Asian Journal of Chemistry; Vol. 26, No. 17 (2014), 5887-5890

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.18309

Emission of Cu, Zn and Cd from Coal in Songzao Coal Mine during the Process of Combustion†

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AJC-15815

By taking the coal samples from seam K1, K2 and K3 of Songzao coal mine in Chongqing as the research objects. Total amount of Cu, Zn and Cd from coal samples and corresponding ash samples were studied. The content of Cu in coal from seam K1 and corresponding ash reach 152.25 and 51.71 mg/kg, while that of Cd in coal from seam K3 and corresponding ash are as low as 1.32 and 0.69 mg/kg, respectively. According to the relative enrichment factors, Cu is found to be the most volatile, while Cd is the least volatile heavy metal element. Relative enrichment factor of Cu in coal of seam K3 is as low as 15.93, while that of Cd in coal of seam K3 is as high as 67.68. By comparing the form content percentage of Cu, Zn and Cd in coal with that in their corresponding ash samples, Cu, Zn and Cd in coal from seam K1, K2 and K3 associated with the organic and sulfide fractions tend to vaporize in the process of coal combustion.

Keywords: Coal combustion, Heavy metal, Emission, Speciation, Sequential extraction.

INTRODUCTION

In the future, coal will keep its important position as a world energy source because of its relatively abundant reserves in comparison to the decreasing reserves of both petroleum and natural gas. In fact, on a global basis, coal is the world's most abundant fossil fuel reserve. In China, coal is the main source of energy and an important industrial raw material. 1/3 of coal consumed in Chongqing is from Songzao coal mine. There are 3 minable coal seams in Songzao coal mine and they are seam K1, K2 and K3 from bottom to top, respectively[1]. The pollutant emissions from coal utilization may cause serious environmental and health risks, so it becomes an important issue with respect to environmental protection.

Besides sulfur, more than 80 trace elements have been discovered from coal until now, among which there are 22 harmful or potentially harmful elements. Some kinds of them will cause considerably serious damage to the ecological environment. In the process of coal combustion, they will be discharged into the atmosphere in different forms and cause environment pollution to the air, water and soil. Once absorbed by living organisms, they will be accumulated for a long time and are difficult to be excreted from body, which carries a great threat on human health[2-7].

Several researches have been done on heavy metal emission in the process of coal combustion in recent years. Koukouzas *et al.*[8] in South Africa determined the content of heavy metal Cd, Cr, Cu, Ni, Mn and Zn in coal combustion process. Labus[9] discussed the release rule of As, Cd, Pb and Zn during the coal combustion process taking coal in Poland as the research object. Liu *et al.*[10] studied the volatilization behaviour of Zn and Cd in flue gas during the process of coal combustion. Ren[11] studied the distribution of the harmful elements in coal maceral and in pyrites. Zhang *et al.*[12,13] studied the content of organic trace mineral sources in coal, analyzed the species distribution of harmful trace elements in the process of coal combustion and studied the release rule of trace elements in the high temperature pyrolyzed coal.

In this paper, the coal samples from seam K1, K2 and K3 of Songzao coal mine in Chongqing are chosen as the research object. The total amount of Cu, Zn and Cd in coal from seam K1, K2 and K3 of Songzao coal mine and corresponding ash samples were studied through doing related experiments. The relative enrichment (RE) factors of Cu, Zn and Cd were calculated and discussed. The brief emission rule was drawn by comparing the form content percentage of Cu, Zn and Cd in coal with that in their corresponding ash samples.

†Presented at 2014 Global Conference on Polymer and Composite Materials (PCM2014) held on 27-29 May 2014, Ningbo, P.R. China

EXPERIMENTAL

Sample preparation: Three kinds of experimental coal samples were obtained from seam K1, K2, K3 in Songzao Mine Area, respectively in Chongqing, China. The coal was processed into fine particles (< 0.2 mm) through the process of reduction and division according to the hard coal and coke-manual sampling. Samples were carefully shifted through a 200-mesh sieve after being naturally air dried.

In addition, three kinds of ash samples were prepared through calcining three kinds of experimental coal samples, respectively in a muffle furnace in air at 900 ºC for 2 h.

Analysis of total amount: Microwave dissolver was used to dispel the sample. The atomic fluorescence electroscopy was used to measure the concentration of heavy metal.

In order to obtain the total content of heavy metal in the coal and ash, 5 mL of conc. HNO_3, 2 mL of conc. H_2O_2 and 3 mL of conc. HF were added to 0.2 g of sample. Then, these mixtures were treated with Microwave Digestion System (MD6). After cooling and filtration, the solutions were diluted to 100 mL with distilled water. The total content can be measured by SK-2002B atomic fluorescence spectrometer[14].

Sequential extraction procedure: Based on the method of sequential extraction in literature[15], heavy metal of Cd, Zn and Cu in coal and ash was divided into four fractions: exchangeable (F1), bound to sulfide (F2), bound to organic matter (F3) and residual (F4). The specific operations are listed below and shown in Fig. 1.

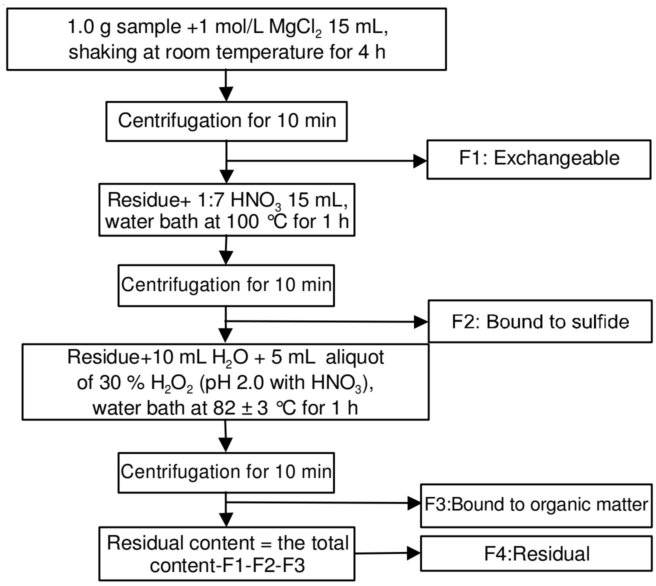

Fig. 1. Flow chart of sequential extraction

(I) Exchangeable: 1 g sample was extracted at room temperature for 4 h with 15 mL of magnesium chloride solution (1 M $MgCl_2$, pH 7.0) with continuous agitation.

(II) Bound to sulfide: The residue from (I) was leached in 15 mL 1:7 (v/v) nitric acid with water bath at 100 ºC for 1 h.

(III) Bound to organic matter: The residue from (II) was extracted in 10 mL H_2O adjusted to pH 2.0 with nitric acid and 5 mL 30 % (v/v) H_2O_2 with water bath at 82 ± 3 ºC for 1 h.

(IV) Residual: Residual content = The total content- F1- F2- F3.

RESULTS AND DISCUSSION

Total amount of Cu, Zn and Cd: The mean value for total amount of heavy metal in coal and ash samples are demonstrated in Table-1. Table shows that the content of Cu is the highest among of these metal elements. Zinc is the second highest value in both coal and ash.The content of Cd in coal and ash is the lowest and is less than 3 and 5 mg/kg, respectively. Moreover, there is a trend that the content of Cu and Cd both in coal and ash decreases in turn from seam K1 to seam K3. The content of Cu in coal from seam K1 and corresponding ash reaches 152 and 51.71 mg/kg. For that of Cd in coal from seam K3 and its corresponding ash are as low as 1.32 and 0.69 mg/kg, respectively.

TABLE-1
CONTENT OF Cu, Zn AND Cd IN COAL AND ASH SAMPLES (mg/kg)

Sample		Cu	Zn	Cd
K1	Coal	152.25	89.23	2.98
	Ash	111.00	58.19	4.33
	Ash*	51.71	27.11	2.02
K2	Coal	105.00	39.28	1.80
	Ash	96.25	64.19	4.08
	Ash*	22.52	15.02	0.96
K3	Coal	88.00	47.54	1.32
	Ash	71.20	112.59	3.49
	Ash*	14.02	22.17	0.69

Note: *Indicates data were calculated based on the content of heavy metal in coal.

Relative enrichment (RE) factor of Cu, Zn and Cd: The relative enrichment factor (RE) was calculated for the ash and it is shown in Table-2. Relative enrichment factors are useful in understanding behaviour of trace elements in terms of their volatility in the process of combustion. A relative enrichment factor, discussed previously, was calculated by the following formula[16]: RE = (element concentration in ash)/(element concentration in coal) × (percentage ash content in coal)/100.

TABLE-2
RELATIVE ENRICHMENT (RE) FACTOR OF Cu, Zn AND Cd

Sample	Cu	Zn	Cd
K1	33.97	30.38	67.68
K2	21.45	38.24	53.06
K3	15.93	46.63	52.05

According to the relative enrichment factors, overall, Cu is found to be the most volatile while Cd is the least volatile heavy metal element. Relative enrichment factor of Cu in coal of seam K3 is as low as 15.93 and that of Cd in coal of seam K3 is as high as 67.68. Higher value of the relative enrichment factors in ash indicates a lower emission rate in the process of combustion.

Speciation analysis of Cu, Zn and Cd: The amount of heavy metal emission from coal combustion is strongly dependent on the modes of occurrence in coal. The mode of occurrence includes information about the specific mineral an element forms, dispersion within a particular host mineral or maceral, the fraction of the coal the element is associated, the oxidation state that element occurs and so on[17]. Figs. 2-7, show form content percentage of Cu, Zn and Cd in coal and ash, respectively and the result of sequential extraction procedure for coal and ash are shown in Table-3.

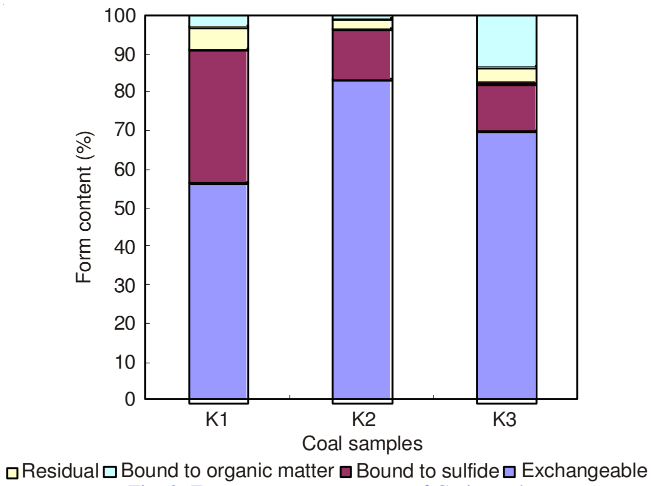

Fig. 2. Form content percentage of Cu in coal

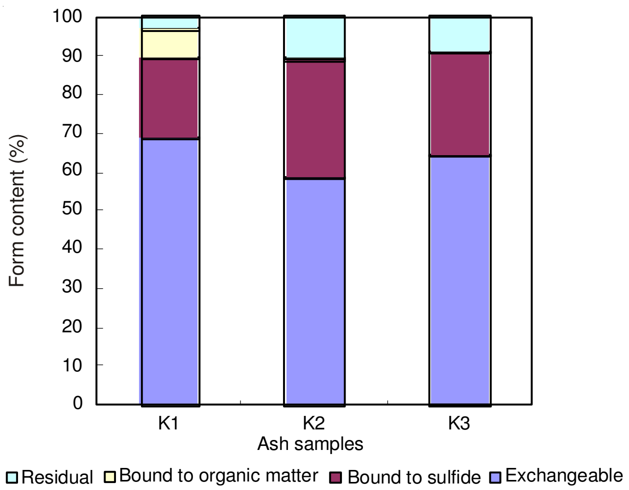

Fig. 3. Form content percentage of Cu in ash

Exchangeable is the most mobile and bioavailable. According to the present study, high concentrations of this fraction

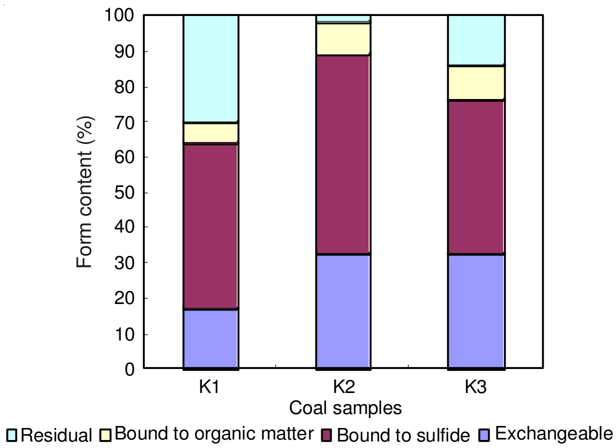

Fig. 4. Form content percentage of Zn in coal

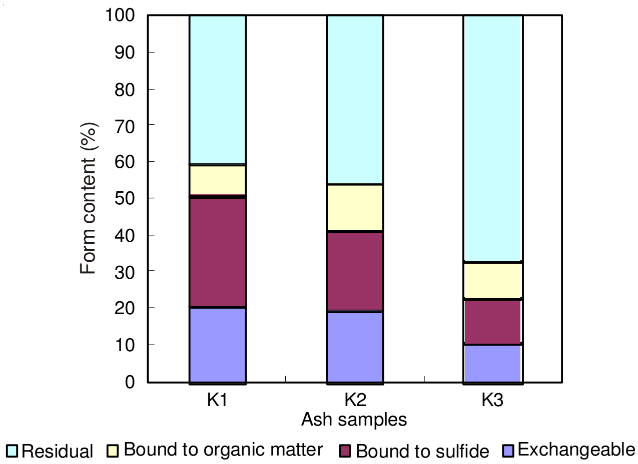

Fig. 5. Form content percentage of Zn in ash

would indicate a higher level of health risk. F2 can also be considered to be a mobile phase of trace elements. F3 explains trace elements were associated with organic matter in coal. In natural environment, organic matter tends to be more stabilized than the binding properties associated with F1 and F2. However, trace elements in F3 are easily released in the process of coal combustion. These trace elements, in F4, are not expected to be released during a reasonable time and they are usually contained in the crystalline structure of primary or secondary mineral.

TABLE-3
RESULT OF SEQUENTIAL EXTRACTION PROCEDURE FOR COAL AND ASH

Sample	Extraction steps	Speciation	Cu (mg/kg)		Zn (mg/kg)		Cd (mg/kg)	
			Coal	Ash	Coal	Ash	Coal	Ash
K1	F1	Exchangeable	86.50	35.52	15.61	5.59	1.75	1.25
	F2	Bound to sulfide	52.50	10.96	41.66	8.18	0.77	0.24
	F3	Bound to organic matter	9.30	3.70	5.15	2.42	0.12	0.07
	F4	Residual	3.95	1.53	26.81	10.92	0.35	0.45
K2	F1	Exchangeable	92.50	13.23	12.84	2.95	1.28	0.71
	F2	Bound to sulfide	15.10	6.81	22.15	3.25	0.35	0.13
	F3	Bound to organic matter	2.60	0.18	3.69	1.98	0.15	0.08
	F4	Residual	0.80	2.30	0.60	6.84	0.03	0.03
K3	F1	Exchangeable	61.50	9.07	15.65	2.26	0.82	0.48
	F2	Bound to sulfide	11.30	3.72	20.83	2.77	0.25	0.10
	F3	Bound to organic matter	3.50	0.00	4.38	2.27	0.15	0.07
	F4	Residual	11.70	1.23	6.67	14.88	0.09	0.04

Note: Data of ash in table 3 were calculated based on the content of heavy metal in coal.

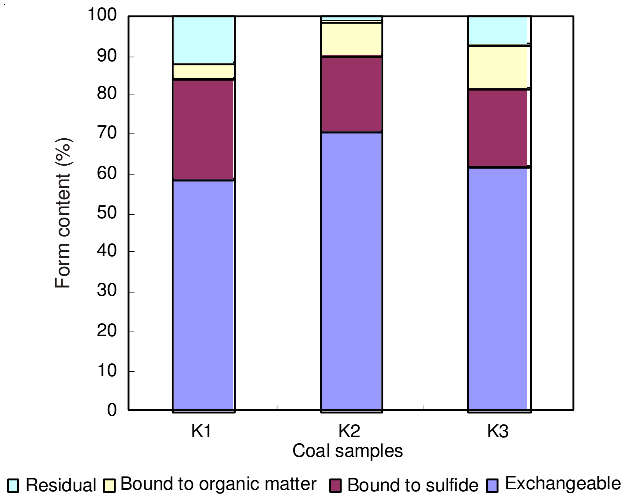

Fig. 6. Form content percentage of Cd in coal

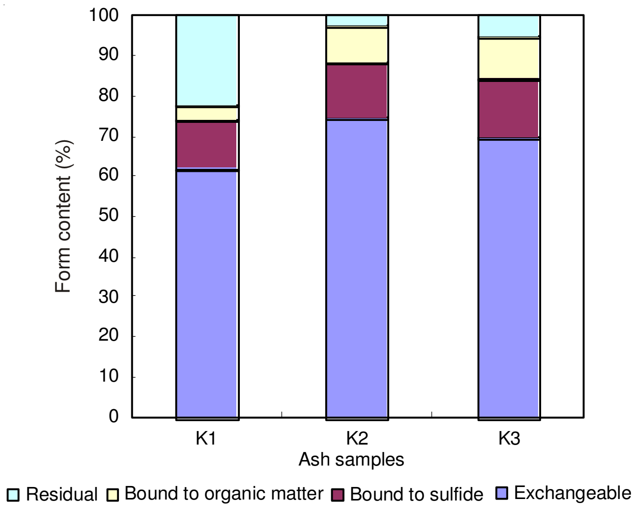

Fig. 7. Form content percentage of Cd in ash

Tables 1 and 3 showed Cu, Zn and Cd had emission rate at different degrees in the process of coal combustion. By comparing the percentage of Cu, Zn and Cd in coal with that in their corresponding ash samples, a brief conclusion can be drawn that those elements which are associated with the coal organic and sulfide fractions tend to vaporize in the process of coal combustion. In detail, Cu, Zn and Cd associated with sulfide fraction were emitted more into the air as their content in coal were more than the content of those associated with the coal organic fraction.

Conclusion

• Copper is the element whose content is the highest and the content of Cd is the least both in coal and ash. The content of Cu in coal from seam K1 and corresponding ash reach 152.25 and 51.71 mg/kg, while that of Cd in coal from seam K3 and corresponding ash are as low as 1.32 and 0.69 mg/kg, respectively.

• According to the relative enrichment factors, Cu is found to be the most volatile while Cd is the least volatile heavy metal element. RE factor of Cu in coal of seam K3 is as low as 15.93, while that of Cd in coal of seam K3 is as high as 67.68.

• Copper, zinc and cadmium in coal from seam K1, K2 and K3 associated with the organic and sulfide fractions tend to vaporize in the process of coal combustion. Those elements associated with sulfide fraction were emitted more into the air in the process of coal combustion.

ACKNOWLEDGEMENTS

This study is financially supported by the National Natural Science Foundation of China (No. 51274262) and National Engineering Research Center of Phosphate Resources Development and Utilization Foundation of China (No. 2012 National Phosphate k002).

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