



Emission characteristics of hazardous components in municipal solid waste incinerator residual ash*

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Abstract: In this study, eight fly ash samples and three bottom ash samples from different areas are collected for analysis of their physicochemical properties and emission content of dioxin precursors and metals. Their surface characteristics, their effects on dioxin precursors, and important aspects of the compositions of residual ash (fly ash and bottom ash) are investigated. Poly-chlorobenzenes (PCBzs) in the fly ash of a fluidized bed incinerator (FBI) are 7.35 to 357.94 $\mu\text{g}/\text{kg}$, and in that of a fire grate incinerator (FGI) are 6.74 to 96.52 $\mu\text{g}/\text{kg}$. The concentrations in bottom ash are the same (i.e., 2.23 to 2.99 $\mu\text{g}/\text{kg}$) regardless of the furnace type. The concentrations of polycyclic aromatic hydrocarbons (PAHs) in FGI fly ash samples (0.293 to 1.783 mg/kg) are less than these in samples from FBIs (1.820 to 38.012 mg/kg). Low boiling point PAHs (mainly 2- and 3-ringed PAHs) and high boiling point PCBzs (mainly H_xCB and P_eCBz) are the major constituents of residual ash. Different distributions of PCBzs and PAHs are mainly dictated by the incineration characteristics of FBI and FGI. Al and Fe, as non-toxic “light metals” are the major constituents of the residual ash, and Ni and Zn as non-toxic heavy metals play important roles in the total heavy metal. Cu, Pb, and Cr are the three major toxic heavy metals. The correlation of the metals and the dioxin precursors is discussed and distinguished.

Key words: Residual ash, Poly-chlorobenzenes (PCBzs), Polycyclic aromatic hydrocarbons (PAHs), Heavy metal, Municipal solid waste incineration (MSWI)

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1 Introduction

Incineration is regarded as an effective thermal treatment for municipal solid waste (MSW) disposal (Besombes *et al.*, 2001; Dyke *et al.*, 2003), and has been developed rapidly in China in the last 10 years. In China, the number of municipal solid waste incinerator (MSWI) plants has increased to 159, and the total disposal capacity reached 145 kt/d by 2013. In practice there are two major furnace types: the fire grate incinerator (FGI) and the fluidized bed incinerator (FBI). However, the emission of by-products,

mainly dioxins and heavy metals, limits the further use of MSW incineration technology (Wei *et al.*, 2011).

Dioxins contain poly-chlorinated dibenzo-*p*-dioxin (PCDDs) and poly-chlorinated dibenzofuran (PCDFs) regarded as trace persistent organic pollutants (POPs). They mainly arise from the transformation of some dioxin precursors such as polycyclic aromatic hydrocarbons (PAHs) and poly-chlorobenzene (PCBzs) (Quina *et al.*, 2008; Li *et al.*, 2001). According to previous studies (Everaert and Baeyens, 2002; Chin *et al.*, 2011; 2012), the dioxin formation process is a catalytic reaction taking place on the surface of residual ash (fly ash and bottom ash), influenced by some metal compounds and their precursors (Weber *et al.*, 2001; Wang *et al.*, 2002). PAHs are a group of multi-ring organic compounds from the organic carbon in the dust, depending upon the

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incineration state of the furnace (Yasuda and Takahashi, 1998; Frey *et al.*, 2003; Johansson and van Bavel, 2003). Sixteen of the total PAHs with carcinogenic and mutagenic characteristics have attracted attention and are listed by the United States Environmental Protection Agency (USEPA). PAHs are mainly found in the small particles of MSWIs, i.e., fly ash and bottom ash (Wilhelm *et al.*, 2001; van Caneghem and Vandecasteele, 2014). As well as PAHs, PCBzs have a strong correlation with dioxin formation, and are considered to be an indicator of dioxins in MSWIs (Yan *et al.*, 2010). PCBzs come from a surface catalytic oxidation reaction in bottom ash and fly ash. A variety of heavy metal compounds are catalytic for the formation of PCBzs and PAHs (Öberg *et al.*, 2007; 2008; Fujimori *et al.*, 2009). Some catalytic metal constituents can cause the formation of dioxins from precursors, and some metallic chlorides, especially Cu, play an important role in catalysing dioxin formation (Gullett *et al.*, 1990; Takaoka *et al.*, 2005). Catalytic heavy metals mainly exist on the surface of fly ash and bottom ash, with silicate-based glass phases and mineral phases (Hagenmaier *et al.*, 1987). The main heavy metals are Cd, Cr, Cu, Hg, Ni, Pb, and Zn, and the different saturated vapor pressures and boiling points of those metals lead to their different distributions in fly ash and bottom ash (Wei M.C. *et al.*, 1998; Wei Y. *et al.*, 2011; Grosso *et al.*, 2011). Considering both the high toxicity of heavy metals and their catalytic ability, the investigation of their distribution in residual ash is important. The distribution characteristics of PAHs and PCBzs in the residual ash and the correlation of them with heavy metals also deserve investigation. Moreover, MSWI furnace types are of

concern because of their direct relationship with the formation of dioxins from precursors. However, the overall emission distribution characteristics of PAHs and PCBzs in the residual ash of the MSW incineration system have not been much discussed and the correlation of PCBzs and PAHs with catalytic metals still needs more study.

In this paper, the basic characteristics of residual ash particles from different MSWI furnaces are discussed and distinguished, including surface characteristics, basic elemental composition, and the mineral composition of residual ash particles. The emission characteristics of dioxin precursors (PCBzs and PAHs) and major metals in MSWI residual ash are respectively investigated, and the effect of furnace types on their emissions characteristics are discussed. Furthermore, correlations between the major metals and precursors are investigated and evaluated to recognize different roles of metals in the incineration process.

2 Materials and methods

2.1 Basic information of samples

Brief information on the sampled incinerators is given in Table 1. All the fly ash samples were collected at the outlet of the bag filter house and the bottom ash samples came from the dry extraction system.

2.2 Detection methods

The particle characteristics of residual ash samples were analyzed by BET surface analyzer (TRISTAR 3020, Micromeritics Inc., USA).

Table 1 Brief information of the sampled MSW incinerators

No.	Location	Raw material	Furnace type	Flue gas cleaning	Disposal ability (t/d)	Fly ash	Bottom ash
MSW11	Ningbo 1#	Waste+coal	Fire grate	SDP+AC+FB+SCR	500	FA1	BA1
MSW12	Hangzhou 1#	Waste+coal	Fire grate	SDP+AC+FB	150	FA2	BA2
MSW13	Deyang	Waste+coal	Fire grate	SDP+FB	200	FA3	
MSW14	Tianjin	Waste+coal	Fire grate	SDP+AC+FB	500	FA4	
MSW15	Hangzhou 2#	Waste+coal	Fluidized bed	SDP+AC+FB	400	FA5	
MSW16	Hangzhou 3#	Waste+coal	Fluidized bed	SDP+AC+FB	400	FA6	BA3
MSW17	Ningbo 2#	Waste	Fluidized bed	SDP+FB	400	FA7	
MSW18	Pinghu	Waste+coal	Fluidized bed	SDP+AC+FB	300	FA8	

AC: active carbon; FB: fabric bag; SDP: semi-dry process; SCR: selective catalytic reduction

Elementary compositions of residual ash samples were detected by an energy dispersive spectrometer (EDS) (EDAX-GENESIS4000, USA). Mineral compositions of residual ash samples were analyzed by X-Ray Diffraction (XRD) (PANalytical-X'Pert PRO, the Netherlands).

PCBzs, PAH, and heavy metals in residual ash were analyzed by different analysis methods. The detection of PCBzs in residual ash samples followed the China National Standard (MEPC, 2002) and that of PAHs followed the USEPA methods 8100, 3540C, and 3660B (USEPA, 1986; 1996a; 1996b). All the residual ash samples were firstly heated and dried under N₂ at 105 °C for 24 h, and then were taken to a pretreatment stage. All the concentration values were based on the dry base of residual ash samples. The detailed pretreatment steps, including solution concentration, multistep purification, and volume measured, were according to the previous studies (Yan *et al.*, 2010; Dai *et al.*, 2014). Then samples in organic solution were injected into gas chromatography with electron capture detector (GC-ECD, 6890N, Agilent, USA) for PCBzs detection and gas chromatography with mass spectrometry (GC-MS, Scientific ISQ, Thermofisher, USA) for PAHs detection. The concentrations of PCBzs and PAHs were calculated by an external standard method.

To release the metals from the residual ash particles, the residual ash samples were first digested with a mixed solution of HCl, HNO₃, and HF (6 ml of 12.4 mol/L, 3 ml of 14.4 mol/L, and 1 ml of 33.3 mol/L, respectively) in a microwave accelerated

reaction system (MARS) (CEM Inc., USA). Then the solutions were used to detect the object metals by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (iCAP 6000, Thermofisher, USA), and their concentrations in the residual ash were calculated.

3 Results and discussion

3.1 Basic characteristics of MSWI residual ash

The basic characteristics of MSWI residual ash were subdivided into surface characteristics, basic element composition, and mineral composition. The surface characteristics of residual ash are listed in Table 2, including average particle diameter, BET surface area, and pore parameter. Overall, the average particle diameters show FBIs>FGIs for fly ash samples and FGIs>FBIs for bottom ash samples. Those differences are caused by the operational characteristics of FBIs and FGIs. Larger raw waste was incinerated in FGIs and larger bottom ash particles were produced there. Moreover, larger and heavier fly ash particles in FBIs could escape from the furnace because of the strong fluidization state, and thus larger fly ash particles were obtained.

The BET surface areas of residual ash samples from FGIs (FA 1–4) range from 2.01 to 8.49 m²/g, and those from FBIs (FA 5–8) range from 1.58 to 5.75 m²/g. The values of the BET surface area from FGIs are a little higher than those from FBIs. As for bottom ash samples, BA1 and BA2 differ a little (2.45

Table 2 Pore characteristics of MSWI residual ash samples

Sample	Average particle diameter (nm)	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Micropore volume (cm ³ /g)	Pore size (nm)	
FGI	FA1	7.07×10 ²	8.49	9.31×10 ⁻³	1.32×10 ⁻³	106.71
	FA2	2.99×10 ³	2.01	4.75×10 ⁻³	2.44×10 ⁻⁴	227.36
	FA3	1.42×10 ³	4.23	6.07×10 ⁻³	1.82×10 ⁻⁴	101.42
	FA4	8.60×10 ²	6.98	1.56×10 ⁻²	1.54×10 ⁻³	256.92
FBI	FA5	3.79×10 ³	1.58	3.42×10 ⁻³	9.20×10 ⁻⁵	270.38
	FA6	4.35×10 ³	1.38	4.35×10 ⁻³	1.30×10 ⁻³	489.19
	FA7	3.06×10 ³	1.96	3.60×10 ⁻³	4.45×10 ⁻⁴	238.74
	FA8	1.04×10 ³	5.75	1.82×10 ⁻²	7.03×10 ⁻⁴	282.57
FGI	BA1	2.38×10 ³	2.45	6.78×10 ⁻³	1.00×10 ⁻⁴	259.11
	BA2	1.80×10 ³	3.44	9.61×10 ⁻³	5.10×10 ⁻⁵	184.12
FBI	BA3	1.11×10 ³	0.52	1.38×10 ⁻³	1.10×10 ⁻⁴	427.14

The pore sizes were measured according to the BJH method

and 3.44 m²/g) but are 5–6 times larger than for BA3 (0.52 m²/g). Moreover, the BET surface areas of bottom ash samples are smaller than those for fly ash samples as a whole.

For the total pore volume of residual ash, the values from FGIs are generally higher than those from FBIs, regardless of fly ash and bottom ash, and the differences among FGI fly ash samples are larger. However, bottom ash samples have less micropore volume than fly ash, and the residual ash from FBIs has a more complex micropore structure than that from FGIs. Rapid release of flammable constituents in raw waste under strong fluidization state of FBIs can cause the abundant formation of micropore structure on the FBI fly ash surface. The pore sizes are ordered as FBIs bottom ash > FGIs bottom ash, as well as FBIs fly ash > FGIs fly ash.

MSWI2 and MSWI6 have the same waste sources and flue gas disposal devices, and the major difference is the type of incineration furnace. FA2 and FA6 are comparatively studied to investigate the effect of furnace type on element distribution. Table 3 showed that O, Si, and Ca are major elements of fly ash, and they constitute the basis of fly ash particles. FA2 contains more non-metallic elements such as S,

Cl; however, FA6 contains more metallic elements such as Al, Mg, and Fe. Among the mineral compositions, CaO is usually used as the additive for SO_x removal in the incineration system (Bodéan and Deniard, 2003), and the addition of SiO₂ used as bed material in FBI (Saxena and Jotshi, 1994; van Caneghem *et al.*, 2012) weakens the pore structure of the fly ash surface. The smaller particle, more crushed surface, and less micropores of FA2 are as shown in Fig. 1.

3.2 Emission characteristics of dioxin precursors PCBzs in MSWI residual ash

PCBzs produced in the incineration process are important dioxin precursors. The total concentration of PCBzs in FGIs fly ash ranged from 7.35 to 357.94 µg/kg with big discrepancies, and FGIs bottom ash contained 2.23 to 2.99 µg/kg PCBzs. For the samples from FBIs, fly ash samples showed smaller discrepancies in PCBzs concentration of 6.74 to 96.52 µg/kg and PCBzs in bottom ash were 2.75 µg/kg. Overall, fly ash contributed the major quantity of PCBzs of residual ash (over 95%), and the concentrations of PCBzs in fly ash were 25–150 times higher than those in bottom ash. Moreover, FBIs

Table 3 Compositions of elemental and mineral compositions in fly ash samples (% in weight)

Element (EDS)	FA2	FA6	Element (EDS)	FA2	FA6	Mineral (XRD)	FA2	FA6
O	20.51	33.40	Na	7.95	3.39	SiO ₂	16.8	51.4
S	4.75	1.92	Mg	1.75	2.61	NaCl	10.0	18.0
Cl	25.80	8.85	K	6.55	2.81	KCl	7.1	5.2
Si	4.28	14.40	Fe	0.73	3.24	CaCO ₃	31.0	16.4
P	1.01	1.69	Zn	0.89	0.98	CaSO ₄	7.7	9.0
Al	2.12	7.33	Ti		0.78	CaClOH	27.4	
Ca	23.65	18.61						

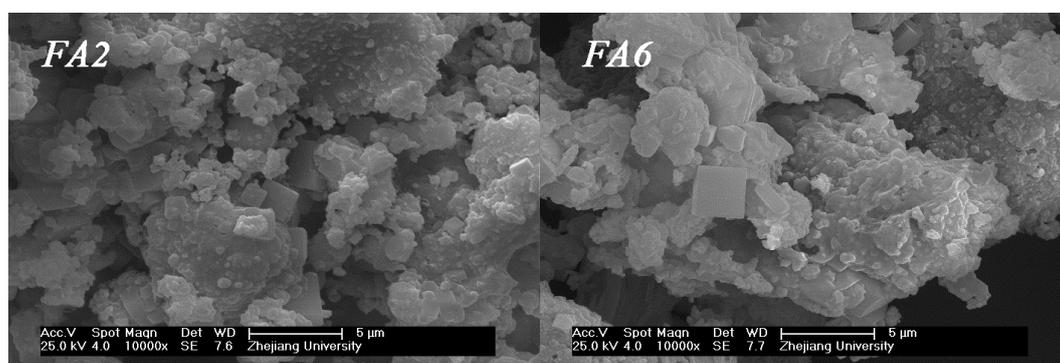


Fig. 1 SEM images of fly ash samples (FA2 and FA6)

showed a better adaptability and were more effective on eliminating the effects of individual differences between plants and on controlling the PCBzs emission of fly ash, in comparison with FGIs. The emission amounts of PCBzs in bottom ash were approximately the same for both the furnace types.

The formation and emission of PCBzs in residual ash was related to the incineration conditions of raw waste in the furnace. According to our results, a sufficient mixture with enough oxygen under a high enough temperature (>850 °C) with long residence time (>2 s) can effectively control the emission of dioxins, as well as PCBzs (McKay, 2002), and is regarded as the principal emission control method (Ma et al., 2013). FBI shows more advantages in PCBzs emission control than FGI owing to its operational characteristics. Moreover, the basic characteristics of residual ash particles can also affect the emissions of PCBzs by means of adsorption and desorption effects (Hagenmaier et al., 1987; Halonen et al., 1995). The complex surface structure and the catalytic metals can apparently accelerate the formation of PCBzs (Gullett et al., 1990; Olie et al., 1998).

By correlation analysis, the total concentration of PCBzs had a partial positive correlation with BET surface area and micropore volume ($R^2=0.63$ and 0.53 , respectively), and negative partial correlation with pore size ($R^2=-0.58$). Complex surface structure and large micropore volume are beneficial to the adsorption of PCBzs, and they also give a strong ability to adsorb and then catalytically produce PCBzs on the surface of residual ash particles. Bottom ash with a simpler surface structure showed less PCBzs concentration than fly ash, and fly ash from FBIs showed a lower emission concentration of PCBzs than that from FGIs.

The percentages of each PCBzs congener are presented in Fig. 2. Chlorobenzene and dichlorobenzene were rarely detected in residual ash because they are highly volatile with low boiling points. Both of them can easily escape from residual ash particles in the high-temperature region of the furnace cavity, and only T_x CBz to H_x CBz were analyzed and discussed below. H_x CB and P_e CBz were commonly the majority of total PCBzs, with proportions of 29.15% to 83.98% in fly ash and 34.76% to 89.49% in bottom ash. The residual ash from FBI had a lower proportion of high

chlorine-substituted PCBzs than that from FGI, which can be attributed to the high temperature and to a thorough mixture with enough oxygen in the FBI furnace cavity conditions unfavorable to the survival of high chlorine-substituted PCBzs. Moreover, the previous crushing of raw wastes for FBI can weaken some unnecessary influence from raw wastes and be beneficial for PCBzs emission control (Li et al., 2001; Frey et al., 2003), by encouraging relatively low PCBzs emission levels in FBI fly ash samples compared with those from FGIs.

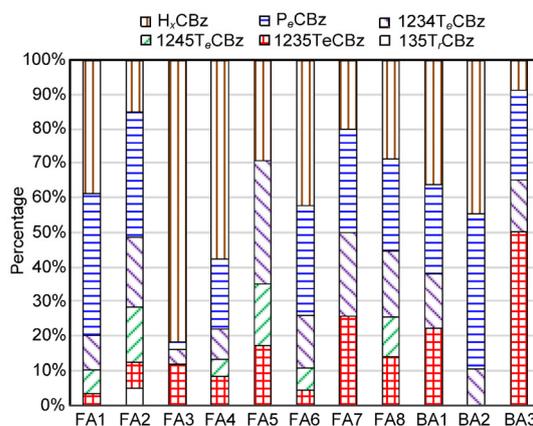


Fig. 2 Distribution of PCBzs (more than three chlorine substituted congeners) in MSWI residual ash samples

3.3 Emission characteristics of PAHs in MSWI residual ash

Taking into account harmfulness and representativeness, only 16 toxic PAHs were analyzed and are discussed below (Kirso et al., 2005).

The concentration of PAHs in FGIs fly ash ranged from 0.293 to 1.783 mg/kg, lower than that of FBIs (1.820–38.012 mg/kg). However, FGI bottom ash contained more PAHs (0.512–1.940 mg/kg) than FBIs (0.299 mg/kg). According to the previous research, PAHs mainly come from the catalytic oxidation of carbon sources on ash particles under high temperature, and mainly exist absorbed on small particles in the gas flow out of furnace cavity (Li et al., 2001; Johansson and van Bavel, 2003). Hence, the concentrations of PAHs in fly ash are much higher than bottom ash. Moreover, the emission amounts of small particles (i.e., fly ash) of FBI were generally much higher than that of FGI, so there was more total PAHs emission by FBI.

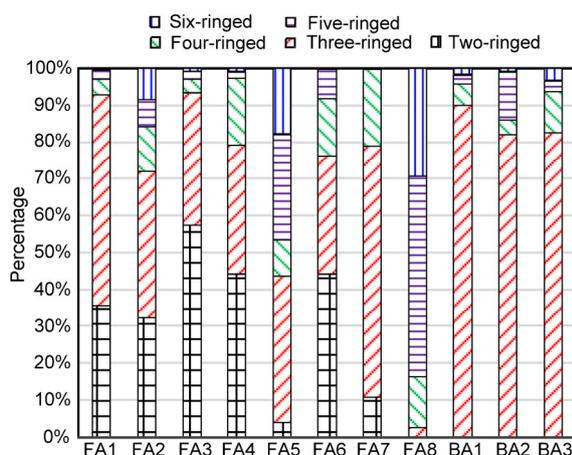


Fig. 3 Distribution of different ringed PAHs (2- to 6-ringed PAH) in MSWI residual ash samples

16 toxic PAHs were divided into five groups (2- to 6-ringed PAHs) according to the number of benzene rings. The physical and chemical characteristics of PAHs with the same ring number were similar, and differently ringed PAHs apparently performed differently from each other (Fig. 3).

For the distribution of PAHs in fly ash, 2- and 3-ringed PAHs with low boiling points were generally in the majority (32.34% to 57.36% and 35.03% to 57.14%, respectively) for FGIs. However, the situation in FBIs was more complex. In FA5 and FA8, the major constituents were 5- and 6-ringed PAHs, and 2-ringed PAHs were not even detected in FA8. Moreover, the major PAHs in FA6 and FA7 were 2- and 3-ringed PAHs, with slightly lower proportions than in FGIs. Overall, fly ash mainly had PAHs with low boiling point. As for the bottom ash samples, all had a majority of 3-ringed PAHs (82.07% to 90.09%) regardless of furnace type, and hardly any 2-ringed PAHs were identified.

Comparing the distribution of PCBzs and PAHs in residual ash, low boiling point PAHs and high boiling point PCBzs were in the majority, which indicated that PAHs and PCBzs are formed by different pathways and play different roles in the incineration process. From previous research (Iino *et al.*, 1999; Böhm and Jander, 1999; Wilhelm *et al.*, 2001), PAHs appear mainly to arise from a primary synthesis from small hydrocarbons with appropriate catalytic and temperature conditions, but one of the most important PCBzs formation pathways was precursor formation depending on the decomposition products of PAHs. In

the other words, the formation of PAHs related to a primary formation mainly determined by the incineration conditions, but the formation of PCBzs depended on the decomposition of PAHs (Weber *et al.*, 2001), and hence they showed some negative correlation to each other in the residual ash.

The synthesis process of PAHs was divided into different stages influenced by reaction temperature; the key temperature points were 600 and 800 °C (Mastral *et al.*, 1999; Liu *et al.*, 2001). With the increase of temperature from 600 °C, the major constituent of 6-ringed PAHs from pyrolysis of waste reduced progressively and was decomposed to 2- and 3-ringed PAHs. However, exceeding 800 °C will destroy 2- and 3-ringed PAHs further. Hence, fewer ringed PAHs (2- and 3-ringed PAHs) were the major constituent in FGI and FBI residual ashes (both with their furnace cavity temperature higher than 800 °C). However, the higher temperature in FBI furnace cavity (Liu *et al.*, 2000; Weber *et al.*, 2001) could reduce the proportions of 2- and 3-ringed PAHs by further breaking them down to some organic fragments (Bauschlicher and Ricca, 2000; Liu *et al.*, 2001). The special case of FA5 and FA8 may be caused by the fluctuation of the furnace operating load, reflected in their very high PAHs emission amounts.

3.4 Emission characteristics of metals in MSWI residual ash

The distribution of Cu in fly ash got much attention due to its strong catalytic effect on the formation of dioxin compounds (Hagenmaier *et al.*, 1987; Gullett *et al.*, 1990). However, the comprehensive distribution characteristics of metals in residual ash need further study. The total metals were divided into “heavy metals” and “light metals” according to molecular weight. Heavy metals in residual ash were simultaneously detected and analyzed as shown in Table 4, including Cu, Mn, Ni, Pb, Sn, V, Zn, As, Cd, and Cr. The light metals, mainly Al and Fe, were also detected in the same way.

The heavy metals were further sorted into toxic heavy metals and non-toxic heavy metals (Table 4). The sources of the metals were the original raw waste, and the incineration process made the metals transfer from waste to residual ash (Park and Heo, 2002).

In fly ash samples from FBI, the concentrations of toxic heavy metals were in the order Cu>Pb>Cr>

As>V>Cd, but that order changed to Pb>Cu>Cr>As>Cd>V in FGI fly ash. Bottom ash showed similar characteristics to the corresponding fly ash, except for an apparent enrichment effect in the case of Cr. Cu, as the indicator of toxic heavy metals, ranged from 89 to 1417 mg/kg in fly ash and 167 to 469 mg/kg in bottom ash. FBIs fly ash also contained more Cu than FGIs as a whole, performing better enrichment of Cu. Among the toxic heavy metals, Cu, Pb, and Cr were in the majority but their concentrations were all lower than those of non-toxic heavy metals.

Non-toxic heavy metals occupied the major proportions in total heavy metal in residual ash with 841 to 7376 mg/kg Ni and 1250 to 6650 mg/kg Zn, much higher than Mn and Sn. Furthermore, it was noticeable that Al and Fe as non-toxic “light metals” were the major constituent of metals in the residual ash sample, from the original raw waste. The concentrations of Al ranged from 44 469 to 108 540 mg/kg and that of Fe ranged from 4020 to 49 336 mg/kg.

This offers the possibility of recovery of Al from its high concentrations in residual ash (Grosso *et al.*, 2011). Moreover, the concentrations of Al and Fe in FBIs fly ash were generally higher than those in FGIs, similar to the case of Cu.

By calculating the correlation coefficient between metals and dioxin precursors (PCBzs and PAHs), metals were divided into two groups. Except for Fe and V, the metals had a positive correlation with the concentration of PCBzs, and Pb, Cd, and Hg had a strong positive correlation (with correlation coefficients of 0.86, 0.97, and 0.92). It was inferred that most metals had catalytic promotion effects on PCBzs formation except for Fe and V. However, the correlation relationships between metals and PAHs were complex. Mn, Sn, V, Cd, and Hg had weak negative correlation coefficients (from -0.06 to -0.18) with PAH concentration, reflecting some inhibition effects on the formation of PAHs, but other metals had the opposite effect. In overall consideration of the

Table 4 Concentrations of metals in residual ash samples (unit: mg/kg)

Sample	Concentration											
	Toxic heavy metals						Non-toxic heavy metals				Light metals	
	Cu	Pb	V	As	Cd	Cr	Mn	Ni	Sn	Zn	Al	Fe
FA1	739 ±45	1534 ±81	48 ±7	311 ±55	157 ±27	316 ±58	668 ±45	6984 ±661	1300 ±292	7047 ±505	90 142 ±3880	17 110 ±751
FA2	208 ±12	356 ±11	31 ±6	271 ±30	40 ±6	91 ±13	381 ±30	6453 ±856	507 ±80	2366 ±94	76 493 ±2974	11 878 ±720
FA3	257 ±5	114 ±2	97 ±20	65 ±10	3 ±0	154 ±20	2917 ±57	327 ±36	81 ±13	687 ±20	47 379 ±1442	39 529 ±3160
FA4	94 ±5	544 ±27	8 ±2	182 ±22	7 ±1	25 ±4	140 ±8	4492 ±744	1431 ±194	8007 ±132	48 902 ±1645	4075 ±261
FA5	588 ±25	610 ±16	74 ±15	69 ±9	14 ±2	278 ±31	908 ±58	840 ±129	349 ±51	3654 ±292	60 115 ±5855	33 218 ±3056
FA6	1501 ±49	727 ±26	74 ±11	180 ±23	23 ±8	372 ±50	805 ±75	3331 ±598	426 ±68	4175 ±82	89 219 ±4892	30 167 ±3192
FA7	1362 ±48	509 ±21	58 ±12	230 ±27	29 ±7	243 ±35	91 ±10	5638 ±553	332 ±62	4323 ±258	87 844 ±6874	24 622 ±2305
FA8	868 ±40	431 ±14	59 ±14	261 ±47	18 ±4	292 ±45	794 ±101	7201 ±1145	324 ±53	4344 ±140	106 635 ±7055	35 875 ±1130
BA1	164 ±14	67 ±4	18 ±5	96 ±18	9 ±1	319 ±57	385 ±47	898 ±124	178 ±36	1230 ±85	20 322 ±1906	12 680 ±1544
BA2	440 ±31	158 ±11	61 ±13	315 ±68	7 ±1	183 ±45	668 ±70	5324 ±805	363 ±80	2522 ±219	82 320 ±9658	29 735 ±2865
BA3	461 ±39	159 ±9	252 ±60	126 ±25	8 ±2	591 ±151	1075 ±97	1725 ±244	492 ±95	1758 ±115	47 031 ±4562	50 471 ±4144

Data are presented as mean±standard deviation (SD), where SD is calculated from the repeated detection of one batch of samples

correlations of PCBzs and PAHs with metals, vanadium is of special interest because of its limited inhibition effects on the formation of both PCBzs and PAHs (Cho and Ihm, 2002). Therefore, vanadium oxide (especially V_2O_5) with its strong catalytic destruction ability was utilized to destroy several chlorinated organic compounds in the present study (Lichtenberger and Amiridis, 2004; Ji et al., 2013). Moreover, Sn, Cd, and Hg demonstrated opposed correlation coefficients between PCBzs and PAHs. It was therefore inferred that those three metals could cause the transformation of PAHs to PCBzs.

4 Conclusions

The different incineration characteristics of FGI and FBI caused different distribution characteristics of dioxin precursors (PCBzs and PAHs) and metals in residual ash. FBI gives partial high temperature and strong gas flow disturbance in the incineration process, and yields a residual ash particle with larger surface area and more complex micropore structure. FBIs have the advantage of eliminating the individual effects of incinerators and raw waste, and can effectively control PCBzs emission in fly ash. Fly ash from FBIs contains more PCBzs (25–150 times higher than bottom ash) with H_xCB and P_eCBzs as major constituents. FBIs cause more PAHs emission than FGIs, and the fewer ringed PAHs (mainly 2- to 4-ringed PAHs) are the major constituents in residual ash. Overall, low boiling point PAHs (i.e., fewer ringed PAHs) and high boiling point PCBzs (mainly P_eCBz and H_xCBz) are the main constituents in residual ash, and PAHs and PCBzs have some negative correlation with each other in residual ash. That result reflects that PAHs belong to primary direct formation of dioxins and PCBzs arise from a secondary process from PAHs. Overall, the proportion of toxic heavy metals (mainly Cu, Pb, and Cr) is lower than that of the non-toxics (Mn, Ni, As, Zn), and both of them are much lower than that of the non-toxic light metals (Al and Fe) in residual ash. Most metals, except for Fe and V, have a positive correlation with the concentration of PCBzs, reflecting some catalytic promotion effects on PCBzs formation, but the correlation relationships between metals and PAHs are complex. Vanadium performs some limited inhibition effects on the formation of both PCBzs and PAHs.

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中文概要

题目：生活垃圾焚烧残灰中有毒成分的排放特性

目的：探索中国生活垃圾焚烧残灰中重金属、氯苯、多环芳烃等有毒成分的排放特性、排放水平及相互之间的关联特性，并认识其产生、排放与焚烧炉型、焚烧条件的关联，以探索控制其危害的有效方法。

方法：1. 对中国几个典型的生活垃圾焚烧炉现场采样，获得多个飞灰和底渣的样品；2. 通过多种不同的检测手段和方法，分别检测残灰的基本物理化学特性、氯苯、多环芳烃和主要金属元素的浓度；3. 结合焚烧炉型和焚烧特性等条件，分析各有毒成分的排放特性和相互之间的关联特性。

结论：1. 氯苯、多环芳烃和重金属受焚烧因素影响，在残灰中的排放特性各不相同，流化床焚烧炉能消除焚烧和原始垃圾的扰动，能控制氯苯在残灰中的排放，但多环芳烃排放控制不如炉排焚烧炉；2. 残灰中主要的有机有毒成分为高氯代氯苯和 2 至 4 环等少环类多环芳烃；3. 氯苯和多环芳烃在残灰中的含量可能因为不同的产生机理而表现出一定的负关联特点；4. 残灰中的金属主要为铝和铁等轻金属，浓度远高于重金属元素，而无毒重金属（主要为 Mn、Ni、As 和 Zn）浓度高于有毒重金属元素（Cu、Pb 和 Cr），且不同金属表现出不同的对氯苯和多环芳烃的催化促进或抑制作用。

关键词：残灰；氯苯；多环芳烃；重金属；生活垃圾焚烧