Characterization of Inorganic Components of Size-Segregated Particles in the Flue Gas of a Coal-Fired Power Plant

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Particulate matter (PM) in the range of 0.03–10 μm were collected with a 13-stage cascade impactor sampler at the outlet of an electrostatic precipitator (ESP) of a 100 MW lignite-fired power plant and were characterized by number and mass size distributions, element, and ion measurements. The number size distribution in the whole range of 0.03–10 μm appeared to be bimodal with peaks at 0.06 and 0.835 μm . The mass size distribution over 13 size-segregated fractions was also bimodal with peaks at 0.06 and 1.8 μm . Four out of 13 fractions (namely, $0.03 < D_p < 0.06 \mu\text{m}$, $0.06 < D_p < 0.1 \mu\text{m}$, $0.7 < D_p < 1.1 \mu\text{m}$, and $1.8 < D_p < 2.7 \mu\text{m}$) were selected to represent the nano, ultrafine, submicron, and fine particles in this research, respectively. In general, the highest concentrations of elements were found in the fine fraction, in which Al and Ca were the most abundant elements, followed by S, Fe, and Na. In the nano fraction, Na and S were found with the highest levels. Enrichment coefficients of pollution elements (As, Pb, S, Se, Sb, and Cd) and some trace metal elements (Zn, Cr, Ni, Cu, V, and Co) suggested that these elements were enriched in the particles with smaller size. pH measurements showed that these flue gas samples were acidic and the acidity became weaker with larger particle size. Sulfate was the most predominant anion and remained at rather high levels due to the lack of desulfurization equipment. The high sulfate/nitrate ratios could be taken as a rudimentary indicator of such coal combustion sources.

1. Introduction

The sources of inhalable particulate matter (PM) include natural sources and anthropogenic sources. Among these sources, the coal-fired power plant is one of the major anthropogenic sources, and some harmful compositions have been found coming from the coal combustion process.¹ A study showed that the new born in the downwind direction of a coal-fired power plant had higher ratios of congenital malformation, in which particles emitted from the power plant played an important role.² Another study found that the high emission contribution of coal-fired power plants induced a relatively small contribution to the average ambient concentration and a significant impact on the urban area.³ In fact, with the importance of coal as a fuel for power generation, there has been prolonged concern about the atmospheric emissions associated with coal combustion over the past few decades. Earlier studies with the aid of 7- or 11-stage cascade impactor samplers reported a bimodal size distribution of the particulate emitted from coal combustion sources.^{4,5} Investigations on the formation mechanisms of particulate matter during coal combustion showed that the submicron particles are formed via

vaporization, condensation, and subsequent nucleation, whereas supermicron particles have a different route of formation (i.e., fragmentation, coagulation, or coalescence).^{6–8} Due to the great threat to public health and the environment, trace elements from the coal combustion were highly attended.^{9,10} A study for mercury emitted from a coal-fired plant indicated that the majority of mercury might go into the flue gas, and the ratio of mercury quantity in the flue gas to that of the total combustion products was about 83%.¹¹ Another study on As, Cd, Co, Cr, Cu, Hg, Fe, Mn, Ni, Pb, Se, and Zn emissions from a coal-fired power plant showed that the mass balance for all the trace elements was below 50% except for the As, Se, and Hg; trace metals emissions were higher in the coal-based power plant than in the fuel oil-fired power plant.¹² Klika investigated the distributions of trace elements and found that most trace elements were highly enriched in the fly ash rather than in the bottom ash; Hg and Cl were the easiest to enter into the gas phase.¹³

Currently, 47.7% of the total coal consumed in China is used for electric power generation, and the amount of coal consumed for power generation is expected to rise in the forthcoming

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Table 1. Tested Coal Compositions

Elemental Analysis ^a (as received, mass %)							
Na	Mg	Al	Fe	Ca	Ti	K	Cl ^b
0.11	0.26	2.23	0.38	1.77	0.26	0.13	0.035
proximate analysis (as received, mass %)				ultimate analysis (as received, mass %)			
moisture				C			
				23.49			
volatile matter				H			
				23.12			
fixed carbon				O			
				17.46			
ash				N			
				35.93			
calorific value (MJ/kg)				S			
				13711.4			
				0.3			

^a Analyzed by ICP-OES. ^b Analyzed by IC.

decade.¹⁴ The available literature indicates that very little is known about the size distribution of trace elements in the PM from coal-fired power plants in China. Only a few papers have been published about the size distribution of major elements and trace elements in the PM from coal-fired boilers¹⁵ and trace element partitioning under laboratory combustion conditions.¹⁶ Most of the power plants in China are now equipped with electrostatic precipitators (ESPs), but desulfurization scrubbers, favoring further reduction of the PM,¹⁷ are not widely installed in the Chinese power plants. It is, therefore, interesting to study the major ionic species and trace element distribution in size-segregated PM from coal-fired power plants in China. In this article, we reported the distribution of 8 ions and 20 elements in the nano, ultrafine, submicron, and fine fractions of the PM from a lignite-fired power plant with an ESP in northeast China and also the number and mass size distributions in the range of 0.03–10 μm .

2. Experimental Section

2.1. Description of the Power Plant. The coal-fired power plant is located in the suburb of Daqing, a northeastern city in China. Its annual coal consumption rate is about 8.2×10^5 tons of local low-sulfur, high-ash lignite. The results of the coal proximate and ultimate analyses as well as the contents of eight other elements in the coal are shown in Table 1. The raw coal was pulverized by a direct-feed fan mill system up to an average diameter of around 100 μm , and the coal powder was combusted with impellerless burners. The coal-fired boiler (model: HG-220/9.8-HM12) is manufactured by the Haerbing Boiler Co. For the PM removal, a twin-chamber ESP with three electric fields was employed. The PM removal efficiency was 99.6%. No desulfurization scrubber was employed, and the flue gas after the PM removal was emitted directly into the atmosphere. During our test runs, the boiler load was kept at 100%.

2.2. Measurements of Operating Parameters. A flue gas analyzer (model MGA5, MRU Inc.) was employed to measure O_2 , CO_2 , CO , NO_x , and SO_2 in the flue gas at the ESP outlet. An exhaust analyzer (model 3012, Laoshan Inc.) was used for the measurements of the flue gas temperature, the flue gas exit velocity, and the vapor content. For the determination of the fly ash concentrations in the flue gas, a particulate sampling system, consisting of a sampling probe, a quartz filter, and a vacuum pump, was employed. The probe with a tubular quartz filter was inserted into the flue gas, and the pumping rate was then adjusted to achieve isokinetic sampling. The

Table 2. Operating Parameters during Test Runs

boiler type	pulverized coal boiler	CO_2 (%)	15
PECDs type	twin chamber three-field ESP	O_2 (%)	11
fuel	lignite	H_2O (%)	13
electricity generated (MW)	100	CO (mg/m^3)	6
test load (%)	100	NO_x (mg/m^3)	708
temp at ESP outlet ($^\circ\text{C}$)	129	SO_2 (mg/m^3)	766
flue gas exit velocity (m/s)	14	total fly ash (mg/m^3)	68

fly ash concentrations were calculated from the flow rate and the filter weight gained before and after sampling. Details of the measured parameters are listed in Table 2.

2.3. Sampling Procedure. A sampling system, consisting of a sampling probe, a PM_{10} cyclone, a 13-stage low-pressure cascade impactor (LPI, Dekati Ltd., Finland), and a vacuum pump, was used to collect size-segregated PM at the ESP outlet. A probe nozzle of 6 mm inner diameter was selected. The sampling probe, the PM_{10} cyclone, and the LPI were wrapped up with an electric-heating band controlled at 120 $^\circ\text{C}$ to avoid vapor condensation. Particles in the flue gas were sucked into the probe nozzle and passed through the PM_{10} cyclone, where particles larger than 10 μm ($D_p > 10 \mu\text{m}$) were removed. The remaining particles in the flue gas in the range of 0.03–10 μm were collected successively onto the 13-stage membranes of the LPI, according to their aerodynamic diameters. Quartz membranes (QR100, Advantec, Japan) were used to collect size-segregated samples for chemical analyses. The quartz membranes were baked at 500 $^\circ\text{C}$ before use to remove any residual organic matter.

2.4. Size Distribution Measurements. An engine exhaust particle sizer (EEPS 3090, TSI Inc.) with 32 channels over a size range of 5.6–560 nm and an aerodynamic particle sizer (APS 3310, TSI Inc.) with 57 channels over a size range of 0.47–30 μm were employed for measurements of number size distributions. Both instruments were connected to a dilution system to achieve normal sampling. Regarding mass size distributions, aluminum foil substrates were used in the LPI sampling cascade system to collect 13-stage samples. The aluminum foil substrates were weighed before and after sampling on a microbalance (Mettler Inc.) with a precision of 1 μg .

For comparison, number and mass distribution measurements for the atmospheric PM were also carried out in a similar way. In the case of ambient PM measurements, neither heating of the LPI sampling system nor dilution during number concentration measurements is needed. Furthermore, pulverized coal and fly ash retained in the PM_{10} cyclone ($D_p > 10 \mu\text{m}$) were also sampled and subjected to analyses.

2.5. Analytical Methods. An inductively coupled plasma–mass spectrometer (ICP-MS, Model Plasma Quad 3, VG Inc.) was employed to determine the trace elements in the PM samples, whereas an inductively coupled plasma–optical emission spectrometer (ICP-OES, Model Optima 2000, Perkin-Elmer Inc.) was used to analyze major and minor elements. Each sample was digested in a high-pressure Teflon digestion vessel at 170 $^\circ\text{C}$ for 4 h with 3 mL of concentrated HNO_3 , 1 mL of concentrated HClO_4 , and 1 mL of concentrated HF. After cooling, the solution was evaporated to dryness, and the residue was finally dissolved and diluted with water to 10 mL. Altogether, 20 elements (i.e., Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, Sb, Se, Ti, V, and Zn) were determined. To ensure data quality, a coal fly ash national standard reference material (GBW 08401) prepared by the analytical laboratory of RCEES was analyzed, and the results of the SRM analysis are presented in the electronic Supporting Information.

For ionic analysis, ion chromatography (DX 600, Dionex Inc.) was employed. Each sample was extracted ultrasonically with 5 mL of deionized water for 40 min, and the solution was filtered

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Figure 1. Particle number size distribution measured: (a, left) by the EEPS 3090; (b, right) by the APS 3310.

through a microporous pinhead filter. The filtrate was analyzed for eight ions, namely Na^+ , K^+ , Mg^{2+} , Ca^{2+} , NH_4^+ , Cl^- , NO_3^- , and SO_4^{2-} .

The coal and fly ash samples were also characterized by ICP-OES. For the determination of chlorides in the pulverized coal samples, a different procedure was adopted.¹⁸

3. Results and Discussion

3.1. Number Size Distribution. The number size distributions of the particulate in the flue gas and the ambient air were measured by the EEPS 3090 and the APS 3310. Figure 1a gives a comparison between the flue gas and the ambient air samples in the range of 5.6–560 nm. The PM in the flue gas exhibited two clearly defined modes: the Aitken mode (5.6–50 nm) with a peak at 9.31 nm and the accumulation mode (50–560 nm) with a peak at 60 nm. The PM number concentrations in the flue gas samples were $6 \times 10^8/\text{cm}^3$ and decreased rapidly with an increase in size. The PM number concentrations in the accumulation mode were rather low as compared with the concentrations in the Aitken mode. The low concentration in the accumulation mode might be explained by coagulation/coalescence of tiny particles with the fly ash particles.¹⁹ On the contrary, in the ambient air only the Aitken mode was observed (Figure 1a) with a peak at 10.8 nm. The total number average concentration of the PM in the ambient air was $3.17 \times 10^6/\text{cm}^3$.

In order to extend the measuring range, the APS 3310 with a size range of 0.47–30 μm was also used to measure the number distributions. Figure 1b gives the PM number distributions both in the flue gas and in the ambient air. Evidently, both curves are similar and have only one peak, at 0.835 and 0.724 μm for the flue gas and the ambient air, respectively. In the particle range with $D_p < 2.8 \mu\text{m}$, the number concentrations in the flue gas were found to be much higher than those in the ambient air, whereas for the range $D_p > 2.8 \mu\text{m}$, the number concentrations of particles in the flue gas and in the ambient air were at the same level. Since the flue gas from coal combustion was directly emitted into the atmosphere without further treatment after the ESP, our finding suggests that the ESP could be effective for the removal of particles with a $D_p > 2.8 \mu\text{m}$, but not for particles with a $D_p < 2.8 \mu\text{m}$.

3.2. Mass Size Distribution. As shown in Figure 2, particles in the flue gas from coal combustion displayed a bimodal mass size distribution with an ultrafine mode and a fine mode with peaks near 0.06 and 1.8 μm , respectively. A similar bimodal distribution was reported by many authors,^{4,5,7} but the peak positions were different from ours. This can be explained by the complexity of factors affecting coal combustion: coal particle

Figure 2. Particle mass size distribution.

Figure 3. Particle number size distribution in the range of 0.03–10 μm .

Figure 4. Element size distributions in different fractions.

size, coal composition, combustion temperature, fuel/air ratio, and so forth.⁷ In our case, the total mass concentration of the PM in the flue gas was about 72 times higher than that in the ambient air. Figure 3 shows the comparison of the number size distribution of particles (with peaks at 0.06 and 0.835 μm) with the mass size distribution (at 0.06 and 1.8 μm) in the same range of 0.03–10 μm . Temperature might be an important factor influencing size distribution measurements. For number size measurements, a dilution channel was used, so the working temperature was close to the ambient temperature. However, for the mass size distribution, the working temperature was close to that of the flue gas.

3.3. Element Characterizations. The element mass concentrations in the PM are shown in Figure 4. For the major and minor elements, most of them had the highest concentrations in the fine fraction, followed by the submicron and the ultrafine fractions; the nano fraction gave the lowest values. Al and Ca were the most abundant elements in the fine fraction, and they accounted for 62% (by element mass). The sum of Ca and Al in the submicron, the ultrafine, and the nano fractions was 45%, 40%, and 39%, respectively. The concentrations of the other crustal elements such as Fe, Mn, Mg, and Ti were also high. A similar element distribution was observed in the submicron and the ultrafine fractions, while, in the nano fraction, Na and S were the two highest elements and accounted for 44% of the total element mass in the nano fraction. The sum of Na and S in the submicron, the ultrafine, and the nano fractions was 20%, 27%, and 12%, respectively. The enrichment of easily vaporized elements (Na and S) in the nano fraction implies a condensation/nucleation formation mechanism.³ On the contrary, the domi-

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Figure 5. Element enrichment coefficients in different fractions. Here, the fly ash is the samples kept in the PM₁₀ cyclone with a $D_p > 10 \mu\text{m}$.

nance of refractory elements (Al, Ca, Ti, and Fe) in the coarser fractions suggests that supermicron particles were formed by the fragmentation of coal and coalescence of mineral matter. In Figure 4, the crustal elements (Al, Ca, Ti, and Fe) generally remained at a rather high level in the four fractions. So, a formula here was used to calculate the soil source contribution:

$$M\% = \frac{M_{\text{soil}}}{PM_i} = \frac{2.20 \times \text{Al} + 2.49 \times \text{Si} + 1.63 \times \text{Ca} + 1.94 \times \text{Ti} + 2.42 \times \text{Fe}}{PM_i} \quad (1)$$

where PM_i is the particle mass in the size range of i . M_{soil} was calculated according to ref 20. Due to the pretreatment for elements in this research, wherever HF was added, the Si content could not be determined by the ICP analysis. Here, the values of Si were calculated according to the ratio of Si/Al in the crust (3.3). As a result, the values of $M\%$ were 44%, 43%, 26%, and 43% for the nano, the ultrafine, the submicron, and the fine fraction, respectively, while, for the coal and the fly ash samples, the values of $M\%$ were 27% and 48%, respectively. The difference in the $M\%$ between the coal and the fly ash samples could be explained by the vaporization/violation of the compositions during the coal combustion.

For better characterization, the enrichment coefficients of all elements determined by ICP-OES/ICP-MS were calculated. Aluminum was used as the reference element. The results were shown in Figure 5. Elements with high volatilities, such as As, Se, Pb, Sb, S, and Cd, had the highest enrichment coefficients in the nano fraction and had fairly large enrichment coefficients (10^2 – 10^3) in the other fractions as well. During combustion, these elements could be subjected to vaporization and condensation, and they were enriched in the nano fraction.¹⁶ The minor elements and some trace elements such as Zn, Cr, Ni, Cu, V, and Co had medium enrichment coefficients (10 – 10^2) in most fractions. Their enrichment in the smaller particle fractions was

Table 3. Results of Ion Chromatography and pH Measurements ($\mu\text{g}/\text{m}^3$)

	nano (0.03–0.06 μm)	ultrafine (0.06–0.1 μm)	submicron (0.7–1.1 μm)	fine (1.1–1.8 μm)
Cl^-	0.51 ± 0.03	1.58 ± 0.08	15.54 ± 0.46	24.27 ± 1.23
NO_3^-	1.1 ± 0.06	2.64 ± 0.02	12.32 ± 0.37	62.97 ± 1.89
SO_4^{2-}	2.48 ± 0.14	4.4 ± 0.1	356.28 ± 14.25	611.69 ± 36.7
Na^+	0.14 ± 0.02	0.67 ± 0.04	8.53 ± 0.43	11.79 ± 0.47
NH_4^+	1.32 ± 0.07	0.61 ± 0.03	4.33 ± 0.26	5.55 ± 0.28
K^+	0.28 ± 0.14	0.82 ± 0.03	4.35 ± 0.26	5.19 ± 0.26
Mg^{2+}	0.13 ± 0.10	0.49 ± 0.01	16.47 ± 0.47	28.33 ± 1.42
Ca^{2+}	0.43 ± 0.02	3.41 ± 0.08	113.42 ± 22.3	232.66 ± 11.63
pH	5.98	6.21	6.33	6.76

not so significant as that of Se, S, and As. Regarding the major crustal elements (Ca, Fe, Mg, Na, K, Ti, and Mn), they had enrichment coefficients close to 1 or less than 1 in all fractions. The refractory nature of these elements led to a fragmentation/coalescence mechanism of particle formation. The enrichment coefficients of the elements in the fly ash retained in the PM₁₀ cyclone were also measured, as shown in Figure 5. The reason for explaining the higher enrichment coefficients of the elements in smaller size-segregated particles was that the enrichment coefficients might be deeply influenced by the combustion temperature¹⁶ and the content of chlorine in the fuels, which could help the gasification of the elements.²¹

3.4. Characterization of Ion Species. Table 3 shows the results of the ion chromatography determinations. As mentioned above, the fuel used for combustion was the local low-chlorine lignite,²² although during the combustion process most of the chlorine was released in the form of HCl²³ and was emitted with the flue gas to the atmosphere; soluble chlorides were detected in the size-segregated particles with medium contents, and the mean values were 0.51, 1.58, 15.54, and 24.27 $\mu\text{g}/\text{m}^3$ in the nano, the ultrafine, the submicron, and the fine fractions, respectively. All the soluble sulfates and nitrates in the PM are of secondary origin, as they were formed in the postcombustion stage. From Table 3, we could see that they are not equally distributed among the various size fractions. The predominance of sulfates in the fine and the submicron fractions was observed. The ratio of $\text{SO}_4^{2-}/\text{NO}_3^-$ in the fine fraction samples usually approached 10. That could probably be attributed to the absence of a desulfurization device. This value was higher than the ratios in ambient PM_{2.5} samples, reported elsewhere.^{24–26} Consequently, the high $\text{SO}_4^{2-}/\text{NO}_3^-$ ratio could be taken as an indicator of the PM emitted from coal-fired power plants.²⁷ Among the cations, Ca^{2+} was the most abundant in the fine and the submicron fractions.

In the nano fraction, we could see a preferential enrichment of NH_4^+ , NO_3^- , and Cl^- . Unlike the situation in other fractions, the ammonium ions had the highest concentration among the cations, and the SO_4^{2-} concentration was of the same order of magnitude as NO_3^- and Cl^- . This suggested a nucleation mechanism in the formation of nanoparticles via the interaction of gaseous NH_3 with the volatile acids—hydrochloric and nitric

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acids. On the contrary, calcium and magnesium sulfates predominated in the submicron and the fine fractions. Here, the NH_4^+ concentration was 1 or 2 orders of magnitude less than that of the alkali and alkali-earth metals, and the levels of nitrates and chlorides were also 1 or 2 orders of magnitude less than that of the sulfates. The refractory nature of the alkaline-earth metals suggested an accumulation mechanism of the formation of alkaline-earth sulfates in the condensed phase.

4. Conclusions

Particle samples in the flue gas were collected by a 13-stage impactor sampler on the outlet of an ESP at a power plant. Mass and number size distributions, size distributions of 20 elements and 8 ions of the flue gas samples, were characterized.

Mass size distribution measurements indicated a bimodal mode with peaks at 0.06 and 1.8 μm . Number size distribution also showed a bimodal mode with peaks at 0.06 and 0.835 μm in the range of 0.03–10 μm .

Elemental analysis of size-segregated fractions indicated that Al and Ca had the highest concentrations in the fine fraction. Generally speaking, crustal elements had the highest concentrations, and the trace/pollution elements had lower concentrations. The element concentrations in these size-fractionated particles were in a descending order: fine > submicron > ultrafine > nano.

Easily vaporized elements (As, Se, Pb, Sb, S, and Cd) were enriched in fractions of smaller size. The crustal elements (Ca,

Fe, Mg, Na, K, Ti, and Mn), on the contrary, were more or less equally distributed in these size-fractionated particles.

Ion chromatography has been proven to be a powerful tool to identify the nitrogen species NH_4^+ and NO_3^- , which are unstable at high temperatures and could not be detected by conventional analytical methods. Results of the ion chromatography studies also shed some light on the particulate formation mechanisms. A preferential enrichment of ammonium, nitrate, and chloride ions in the nano fraction suggests a nucleation mechanism of nanoparticle formation, whereas the predominance of sulfates of refractory alkali-earth metals in the coarser fractions is reminiscent of an accumulation mechanism in the condensed phase. The high ratio of sulfates to nitrates could be used as an indicator of coal-fired emission sources.

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Supporting Information Available: Table of the analytical results of a coal ash SRM. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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