



## Content and Distribution of Trace Elements and Polycyclic Aromatic Hydrocarbons in Fly Ash from a Coal-Fired CHP Plant

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### ABSTRACT

The levels of trace elements and polycyclic aromatic hydrocarbons (PAHs) in fly ash generated by coal combustion have received considerable attention in recent years, due to their potential environmental impact. Sixteen high priority PAHs and 14 trace elements in coal fly ash were measured. The particle sizes of fly ash showed a bimodal distribution, and most ash particles were within a range of 20–25 µm in diameter. The fly ash exhibited high contents of CaO and SO<sub>3</sub>, which was influenced by the desulfidation treatment of limestone. The Be, Cu, Ni, V, Se, Mo and Cd contents increased significantly with decreasing particle sizes of fly ash, while those of Zn and Pb showed no obvious trends. PAHs with three- and four-rings were the dominate species in all the fly ash. The amount low molecular weight PAHs with two-, three- and four- rings was inversely correlated with the particle sizes of the fly ash.

**Keywords:** Trace elements; Polycyclic aromatic hydrocarbons; Fly ash; Coal-fired power plant; China.

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### INTRODUCTION

Coal remains the most important energy source for many countries, especially China. From 1980 to 2011, more and more coal was produced and consumed in China (Liu *et al.*, 2004; Vejehati *et al.*, 2010). In 2011, about 3.6 billion tons of coal were consumed in China, accounting for nearly half of the total world coal consumption, and ranking first in the world (USEIA, 2011). More than half of the total coal consumption in China was attributed to electric utilities, and the proportion will increase in the foreseeable future in order to meet the enormous demands for energy supply (You and Xu, 2010). Unfortunately, increasing use of coal has created enormous social, economic, and environmental costs, as estimated by Epstein (Epstein *et al.*, 2011). “The life cycle effects of coal and the waste stream generated are costing the U.S. public a third to over one-half of a trillion dollars every year. Furthermore, accounting for the damages caused by coal combustion doubles to triples the price of the electricity per kWh generated.”

Combustion of coal for power plants produces a tremendous amount of contaminant. A conventional plant

of 1,000 MW for example produces about 1 million tons of contaminant per year, such as SO<sub>x</sub>, NO<sub>x</sub>, CO<sub>2</sub>, acid gases, organic hazardous air pollutants (HAPs) as well as some solid wastes, such as fly ash, bottom ash, boiler slag, gasifier ash and slag, and flue gas desulfurization (FGD) solids (Mukherjee *et al.*, 2008; Agrawal *et al.*, 2010). Coal combustion by-products (CCPs) with the gangue and calcium carbide slag has been regarded as the top three industrial wastes in China. Fly ash accounts for about 80% of the total CCPs production in pulverized coal fired power plants (Janvijitsakul and Kuprianov, 2008).

China is the world largest producer of fly ash and predicted production in 2020 will reach 570–610 million tons (Barnes *et al.*, 2004; Cao *et al.*, 2008). Fly ash has wide application in many products and industries (Dirk, 1996; Queralt *et al.*, 1997; Moreno *et al.*, 2002; Meawad *et al.*, 2010). Nevertheless, the utilization rate of coal fly ash remains low in China; a large portion of fly ash ends up landfills and has created detrimental environmental impacts (Fu, 2010; Stant, 2010). The environmental effects of fly ash have evoked more and more interest, especially for potentially hazardous trace elements and polycyclic aromatic hydrocarbons. Although those contaminants are present at low contents in fly ash, the large quantities of coal consumption worldwide will aggregate huge amount of emissions entering the environment (Helble, 2000).

Combined heat and power plant (CHP) is considered an important part for the development for coal-fired power

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plants (Wang, 2007). Most studies on pollution from coal burning power plants have focused on large industrial coal-fired plants. There are a limited number of studies concerning the CHP plants because of the relatively small amount of coal consumed. However, most coal-fired CHP plants are located in the center of cities and may cause higher health risks (Peng *et al.*, 2008). In order to minimise the potential environmental risk of CHP plant, it is essential to understand the behaviour of trace elements in fly ash during the combustion process. Based on the analyses of coal and fly ash samples, we studied in detail the contents of trace elements, chemical composition and PAHs in fly ash to provide a more integrated knowledge on the environmental impact of fly ash. The present paper is an attempt to present more information about fly ash from CHP plant.

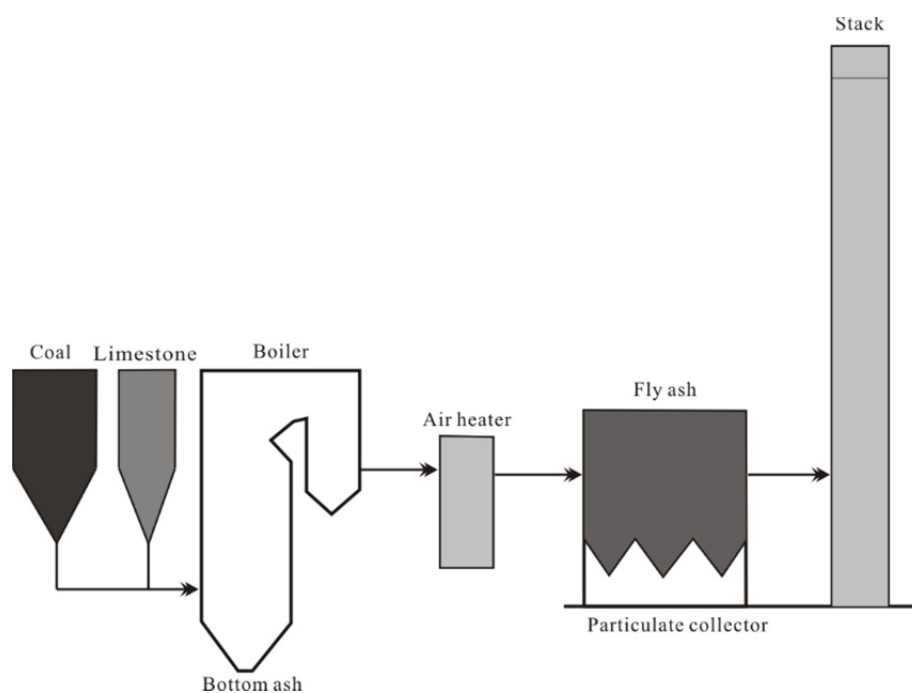
## SAMPLES AND METHODS

Coal and fly ash samples were collected from a CHP plant fueled by pulverized coal at Anhui, China. Coal is dried and crushed before transporting to the fluidized-bed combustion boiler. Limestone is added directly to the fluidized bed as a desulfurizer (Fig. 1). High-efficiency electrostatic precipitators (ESPs) clean the flue gases with particle removal efficiency of 99%. Feed coals are mainly from the Huainan Coalfield. The coal chemical characteristics were discussed by Chen *et al.* (2011) and Li *et al.* (2013). The fly ash samples were obtained from the hopper of electrostatic precipitators and stored in sealed containers to prevent contamination and weathering. Upon return to laboratory, ash samples were first dried at 105°C overnight. Subsequently, the dried fly ash samples were sieved using 100, 120, 170, 240 mesh sieves (BS410-2-2000) and then homogenized. Accordingly, five size classified fractions, namely FA1 (> 150 µm), FA2

(125–150 µm), FA3 (90–125 µm), FA4 (63–90 µm) and FA5 (< 63 µm) were obtained.

Accurate and comprehensive data of coal quality parameters may help to understand the behaviors of element during combustion (Ctvrtnickova *et al.*, 2009). Table 1 summarizes the results of the proximate ultimate analyses. The ash yield of the feed-coal ranges from 15 to 26% with an average value of 22%, and the coals are classified as lower to medium ash coal, based on the Chinese Standard (GB/T 15224-2004). Sulfur oxides released from coal combustion may cause serious environmental pollution and corrosion issues (Thomas, 2012). Meanwhile, higher sulfur content in coal tends to produce fly ash with greater levels of the elements (As, Cd, Hg, Mo, Ni and Pb), which are associated mostly with sulphide minerals (Goodarzi, 2006). The sulfur content of the feed-coal ranges from 0.18 to 0.40%, with a mean value of 0.28%. According to the Chinese Classification for Coal Quality (GB/T 15224-2004), the coal is categorized as special low-sulfur coal.

The coal and fly ash samples were analysed for trace element following the method reported by Chen *et al.* (2011) and Li *et al.* (2013). Content of trace elements (Be, Co, Cr, Cu, Ga, Ni, Pb, V, Zn, Mo and Cd) was determined by inductively coupled-plasma mass spectrometry (ICP-MS) after digestion by an acid mixture of HNO<sub>3</sub>:HCl:HF (3:1:1) in a microwave oven. Selenium (Se) was determined by atomic fluorescence spectrometry (AFS-9230) after ash dissolution in mixture acids of HNO<sub>3</sub>:HClO<sub>4</sub>:HCl = 8:2:5. The content of major elements was determined by X-ray fluorescence spectrometry (XRF) following the method ASTM D4326-2001. The accuracy of the analytical method was determined by analyzing standard reference materials SARM 19 (coal) and NBS1633b (fly ash). The uncertainty was estimated to be within ± 5%.



**Fig. 1.** A schematic diagram of the CHP Plant.

**Table 1.** Proximate and ultimate analysis of feed-coals.

	M <sub>ad</sub> (%)	A <sub>d</sub> (%)	V <sub>daf</sub> (%)	Q <sub>net,d</sub> (MJ/Kg)	S <sub>t,d</sub> (%)
Range	1.67~2.16	15.44–26.96	36.98–45.59	21.89–28.09	0.08–2.37
Mean	1.85	22.36	40.35	25.34	0.77
	C <sub>daf</sub> (%)	H <sub>daf</sub> (%)	N <sub>daf</sub> (%)	S <sub>daf</sub> (%)	O <sub>daf</sub> (%)
Range	83.44–85.86	5.45–6.09	1.36–1.52	0.18–0.40	6.25–7.61
Mean	84.56	5.84	1.41	0.28	6.81

M<sub>ad</sub>: Moisture content of coal (air dry basis); A<sub>d</sub>: Ash content of coal (dry basis); V<sub>daf</sub>: Volatile content of coal (dry ash-free basis); Q<sub>net,d</sub>: Low calorific capacity of coal; S<sub>t,d</sub>: Sulfur content of coal (air dry basis); C<sub>daf</sub>: Carbon content of coal (dry ash-free basis); H<sub>daf</sub>: Hydrogen content of coal (dry ash-free basis); N<sub>daf</sub>: Nitrogen content of coal (dry ash-free basis); S<sub>daf</sub>: Sulfur content of coal (dry ash-free basis); O<sub>daf</sub>: Oxygen content of coal (dry ash-free basis).

Method for PAHs analysis is consistent with the previous analysis process, which has been described previously (Wang *et al.*, 2010a, b; Liu *et al.*, 2012; Wang *et al.*, 2013), 15 g of each sample were extracted in a Soxhlet extractor with 250 mL dichloromethane for 48 h. Activated copper piece was added for desulfurization. The extract was preconcentrated to a volume of 1 mL by rotary evaporation, and then dissolved into 1 mL hexane. The concentrated solution (~2 mL) was injected to pass through a purifying tube packed with silica gel and neutral alumina. After eluting with 70 mL of the methylene dichloride-hexane (30:70 v/v) mixture, the PAH fractions were concentrated to 1.5 mL under a gentle N<sub>2</sub> stream.

Determination of PAHs was conducted on a Shimadzu model 2010 GC-MS instrument equipped with an AOC-20i auto injector (Shimadzu, Japan), using electron impact mode (70 eV) in the selected ion monitoring mode. The DB-5 column of 60 m × 0.25 mm inner diameter (0.25 μm film thickness) was used to separate the individual target compound. The GC temperature increased from 60 to 200°C at 5 °C/min, to 250°C at 2 °C/min, and then to 290°C at 20 °C/min and hold for 20 min at 290°C. The carrier gas He was fed at a constant flow rate of 1.5 mL/min.

The quantitative analysis was done by the internal calibration method (five-point calibration) and PAHs identification was performed by comparison of their retention time with standards. A mixture of internal standards 2-fluoro-1, 1-biphenyl, p-terhenyl-d14, and dibenzo(a,h)anthracene-d14 was added to the sample just before injection. 2-Fluoro-1 and 1-biphenyl were used for Naph, Acy, Acen, Flu; p-terhenyl-d14 was used for Phen, Anth, Flan, Pyr, B[a]A, Chry, B[b]F, B[k]F, and B[a]P; dibenzo(a,h)anthracene-d14 was used for IP, DB[ah]A, and B[ghi]P.

Reagent blanks, duplicate samples and the standard additions were analyzed along with samples through the procedures of extraction and cleanup. Reagent blank samples contained no detectable amounts of the monitoring PAHs. Surrogate standards containing five deuterated PAHs (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12) were added to all samples before extraction to determine the recovery rate of the analysis process. The surrogate recoveries were 67.2 ± 4.52% for naphthalene-d8; 75.4 ± 4.67% for acenaphthene-d10; 88.1 ± 6.41% for phenanthrene-d10; 94.8 ± 4.35% for chrysene-d12; and 98.5 ± 6.59 for perylene-d12 with fly ash samples. Meanwhile, recoveries of 16 PAHs in the

NIST1941 reference sample were between 80 and 120% of the certified values provided by the NIST.

## RESULTS AND DISCUSSION

### Particle Size Distribution of the Fly Ash

Particle size is one of the most important factors for fly ash. Fine-sized fly ash is more persistently available in the atmosphere than coarse fly ash and may cause respiratory illnesses such as asthma, pneumonia and heart diseases (Reynolds *et al.*, 2003; Iordanidis *et al.*, 2008; Harris and Davidson, 2009; Ruhl *et al.*, 2009; Zhang *et al.*, 2012). Particle size distribution of fly ash was measured by a Laser diffraction particle size analyzer. The result for a selected fly ash sample is shown in Table 2 and Fig. 2. Particle sizes of fly ash range from 0.3 to 250 μm with a major fraction in the range of 20–25 μm. The existence of bimodal distribution for coal fly ash particles has been shown by many investigations (Lind *et al.*, 2003). Two maxima peaks are seen in Fig. 2, with the first occurring at the range of 0.5–0.6 μm and second one occurring at 20–25 μm in diameter.

Vaporization, condensation, and nucleation of inorganic constituents in the fuel gas are thought to be the responsible mechanism for the formation of the 0.5–0.6 μm peak, whereas the 20–25 μm peak is formed from the fusion and coalescence of inorganic material (Linak and Wendt, 1994; Lighty *et al.*, 2000; Yu, 2004). Other studies show that the addition of limestone can also cause the bimodal particle distribution system (Lin *et al.*, 2002).

### Chemical Compositions of Fly Ash

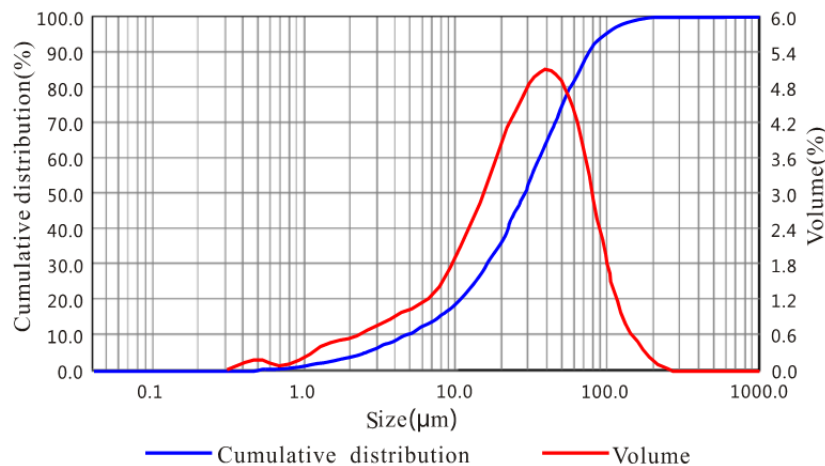
The chemical compositions of the fly ash were analyzed by XRF (Table 3). SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaO are the dominant compositions of fly ash, which account for more than 70 wt.% of the fly ash. MnO, TiO<sub>2</sub>, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, Na<sub>2</sub>O, SO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and MgO are present at trace levels, below 5 wt.%. According to the ASTM C618, this fly ash is classified as Class F for having a low content of calcium oxide and more contents of silica, alumina and iron oxide (more than 70%). These fly ashes are more suitably used for concrete production because the high content of silica and alumina can enhance fly ash strength and resistance to weathering (Ma *et al.*, 1999).

The average chemical compositions of fly ash samples are comparable with China's coal ash (Yuan and Zhang, 1998; Gu, 2004), excepting for CaO and SO<sub>3</sub>, probably due

**Table 2.** Particle size distribution of size fractionated fly ash.

Undersize (%)			D <sub>10</sub> (μm)	D <sub>50</sub> (μm)	D <sub>90</sub> (μm)	AMD (μm)
< 10 μm	< 50 μm	< 100 μm				
3.43	75.37	95.87	4.62	27.96	75.39	40.08

D<sub>10</sub>: 10% of the particles is smaller than this diameter (μm); D<sub>50</sub>:50% of the particles is smaller than this diameter (μm); D<sub>90</sub>: 90% of the particles is smaller than this diameter (μm); AMD: Average Mean Diameter (μm).

**Fig. 2.** Typical particle size distribution of the fly ash.**Table 3.** Chemical composition of fly ash produced from power plant (wt.%).

Samples	Fe <sub>2</sub> O <sub>3</sub>	MnO	TiO <sub>2</sub>	CaO	K <sub>2</sub> O	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	MgO	Total
FA1	3.68	0.01	1.05	6.97	0.79	3.01	0.12	48.11	22.53	0.28	0.64	87.19
FA2	3.81	0.01	1.05	6.75	0.79	2.86	0.13	48.47	22.88	0.30	0.63	87.68
FA3	3.90	0.01	1.05	6.58	0.79	2.70	0.13	48.16	22.97	0.35	0.63	87.27
FA4	4.06	0.01	1.06	6.86	0.76	2.85	0.13	47.79	22.47	0.30	0.66	86.95
FA5	4.33	0.02	1.09	7.28	0.70	3.01	0.16	47.20	22.04	0.30	0.66	86.79
FA <sub>China</sub> <sup>a</sup>	7.56	0.06	1.29	3.32	1.21	0.71	0.28	49.22	27.80	0.45	0.84	92.74
FA <sub>China</sub> <sup>b</sup>	7.00	-	-	2.80	1.30	0.30	-	50.60	27.20	0.50	1.20	-

FA<sub>China</sub><sup>a</sup>: Chemical composition of Chinese coal fly ash, based on 365 samples (Yuan *et al.*, 1998);

FA<sub>China</sub><sup>b</sup>: Chemical composition of Chinese coal fly ash (Gu *et al.*, 2004).

to the addition of limestone in the boiler to minimize the emission of SO<sub>2</sub> from the exhaust gas. The high levels of SO<sub>3</sub> in concrete materials application (generally > 3.5 wt.%) are not desirable owing to the formation of ettringite.

Most of the contents of major oxides such as TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, MnO, CaO, MgO and P<sub>2</sub>O<sub>5</sub> increase with the decrease in particle size, which may relate to the higher surface area of the finer particles (Raclavska *et al.*, 2009).

### Trace Elements in Coal and Fly Ash

Information on trace element contents in coal and fly ash is essential to understand their behaviors during coal combustion. During the formation of fly ash, several trace elements can be enriched relative to the original coal (Meij, 1994; Meijandte Winkel, 2007). Table 5 gives a comparison of coal fly ash and coal in this study with others. Cadmium was the least present in ash, while Barium showed the highest levels. Most elements in the fly ashes show comparable contents to that of European fly ash. Mean contents of most elements except for Mo and Cd in ash

samples fall within the ranges of India fly ash reported by Asokan *et al.* (2005). In the case of coal, only the content for Cu is higher as compared to world, Chinese and Huainan coals (Ketris and Yudovich, 2009; Chen *et al.*, 2011; Dai *et al.*, 2012; Li *et al.*, 2013).

Complex physical and chemical processes of trace elements have occurred in coal combustion process at high temperature phase, and some elements reassigned between different combustion products. In general, behavior of trace elements in coal combustion results from many factors, such as, their affinities and contents in coal, operating conditions and emission control devices (Sarkar *et al.*, 2006; Dai *et al.*, 2010). To elucidate the behavior of the trace elements during coal combustion, a relative enrichment factor was calculated by the following formula: RE = (element content in fly ash)/(element content in coal) × (% ash content in coal)/100. The relative enrichment factor (RE) (Meij, 1994) of trace elements is shown in Table 6. Based on the value of RE factor, trace elements can be grouped into three classes, Class I is around 1.0 (not volatilize during combustion);

**Table 4.** Physical properties of Fly Ash.

Samples	BET Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Pore Size (Å)
FA1	3.0996	0.015729	119.3848
FA2	3.5357	0.018957	123.9240
FA3	4.3331	0.018413	105.7401
FA4	5.2378	0.019481	93.9207
FA5	5.8639	0.019879	85.7934

**Table 5.** Content of trace element in coal and fly ash (mg/kg).

	FA1	FA2	FA3	FA4	FA5	FA <sub>India</sub>	FA <sub>Europe</sub>	Coal	Coal <sub>world</sub>	Coal <sub>China</sub>	Coal <sub>Huainan</sub>
Be	3.7	4.2	4.5	4.5	4.8	Nd	8	1.7	1.6	2.11	Nd
Co	16.75	28.75	19.53	4.64	9.78	7–128	35	5.87	5.1	7.08	11.37
Cr	84.8	80.4	78.5	76.8	76.7	10–353	148	29.7	16	15.4	34.47
Cu	81.3	89.8	106.6	109.5	116.1	39–1000	86	49.8	16	17.5	17.62
Ga	105.28	167.09	115.36	33.79	53.54	Nd	Nd	8.48	5.8	6.55	Nd
Ni	55.4	52.4	53.7	55.4	56.0	29–265	96	38.0	13	13.7	20.70
Pb	46.4	47.2	48.3	46.0	45.9	10–144	80	21.5	7.8	15.1	15.81
V	106.1	127.4	140.2	141.6	145.2	40–190	228	37	25	35.1	19.07
Zn	101.8	85.1	71.2	43.9	89.5	10–250	154	21.4	23	41.4	19.69
Se	2.78	2.09	2.74	3.21	3.06	1–10	7	6.64	1.3	2.47	5.5
Mo	6.05	7.11	8.57	9.23	8.78	8–100	11	2.40	2.2	3.08	ND
Cd	0.59	0.88	0.74	0.73	0.74	1–26	2	0.39	0.22	0.25	ND

Nd: no data;

FA<sub>India</sub>: Concentration of trace element in India fly ashes (Asokan *et al.*, 2005);

FA<sub>Europe</sub>: Mean concentration of trace element in European pulverized coal combustion fly ashes (Moreno *et al.*, 2005);

Coal<sub>China</sub>: Mean concentration of trace elements in Chinese coals (Dai *et al.*, 2011);

Coal<sub>world</sub>: Mean concentration of trace elements in world coals (Ketriss and Yudovich, 2009);

Coal<sub>Huainan</sub>: Mean concentration of trace elements in Huainan coals (Chen *et al.*, 2011).

**Table 6.** Relative enrichment factor of trace elements in fly ash.

	FA1	FA2	FA3	FA4	FA5
Be	0.49	0.55	0.59	0.59	0.63
Co	0.64	1.10	0.74	0.18	0.37
Cr	0.64	0.61	0.59	0.58	0.58
Cu	0.37	0.40	0.48	0.49	0.52
Ga	2.78	4.41	3.04	0.89	1.41
Ni	0.33	0.31	0.32	0.33	0.33
Pb	0.48	0.49	0.50	0.48	0.48
V	0.64	0.77	0.85	0.86	0.88
Zn	1.06	0.89	0.74	0.46	0.94
Se	0.09	0.07	0.09	0.11	0.10
Mo	0.56	0.66	0.80	0.86	0.82
Cd	0.34	0.50	0.42	0.42	0.42

Class II is around 0.7 (volatilize during combustion); and Class III elements with a very low RE factor (almost entirely volatilized during combustion). According to the data, Se was found to be the most volatile, whereas Ga was the least. Most elements (except Ga) had an RE value less than 1, indicating that a portion of the trace elements have not been effectively captured by fly ash, and were directly released from the chimney.

The relationship of element content and the fly ash particle size have been widely studied since the content of some elements is high in small particles and these particles are

hard to remove from flue gas (Sarkar *et al.*, 2006; Dai *et al.*, 2010). Most elements show a pronounced trend of increased content with decreasing particle size, such as: Be, Cu, Ni, V, Se, Mo and Cd, while the content of Ba, Co, Zn and Pb shows an imperceptible change with decrease of particle size. During the combustion process, some vaporized elements (such as, Se and Cd) or their compounds are volatilized and existed as gas phase when the temperature increased, and were captured by fly ash through physical molecular adsorption and condensed on the surface of particles during cooling of combustion gas, which summarize as vaporization-heterogeneous condensation mechanism (Damle *et al.*, 1981; Ho *et al.*, 1992; Chen *et al.*, 2001). Meanwhile the contents of volatile elements from the particle surface are considerably higher than the interior (Fisher *et al.*, 1976). Study of Seames (2003) indicates that, volatilized trace elements are more easily adhere to the particle with high surface areas (Table 4). While for other less volatile elements, chemical reaction is the major adsorption mechanism and shows a less clear trend with the particle diameter of fly ash.

#### Total 16 PAHs in Fly Ash

PAHs, a generic term for organic compounds consisting of two or more connected benzene rings, are severely atmospheric pollutants. Some PAHs with high molecular weight, such as benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and dibenz[a,h]anthracene, are deemed to be

epidemiology, carcinogens and mutagens (Menzie *et al.*, 1992; Talaska *et al.*, 1996; Hannigan *et al.*, 1998; Okona-Mensah *et al.*, 2005; Zhang *et al.*, 2009). Incomplete coal combustion is regarded as an important factor leading to the formation of PAHs (Laflamme and Hites, 1978). The contents of PAHs in fly ash may correlate with parameters such as feed coal properties, combustion conditions and particle removal equipment (Liu *et al.*, 2000). The contents of the 16 PAHs identified as priority pollutants by the USEPA in ash samples are summarized in Table 7. The levels of PAHs vary widely in different fly ash particles. The total amounts of 16 PAHs in the different ash samples are in the range of 3470 to 4800  $\mu\text{g}/\text{kg}$ , while Phenanthrene was the dominant species in fly ash samples. The highest values of the amounts of 16 PAHs are found for the FA4 samples. The most carcinogenic and mutagenic PAH benzo[a]pyrene ranges from 47 to 73  $\mu\text{g}/\text{kg}$ . The amount of carcinogenic PAHs varies between 167 and 321  $\mu\text{g}/\text{kg}$ , which accounts for 4.2 to 6.8% of the total amount of PAHs found in the ash extracts.

In this study the contents of PAHs in fly ash from coal fueled thermal power stations were 43 to 936  $\mu\text{g}/\text{kg}$ , with a mean value of 354  $\mu\text{g}/\text{kg}$  (Sahu *et al.*, 2009). Kong *et al.* (2011) shows the total amounts of PAHs from coal-fired power plant was 70866  $\mu\text{g}/\text{kg}$ . Values between 38560  $\mu\text{g}/\text{kg}$  and 43929  $\mu\text{g}/\text{kg}$  have been reported by Liu *et al.* (2000). These results show that the contents of PAHs in fly ash vary greatly. This relates to different parameters, including combustion conditions, excess air ratio, residence time, addition of limestone, and the properties of feed coal. For this reason, each coal-fired power plant has its own characteristics.

Combustion temperature and excess air ratio have great influence on PAHs emissions from FBC systems (Liu *et al.*, 2000). Previous studies have shown that PAHs emissions first increase, and then decrease with increasing temperature

reaching a maximum at 800°C, which is the temperature used at this power station. At the low temperature, PAHs are mainly from coal pyrolysis and appear as low molecule PAHs. With an increase of temperature, larger PAHs are produced due to the combination of smaller PAHs; however, at high temperature (above 800°C), the PAHs emissions decrease due to complete combustion. Excess air ratio is an important factor of combustion. With the increase of the excess air ratio, more PAHs will be prone to oxidation. The presence of limestone in this study can increase the agglomeration tendency and reduce the combustion efficiency. Hence, the PAHs formation increased.

#### PAH Patterns in Fly Ash

The percent mass and content of PAHs distributed in each size-fractioned fly ash are shown in Fig. 3 and Fig. 4. The three and four rings PAHs were found to be the predominant species in all fly ash samples, accounting for more than 80% of the total PAHs, which agrees with the data reported by other studies (Zhao *et al.*, 2000; Arditoglou *et al.*, 2004; Sahu *et al.*, 2009).

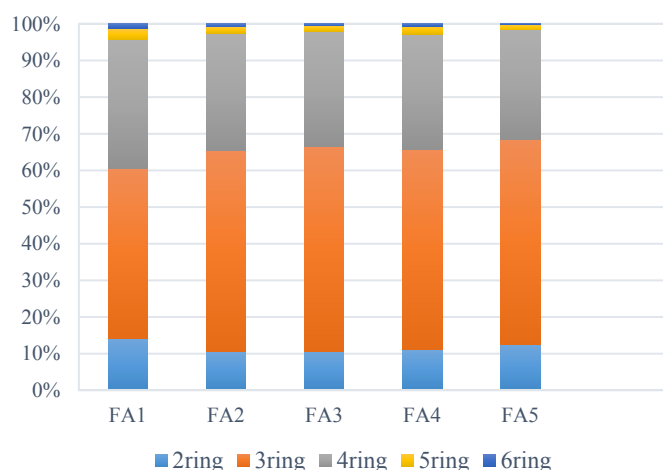
Based on the correlation between PAHs contents and the particle sizes, two groups of PAHs can be recognized. Low molecular weight (MW) PAHs, like two, three and four rings increase with the decrease of ash particle size, and show the highest value in the FA3. The major reasons for this enrichment may relate to the combustor residence time and the surface area for the fly ash. More PAHs could be absorbed on finer particles owing to their larger surface area, leading to a higher percentage of the PAHs contacting with particles (Mastral and Callen, 2000). Meanwhile, smaller particles are characterized by short residence time and faster cooling rate, resulting in a more reactive structure (Liu *et al.*, 2000; Iyer and Scott, 2001; Kong *et al.*, 2011). Another group of PAHs with five and six rings decreases

**Table 7.** Content of PAHs in fly ash from coal-fired CHP plant ( $\mu\text{g}/\text{kg}$ ).

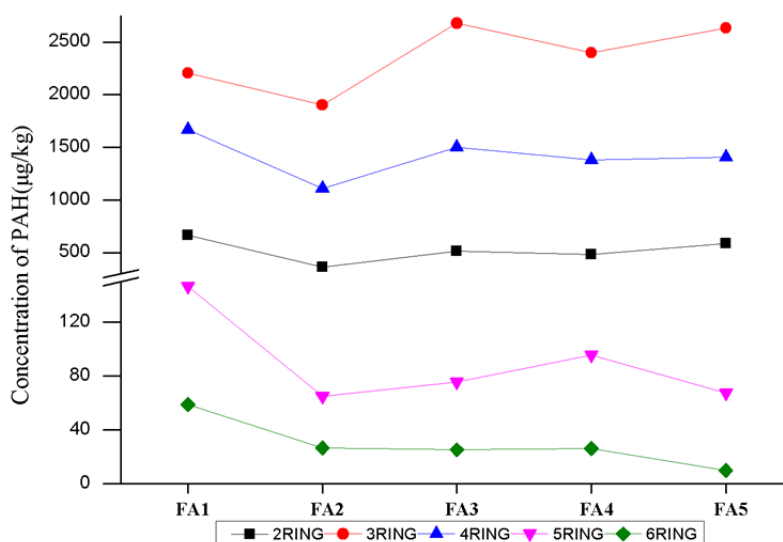
Compound	FA1	FA2	FA3	FA4	FA5
Naphthalene	666.9	363.4	512.5	484.7	585.3
Acenaphthylene	101.4	66.8	92.3	80.6	86.6
Acenaphthene	76.5	44.1	60.0	49.3	55.8
Fluorene	ND	561.0	859.8	732.4	860.2
Phenanthrene	1817.0	1108.2	1492.8	1376.7	1462.4
Anthracene	210.6	121.9	175.0	159.5	170.8
Fluoranthene	635.7	439.1	591.0	535.9	545.8
Pyrene	880.2	581.3	792.4	728.2	735.9
Benz[a]anthracene*	72.8	47.1	64.8	60.0	63.3
Chrysene*	79.9	41.4	54.2	59.1	62.2
Benzo[b]fluoranthene*	89.4	34.6	51.1	55.4	67.2
Benzo[k]fluoranthene*	18.6	11.3	ND	13.9	ND
Benzo[a]pyrene*	38.7	18.9	24.3	26.1	ND
Indeno[123-cd]pyrene*	13.4	7.1	8.2	8.5	9.8
Dibenz[a,h]anthracene*	7.9	6.7	ND	ND	ND
Benzo[g,h,i]perylene	37.5	12.7	17.0	17.5	ND
Total carcinogenic PAH	320.7	167.2	202.8	223.1	202.4
Total PAH	4746.4	3465.6	4795.4	4387.7	4705.2

ND: Not Detected.

\* Carcinogenic PAHs.



**Fig. 3.** Percentage distribution of PAHs with different benzene rings.



**Fig. 4.** Content of PAHs in fly ash with different particle size.

in their contents with the decrease of particle sizes. This is in contrast with the previous study which shows a reverse relationship between content and particle size for all PAHs (Arditsoglou *et al.*, 2004). This difference can be interpreted by the highly developed internal surface of coarse ash particles, which could enhance sorptive capacity for PAHs, particularly the high molecular weight PAHs (Griest and Tomkins, 1986; Janvijitsakul and Kuprianov, 2008). Meanwhile, PAHs with different molecular weight have different vapor pressures. High molecular weight PAHs of lower vapor pressures had more difficulty escaping into the vapor phase upon adsorption onto particles; but low molecular weight PAHs with higher vapor pressures redistributed more easily among different size particles (Chen *et al.*, 2004).

## CONCLUSION

Contents of trace elements and 16 PAHs in coal fly ash taken from a coal-fired CHP plant were determined in the present paper. The result showed that contents of Be, Cu,

Ni, V, Se, Mo and Cd increased significantly with the decrease of particle sizes, while those of Zn and Pb showed no obvious trends. The total PAHs levels ranged from 3465 µg/kg to 4795 µg/kg, and Phenanthrene was the dominant PAH in all ash samples. More than 80% PAHs existed as three and four rings. An inverse relationship of content with particle size was observed for low molecular weight PAHs, with two rings, three rings and four rings, while the other PAHs with five and six ring showed the opposite trend. The addition of limestone may affect particle size distribution, chemical composition and content of PAHs in coal fly ash.

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