of OC and EC were observed, while in other CFBs they displayed a bimodal distribution. Linak *et al.* (2002) found that pulverised coal fly particle has a trimodal PSD with sub-micrometre region, fine region, and super-micrometre region. In addition, there were differences about the average mass percentage of OC and EC for different CFB boilers. Approximately 3.5%, 1.9%, 6.3% and 1.8% of the OC were emitted from CFB1, CFB2, CFB3 and CFB4, respectively. EC displaying an analogical change based on the four sampled boilers, and approximately 0.49%, 0.17%, 0.48% and 0.20% in the $\text{PM}_{2.5}$ emitted from the four CFB units. The four boilers used the same combustion method, but CFB3 and CFB4 employed electric-bag precipitator, whose dusting ways are from CFB1 and CFB2. So dust removal technology might affect the mass distribution of OC and EC in different sizes.

Fig. 6. Particle size distribution for OC, EC, OC and EC fragments in different CFBs.

The evaporation from OC1 and OC2, considered as volatile organic compounds and semi volatile organic compounds, respectively, occurred below 250°C (Duan *et al.*, 2012). Therefore, OC1 and OC2 were stable at relatively low temperatures. In our work, CFB3 and CFB4 presented similar combustion methods; furthermore, CFB3 and CFB4 were equipped with the same electric bag. In CFB3 and CFB4, the mass distribution of the organic carbon fraction (OC1, OC2, OC3 and OC4) were remarkable distinction. In CFB3 (Fig. 6), the OC3 displayed an obvious double peaks consisting of one sub-micrometre region with peaks at $PM_{0.13-0.24}$ and a fine peak at $PM_{0.95-1.52}$, and OC2 had one peak with $PM_{0.08-0.13}$ at a gas temperature of 50°C. In CFB2 (Fig. 6), the OC1, OC2, OC3 and OC4 had similar size distribution trends with peaks near 1 and 2.5 μm at a gas temperature of 160.2°C. In CFB3 (Fig. 6), in the size range of 0.006–0.08 μm , 0.24–0.95 μm and 2.44–6.89 μm , the mass percentage of OC1 was higher than that of OC2, OC3 and OC4, and this trend was inconsistent with those in CFB4. In CFB1 equipped with bag dust cleaning (Fig.6), mass percent of OC2 were higher than those of OC1, the temperature in the CFB1 flue gas was approximately 74°C. The results may indicate that the particle filtration device and temperature could affect the mass distribution of carbonaceous fraction (OC1, OC2, OC3, OC4) in different sizes.

Fig. 6 also shows the mass percentage of EC fractions for the four CFB units. The mass percentage of EC1-3 varied widely at various particle sizes. In all samples, the mass percentage of EC1 was high in different particulate sizes, followed by EC2 and EC3. EC1 was the dominant among

EC fractions in CFBs. The EC1 emitted may be related to the exhaust humidity and temperature. In CFBs, the maximum mass of EC1 obtained in CFB1 (0.42% in $PM_{0.95-1.52}$), CFB2 (0.5% in $PM_{2.44-4.10}$), CFB3 (1.33% in $PM_{0.13-0.24}$), and CFB4 (0.37% in $PM_{0.37-0.61}$) samples were comparable. The mass percentages of EC2 in the CFBs were lower than those of EC1, and similar size distributions were observed from the mass percentages of EC1 and EC2 in the four CFBs. The mass percentage of EC3 was equal to zero. Among the boilers, emissions of EC1 from CFB3 were the highest. The temperature in the CFB3 flue-gas was approximately 50°C, which was lower than that in other CFBs. Simultaneously, the humidity from the flue gas of CFB3 reached 11% and was the highest level in all CFBs, potentially causing additional EC1 emissions.

3.2 Comparison of OC/EC Ratios among Various Boilers and Particle Sizes

The OC/EC ratio is an important factor for determining source characteristics (Cao *et al.*, 2009). The observed correlations of OC with EC for their mass percentages in the four CFB units are plotted to show an overview of the relationships in Fig. 7. A good correlation was shown between the OC and EC in different size fractions for the four CFBs. The higher correlation coefficients were computed for CFB3 (0.699) and CFB4 (0.625). The different correlations manifested that the influence factor for OC emissions was differ from that of EC, suggesting the relative contribution of OC and EC to the composition of PM for CFB units under different working conditions. In addition, slopes between OC and EC were estimated as 0.511 and 0.482 for CFB1 and CFB2, respectively. It is noted that the correlation of OC and EC was commonly prominent in the four CFB units. In Table 2, the OC/EC from fuel gases with different particle sizes from the four CFBs is listed. It was found that the OC/EC in different particle size varied significantly. It may have been caused by the dust-cleaning method and efficiency. At the same particle size fraction, it was observed that the ratio of OC to EC showed important differences because OC powerfully rely on air pollution control devices and coal property (Wierzbicka *et al.*, 2005). So air pollution control devices could influence the PSD of OC and EC, and transform the OC/EC ratios in the flue gas.

4 CONCLUSION

Based on this work, the particulate matter with the mass percentage and size-classification particles emitted from four boilers of the same types were collected and characterised. Measurements in the stacks were obtained for an ELPI with a stage dilution sampling system.

Fig. 7. Correlation between OC and EC in the four CFBs.

Table 2. OC/EC ratio in different particle-size bins in the four CFB boilers.

Particle size	CFB1	CFB2	CFB3	CFB4
0.006–0.08	15.04	12.57	10.05	13.50
0.08–0.13	14.57	8.28	8.12	10.20
0.13–0.24	10.55	8.23	7.43	7.37
0.24–0.37	19.83	23.58	23.19	10.33
0.37–0.61	19.50	9.60	4.92	12.34
0.61–0.95	19.00	9.11	5.98	14.75
0.95–1.52	9.58	26.00	10.59	14.50
1.52–2.44	13.24	17.29	6.69	11.74
2.44–4.10	8.29	22.07	10.13	9.56
4.10–6.89	8.41	12.33	10.31	6.07
6.89–10.23	6.54	9.93	17.86	11.72

It was noted that Ca, Fe, Na, S, SO_4^{2-} , Na^+ , Ca^{2+} , NH_4^+ and OC, which mainly concentrated in sizes 0.1–2.5 μm in aerodynamic diameter, appeared at relatively high levels in PM from flue gas; The mass distributions of element in different sizes in CFBs after ESP displayed a bimodal distribution, and the highest level contained a fine mode region. In addition, the content of OC2 and OC3 in $\text{PM}_{0.13-0.24}$ appear single peak, mass percentage of SO_4^{2-} , NH_4^+ , Ca^{2+} , Na^+ , OC, EC, OC1 and EC3 presented a bimodal distribution, and Cl^- , NO_3^- , OC4, EC1 and EC2 had similar size distributions with trimodal distribution; It demonstrates that air pollution control devices can effectively change PM size distribution and associated main chemical compositions. Our results can better quantify chemical compositions from CFB boiler in China. Also, due to the complex conditions and numerous influencing factors of field measurements, chemical compositions of PM based on field tests for real CFB boiler are still limited. Therefore, in order to more accurately assess the relationship between the emissions characteristics and air pollution control devices of CFB boiler on primary air pollutants emissions, a lot of field tests need be conducted.

ABBREVIATIONS

PSD	particle size distributions
CFB	circulating fluidized-bed
ELPI	electrical low-pressure impactor
OC	organic carbon
EC	elemental carbon
PECDs	particulate emission control devices
CFPPs	coal-fired power plants
FGD	flue gas desulphurization
T	temperature
RH	relative humidity
ESP	electrostatic precipitators
ESB	electrostatic bags
SDFGD	semi-dry flue gas desulphurization
DFGD	dry flue gas desulphurization
AD	ammonia desulphurization
SCR	selective catalytic reduction
SNCR	selective non-catalytic reduction
APCDs	air pollution control devices
SO_2	sulfur dioxide
NH_3	ammonia
NO_x	nitrogen oxides
WESP	wet electrostatic precipitator
PM	particulate matter

ADDITIONAL INFORMATION

Declaration of Conflicts of Interest

The authors declared that they have no conflict of interests

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