Aerosol and Air Quality Research, 16: 1569–1578, 2016

ISSN: 1680-8584 print / 2071-1409 online
doi: 10.4209/aaqr.201

Mass Concentrations of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans (PCDD/Fs) and Heavy Metals in Different Size Fractions of Hospital Solid Waste Incinerator Fly Ash Particles

Guoxia Wei[1], Hanqiao Liu[2*], Rui Zhang[2], Yuwen Zhu[2], Xian Xu[2]

[1] *School of Science, Tianjin Chengjian University, Tianjin 300384, China*
[2] *School of Energy and Safety Engineering, Tianjin Chengjian University, Tianjin 300384, China*

ABSTRACT

Hospital solid waste incinerator (HSWI) fly ash is an extremely complex mixture because it contains carbon constituents, toxic heavy metals, and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). We investigated the distribution of carbon constituents, PCDD/Fs, and heavy metals in the five different particle size fractions (+106 μm, –106 + 75 μm, –75 + 38 μm, –38 + 25 μm, and –25 μm) of HSWI fly ash. The loss on ignition (LOI) in the particle size fraction of –25 μm was higher than that in the particle size fractions of other sizes. Moreover, 82.63% of the fly ash particles were in the size range of –75 + 25 μm, and this particle size range was suitable for direct flotation treatment. Because powder-activated carbon adsorbed a higher amount of low-chlorinated PCDD/Fs in the gaseous phase, the concentration of each PCDD/F congener, particularly of low-chlorinated PCDD/Fs, generally increased with a decrease in the particle size. The total toxic equivalent (TEQ) of the fraction of –75 μm did not satisfy the landfill site standard (3 ng-TEQ g^{-1}). The highest concentration of Pb, Zn, and Cd was observed in the fraction of –38 + 25 μm rather than in the fraction of –25 μm. The exchangeable speciation of Zn, Pb, and Cd was relatively high in the particle size fraction of –75 μm. The carbonate speciation of Pb and Zn was the highest in the particle size fraction of –38 + 25 μm**.** The leaching concentrations of Pb and Cd in all particle size fractions exceeded landfill allowable thresholds.

Keywords: Hospital solid waste incinerator; Fly ash; Size distribution; Heavy metals; PCDD/Fs.

INTRODUCTION

Hospital solid waste is classified as a hazardous material in China because it contains infectious, radioactive, and toxic substances from hospitals, laboratories, and clinics (Javied *et al*., 2008). The annual generation of hospital solid waste in China is approximately 1.65 million tons (Xie *et al*., 2009). The proportion of plastic, chlorine, and heavy metals is higher in hospital solid waste than in municipal solid waste (Wang *et al*., 2003; Chen *et al*., 2013). Incineration is currently the most common technology used for hospital solid waste disposal in China. However, hospital solid waste incinerators (HSWIs) are considered as one of the major emission sources of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) (Yan *et al*., 2011). A powder-activated carbon (PAC) injection followed by baghouse filtration is a key technology to remove PCDD/Fs from flue gases (Ji *et al*., 2013). Therefore, numerous PAC injections are injected into the exhaust gas to absorb PCDD/Fs from flue gases so as to meet the strict emission regulations of hospital solid waste incineration (< 0.01 ng I-TEQ Nm^{-3}) (Liu *et al*., 2013). After the adsorption of PCDD/Fs on PAC, PAC with fly ash is then collected in the bag filter and removed as fly ash (Wang *et al*., 2009). In addition, PCDD/Fs are easily adsorbed on the surface of unburned carbon present in HSWI fly ash. The carbon constituents including PAC and unburned carbon are indicated as the major sources of PCDD/Fs in fly ash because of their large adsorptive surface area and their role in denovo synthesis (Kakuta *et al*., 2007).

The resulting mixture of ash particles and injected PAC, which constitutes the physical and chemical properties of HSWI fly ash, is very complex. However, little attention has been paid to the effect of high PAC content on the distribution of PCDD/Fs and heavy metals in HSWI fly ash. Studies on HSWI fly ash have primarily focused on the determination of the bulk chemical composition of fly ash particles. The chemicals primarily evaluated were PCDD/Fs, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, and some inorganic compounds such as heavy metals and

* Corresponding author.
Tel.: 0086-22-23085107; Fax: 0086-22-23085555
E-mail address: lhqlkx@126.com

metal complexes (Huang *et al*., 2007; Zhao *et al*., 2008; Kim *et al*., 2011; Wei *et al*., 2014; Xiong *et al*., 2014).

The particle size distribution is a crucial physical feature of fly ash. It is noted that the particle size distribution mentioned in this paper is the particle size distribution of hospital solid waste incinerator fly ash particles, which differ from the traditionally defined particle sizes in the air-quality community. A study reported that the chemical composition of fly ash is dependent on its particle size (Buekens *et al*., 2011). Kim *et al*. (2011) indicated that the particle size influenced the transport pathway of pollutants and the adsorption characteristics of toxic chemicals. Sukandar *et al*. (2006) reported that approximately 80% of HSWI fly ash had a particle size of –100 μm and that the concentration of Hg and Sn in fly ash tended to increase in small particle size fractions. Gidarakos *et al.* (2009) reported that the heavy metals were present in higher percentages in the thin sieves. However, Thipse *et al*. (2002) reported that the maximum values of Pb and Hg were obtained in the size range of –300 + 150 μm in municipal solid waste incinerator (MSWI) fly ash. Therefore, the classification of particles in these size fractions can significantly reduce the amount of these toxic metals in the remaining fly ash. Gilardoni *et al*. (2004) considered that small-size fly ash particles, which constitute most of the surface area, were the main contributors to the levels of chlorinated aromatic compounds in flue gases. Lu *et al*. (2007) considered that small-size MSWI fly ash particles have more active surface sites; thus, they can easily absorb reaction intermediates and catalysts to facilitate the increased formation of PCDDs/Fs. Furthermore, Lu *et al*. (2012) reported that all PCDDs, PCDFs, 2,3,7,8-PCDDs, and 2,3,7,8-PCDFs in MSWI fly ash increased with decreases in the particle size. Therefore, different fly ash fractions have different chemical and physical compositions and vary in their suitability for subsequent treatments (Dahl *et al*., 2010).

HSWI fly ash has become a crucial public concern in China because of its high toxicity. In our previous study, we developed the column flotation method, an efficient and inexpensive disposal method, for the treatment of HSWI fly ash containing a high carbon concentration (Liu *et al*., 2013). Numerous studies have investigated aspects of flotation kinetics while particularly focusing on particle size (Abkhoshk *et al*., 2010; Jorjani *et al.*, 2013; Zhang *et al*., 2013). The particle size is a crucial parameter contributing to the efficient performance of the flotation process. Therefore, it is necessary to focus on PCDD/Fs and heavy metals in fly ash as a function of particle size. In this study, we investigated the relationship between particle size and PCDD/F and heavy metal distribution to evaluate the separation behavior of toxic chemicals during subsequent flotation treatments.

MATERIALS AND METHODS

Raw Materials

The fly ash sample was obtained from a 20 t d^{-1} gyration kiln incinerator from the HSW incineration center located in northern China (Fig. 1). The incinerator was equipped with a PAC injection, and bag filters were used as air pollution control devices (APCDs) for controlling PCDD/Fs. A fresh and dry fly ash sample was collected from the hopper of the bag filter; therefore, it contained PAC that was injected into the flue gas duct before using bag filters. The ash sample was collected and dried at 105°C for 24 h. Table 1 shows the chemical composition and bulk concentration of heavy metals in the fly ash sample. Data on concentration of heavy metals in hospital waste ash from incinerators of various countries of the world has been compiled from literature and represented in Table 2. The comparison shows that concentration of heavy metals in hospital solid waste incinerator fly ash of China is relatively higher than that in fly ash of other countries of the world. The chlorine level in the fly ash sample was > 20 wt%, which was related to the usage of polyvinylchloride disposable infusion devices and NaCl frequently used in medical treatments.

Methods

The sieving analysis was performed through mechanical shaking by using a stainless steel screen with openings of 150, 200, 400, and 500 meshes (i.e., 106, 75, 38, and 25 μm,

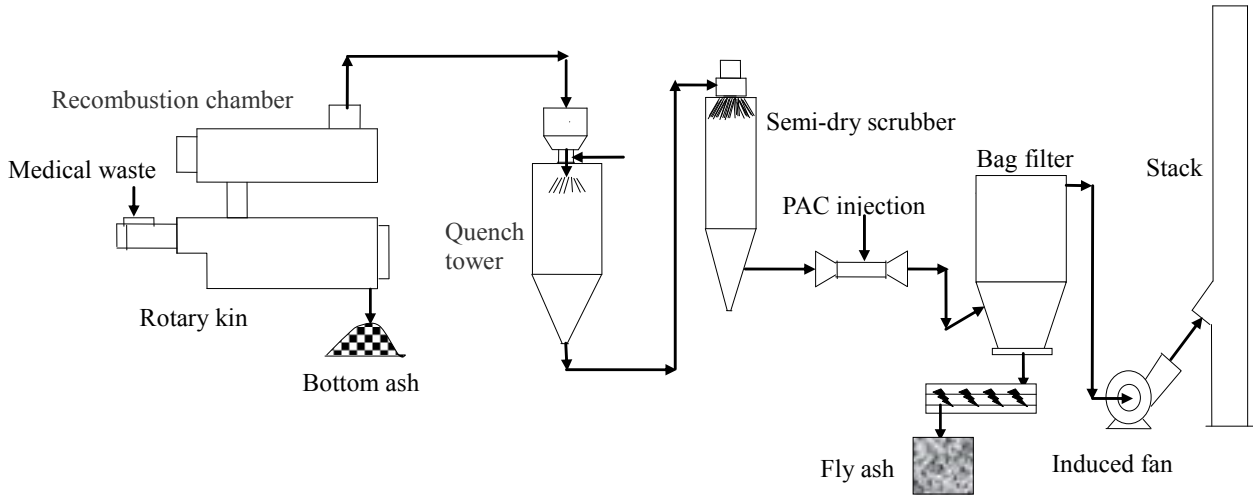

Fig. 1. Flow scheme of incinerator for hospital solid waste.

Table 1. Chemical composition and concentration of heavy metals in the fly ash.

Major components	Mass fraction (%)	Heavy metals	Concentration (mg kg^{-1})
SiO_2	17.1	Pb	1410.2
CaO	24.4	Zn	5235.3
Al_2O_3	2.9	Cu	1022.0
Fe_2O_3	1.8	Cd	88.7
MgO	1.8	Cr	112.1
K_2O	2.8		
Na_2O	15.2		
SO_3	6.4		
Cl	20.4		
TiO_2	1.3		
F	2.6		

respectively). The application of mechanical shaking was limited to a minimum of –25 μm (no further fractionation for particles smaller than –25 μm) as numbers below this were too small for measurement. Then, fly ash and PAC were sieved into five different fractions (i.e., +106, +106 + 75, –75 + 38, –38 + 25, and –25 μm). The weight distribution and carbon content [loss on ignition (LOI)] of each fraction were determined. The concentration, speciation, heavy metal leaching concentration, and PCDD/F concentration and distribution were analyzed in each dimensional range of fly ash. LOI was determined as the weight lost when the subsample was kept at 600 ± 25°C for 3 h in accordance with the standard for pollution control (GB18485–2014).

Analysis of PCDD/Fs

The concentration of 17 toxic PCDD/F congeners (2,3,7,8-substituted) was analyzed using isotope dilution analysis through high-resolution gas chromatography–high-resolution mass spectrometry (HRGC–HRMS). HRGC was equipped with a DB-5 ms fused-silica capillary column (L = 60 m, id = 0.25 mm, and film thickness = 0.25 μm) and a splitless injection. The high-resolution mass spectrometer was equipped with a positive electron impact source. The analyzer mode of selected ion monitoring had a resolving power of 10,000. The electron energy and source temperature were 38 eV and 250°C, respectively. Prior to the analysis, the samples were ground for homogenization and subsequently subjected to treatment procedures. The sample pretreatment was conducted according to the modified version of the US EPA Method 23 (20). The $^{13}C_{12}$ isotopically labeled internal standard solution was purchased from Cambridge Isotope Laboratories. The total toxic equivalents (TEQ) of dioxin congeners in the sample were calculated on the basis of international toxic equivalency factors.

Analysis of Heavy Metals

The heavy metals such as Pb, Zn, and Cu were analyzed using an atomic absorption spectrometer (AA800) after sample digestion. A modified version of the sequential extraction procedure developed by Tessier was used for the partitioning of heavy metal speciation. (Liu *et al*., 2014). This method focused on the breakdown of materials into varied speciations that could be selectively dissolved using particular extraction agents. The chemical speciation in the fly ash samples was divided into exchangeable fraction, carbonate fraction, Fe–Mn oxide fraction, organic matter fraction, and residue fraction. The leaching test was conducted in accordance to the Chinese solid waste extraction procedure for leaching toxicity–acetic acid buffer solution (HJ/T300–2007), which is reported in our previous study (Abkhoshk *et al*., 2010). To ensure validity and reliability of data, all tests were performed at minimum in duplicate and results were calculated as the average of three measurements.

RESULTS AND DISCUSSION

Particle Size Distribution

Fig. 2 shows the weight distribution and carbon content (i.e., LOI) of each particle size fraction of fly ash and PAC. Approximately 98% of the fly ash had a particle –106 μm, which was finer than that reported in the literature (Sukandar *et al*., 2006; Liu *et al*., 2013). This difference might be attributed to different feeding wastes, incinerator operating conditions, and air pollution control devices. Moreover, 89.3% of the fly ash particles had a diameter of –75 μm, and the distribution of carbon constituents in this size range was 90.4%. This could be attributed to the high amount of PAC injected into the APCDs of the incinerator. Moreover, 86.6% of the PAC particles were in the same size range. The overall LOI of raw fly ash was 12.62%, and LOI decreased with an increase in the particle size. Because fine PAC was enriched in the fraction of –25 μm, LOI in this fraction was 19.35%, which was 6.73% higher than the average LOI. This result was inconsistent with that of coal fly ash whose carbon constituents were enriched in the coarse size fraction (Liu *et al*., 2013). Froth flotation was primarily applicable for treating fine-grained material with a particle size range of –300 + 10 μm, and the optimum particle size range was –75 μm (Dermont *et al*., 2010). Therefore, the particle size of fly ash was highly suitable for froth flotation without the grinding pretreatment.

Distribution of PCDD/F Congeners in Bulk Fly Ash

Fig. 3 illustrates the percentage distribution of 17 major PCDD/F congeners in bulk fly ash. The dominant homologs in fly ash were 1,2,3,4,6,7,8-HpCDD (13.34%), OCDD (16.84%), 2,3,7,8-TeCDF (8.36%), 1,2,3,4,7,8-PeCDF (11.97%), 1,2,3,4,6,7,8-HpCDF (10.33%), and OCDF

Table 2. Concentration of heavy metals in hospital solid waste incinerator ash of various countries of the world.

Country/city	Material	Concentration of heavy metals (mg kg^{-1})					Reference
		Zn	Cr	Cd	Cu	Pb	
Pakistan	Bottom Ash	24.1	9.0	1.4	1.7	1.1	Anjum *et al.* (2014)
Morocco/Rabat	Bottom Ash	281.8–1361.3	0.5–786.5	0.0–2.0	NT	48.5–4063.3	Bakkali *et al.* (2013)
China	Bottom Ash	2600.0–30700.0	34.4–895.0	< 100.0	70.0–2300.0	70.0–2100.0	Zhao *et al.* (2008)
	Fly Ash	28800.0–121000.0	< 100.0	28.9–635.0	420.0–2900.0	900.0–5400.0	
Japan	Fly Ash	1386.3–2076.2	7.8–22.0	10.0–16.2	204.4–360.2	321.4–513.5	Sukandar *et al.* (2006)
Italy/Rome	Fly Ash	3200.0	109.0	85.0	173.0	964.0	Lombardi *et al.* (1998)

NT: not tested.

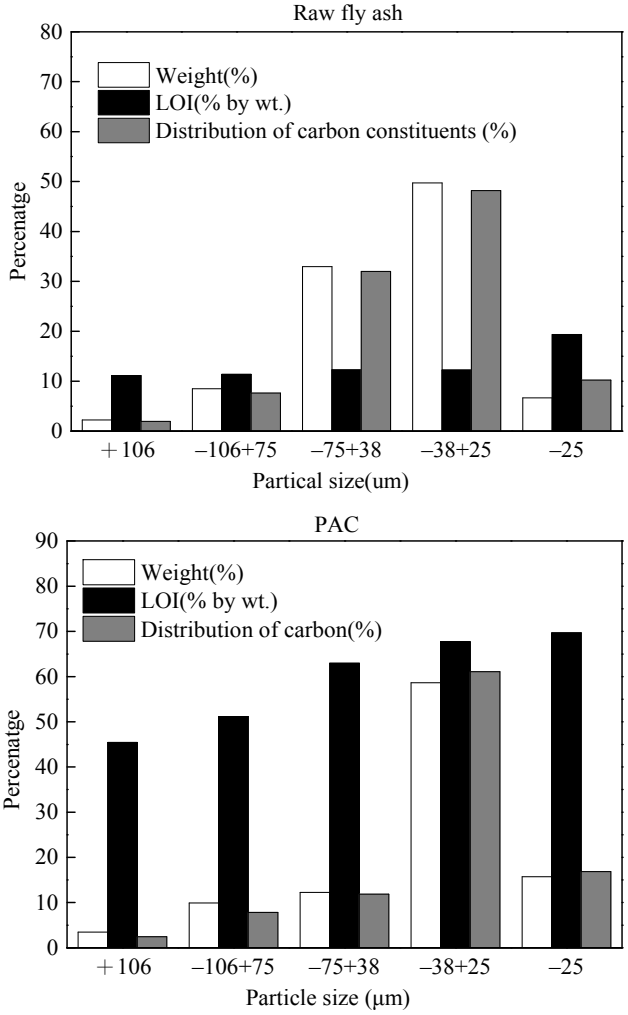

Fig. 2. Weight distribution and LOI of each size fraction in fly ash and PAC.

(8.28%). The PCDF compounds were higher than the PCDD compounds which attributed to the high chlorine content in the hospital solid waste. Wang confirmed that when the chlorine content in the feeding wastes of incinerators exceeded the threshold value at 0.8%–1.1%, the formation rate of PCDFs exceeded that of PCDDs (Wang *et al*., 2003). Moreover, the ratio of PCDDs/PCDFs was 0.57, indicating that the main route of PCDD/F formation was the de novo synthesis in the postcombustion zone (Du *et al*., 2013). However, low-chlorinated PCDF congeners were the dominant contributors to the TEQ of fly ash. By contrast, highly chlorinated PCDD/F homologs contributed little to the total TEQ. In particular, 2,3,4,7,8-PeCDF was the highest contributor (31.4%) to the total TEQ. The 2,3,4,7,8-PeCDF congener has been the dominant contributor to TEQ in the fly ash of both MSWI and HSWI; this result was in accordance with that reported for other fly ash samples (Zou *et al*., 2013; Chang *et al*., 2013).

PCDD/F Congener Distribution of Different Particle Size Fractions

Fig. 4 presents the concentration of each PCDD/F congener

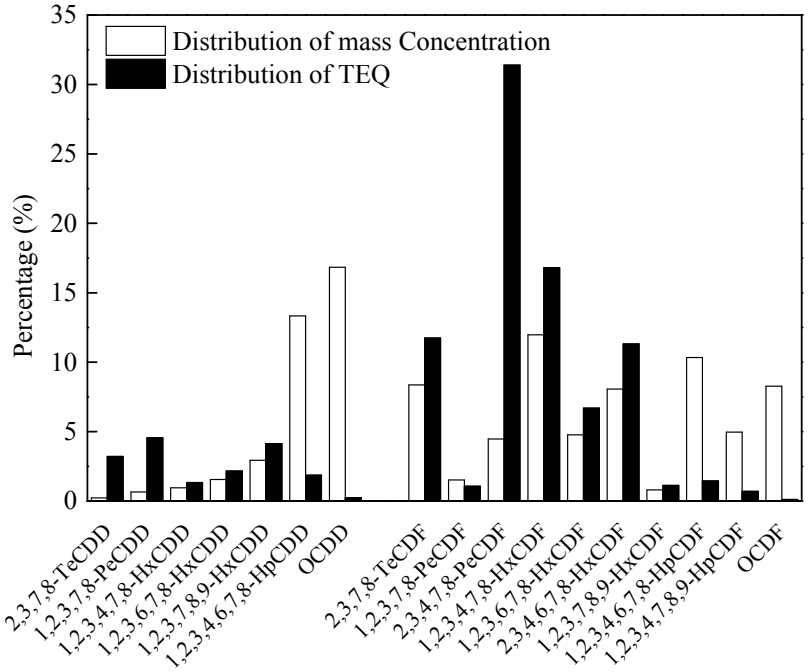

Fig. 3. Mass and TEQ distribution of PCDD/Fs congener in the bulk fly ash.

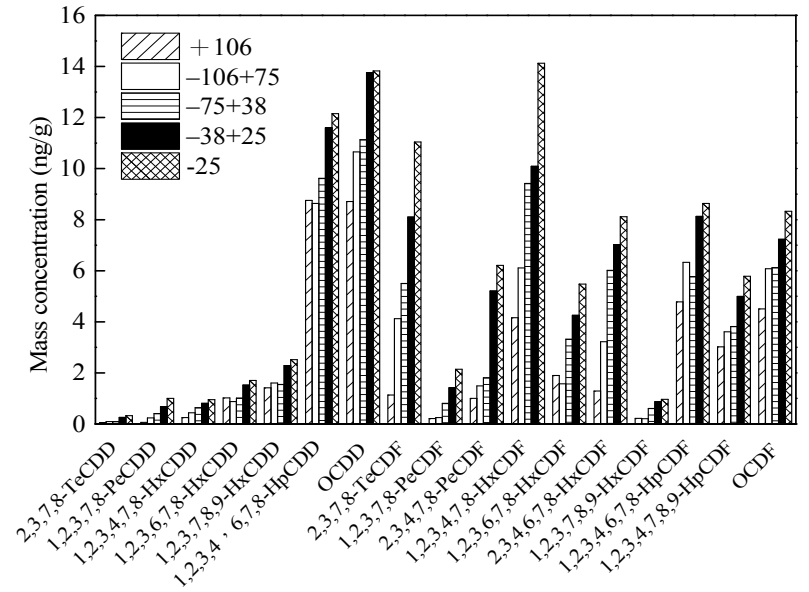

Fig. 4. Concentration of each PCDD/Fs congener for different size fractions.

of different particle size fractions conducted for fly ash. Each PCDD/F congener appeared to increase when the fly ash particle size decreased; the maximum was obtained with the smallest particles (–25 μm). Furthermore, the fractions of low-chlorinated compounds, such as PeCDD, TeCDF, PeCDF, and HxCDF, increased when the particle size decreased. This can be attributed to the high PAC content in small-size fly ash particles. PAC could effectively remove gaseous-phase PCDD/Fs; however, it could not effectively remove particle-bound PCDD/Fs (Atkinson *et al*., 2015). The low-chlorinated PCDD/F congeners with high vapor pressure had a higher mass fraction in the gaseous phase; however, the highly chlorinated PCDD/F congeners were primarily associated with particulates (Du *et al*., 2013; Pan *et al*., 2013). Gaseous-phase PCDD/Fs were easily adsorbed onto PAC particles in the flue gas flow and subsequently filtrated by the bag filter. However, most PCDD/Fs in the solid phase were removed by the bag filter through inertial impaction, direct interception, and Brownian diffusion mechanisms (Chang *et al*., 2009).

Total PCDD/F Concentration in Different Particle Size Fractions

The total PCDD/F concentration in fly ash was 78.8 ng g^{-1},

which was equivalent to 5.61 ng-TEQ g^{-1}. The TEQ of PCDD/Fs was much higher than that of municipal solid waste incinerator fly ash (Liu *et al*., 2013). Fig. 5 shows total PCDD/F concentrations and TEQ values for the different particle size fractions of fly ash. When the particle size of fly ash decreased from +106 μm to –25 μm, the PCDD/F concentration of the fly ash increased from 42.50 ng g^{-1} to 103.29 ng g^{-1}, respectively, and the TEQ value of the particle size of –25 μm increased by 4.6 times that of the particle size +106 μm. Because the fine particles of the fly ash contained a relatively high content of PAC, a high amount of low-chlorinated PCDD/Fs was adsorbed in the gaseous phase. The low-chlorinated PCDD/Fs had a relatively high toxicity factor. This could explain the presence of high TEQ values for fine fly ash particles. All TEQ values in the fraction of –75 μm exceeded the regulation limit (3 ng I–TEQ g^{-1}) for a landfill in China (Liu *et al*., 2014). Therefore, for the removal of PCDD/Fs, the fraction of –75 μm should be particularly considered in the flotation treatment of fly ash.

Heavy Metal Concentration in Different Particle Size Fractions

The concentration of heavy metals in five different particle size fractions is shown in Fig. 6. The heavy metals Pb, Zn, and Cu predominantly had a higher concentration in fly ash, followed by Cd and Cr. The heavy metals such as Cu, Pb, and Zn were probably used for the production of alloys for medical equipment such as needles (Sukandar *et al*., 2006). Cu had a relatively high boiling point, but it was thought that Cu is partially converted into $CuCl_2$ and then entered into fly ash. Cr is a nonvolatile heavy metal, and a small amount of Cr is possibly carried into fly ash by solid particles in flue gases.

We observed that the concentration of heavy metals was different for different particle size fractions of fly ash. Pb and Zn had a similar concentration distribution as a function of the particle size. The highest values of both Pb and Zn were obtained for the fraction of –38 + 25 μm, followed by the fraction of –75 + 38 μm. The concentration of Cd initially increased and then decreased with a decrease in the particle

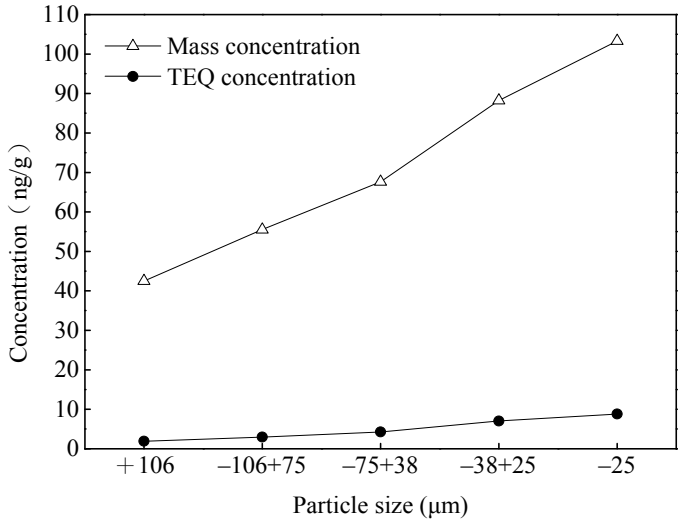

Fig. 5. Mass concentration and TEQ concentration of PCDD/Fs in different size fractions.

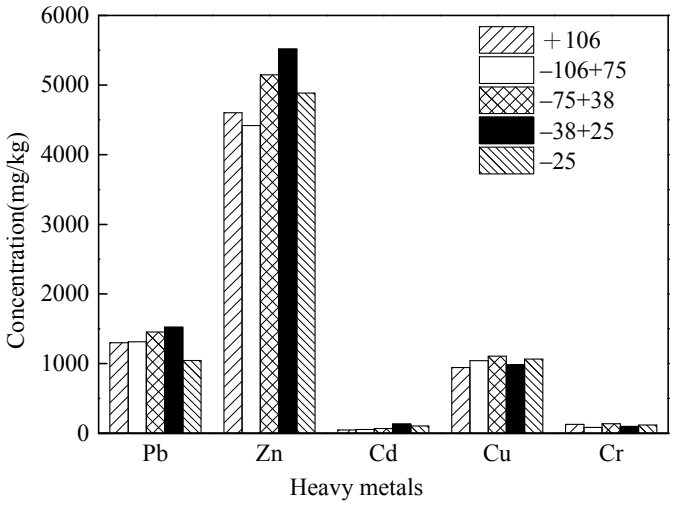

Fig. 6. Heavy metal concentrations in different particle size fractions.

size, and the maximum value was obtained in the fraction of –38 + 25 μm. This result was consistent with that reported in the literature that Cd, Pb, and Zn mainly comprised the fine fraction of fly ash (Kim *et al*., 2002). However, the highest values of Pb, Zn, and Cd were not observed in the smallest size fraction (–25 μm) in our study, which might be related to high PAC content in the fraction of –25 μm. Because vaporized metal chlorides condense and aggregate on the surface of fly ash before PAC injection, a high content of PAC mixed with a fly ash fraction of –25 μm might dilute heavy metals such as Pb, Zn, and Cd (Gilardoni *et al*., 2004).

No significant differences were observed in Cu and Cr concentrations among different particle size fractions. In particular, Cu had a high affinity for chlorine and thus played a catalytic role and easily promoted the formation of PCDD/Fs. This observation was not consistent with those reported in previous studies. For instance, Sukandar *et al*. (2006) reported that Cu concentration was higher in small-sized particles. Thipse *et al*. (2002) indicated that the Cr concentration in particles increased with an increase in the particle size. The relationship between the concentration of heavy metals and the particle size of fly ash is complex because it depends on several factors such as feeding waste composition, incinerator type, operating conditions, and flue gas cleaning device and PAC injection efficiency (Gilardoni *et al*., 2004; Sukandar *et al*., 2006; Dahl *et al*., 2010).

Speciation Distribution of Heavy Metals in Different Particle Size Fractions

The speciation distribution of heavy metals in different particle size fractions of fly ash is shown in Fig. 7. Pb was one of the major heavy metals in fly ash and had high toxicity. Pb retained a fairly uniform distribution in each dimensional range. Fine particles (particle size of –75 μm) had a relatively high exchangeable form. The exchangeable and carbonate-associated Pb was the highest in the particle size fraction of –38 + 25 μm. The leaching of Pb with an acid solution is a crucial concern because of its high carbonate speciation.

Zn had a high exchangeable fraction, which could be attributed to $ZnCl_2$ formation. Zinc oxides easily reacted with NaCl to form low-boiling point (732°C) $ZnCl_2$, which adsorbed the fine fly ash particles. Carbonate-associated Zn was the highest (33.2%) in the particle size fraction of –38 + 25 μm. The residual speciation in each particle size fraction was relatively low.

The dominant and secondary speciation of Cd were exchangeable (29.8%–38.9%) and carbonate (18.2%–28.5%) fractions, respectively. Both the exchangeable and carbonate fractions of Cd were higher in the particle size fraction of –75 μm.

The exchangeable speciation of Zn, Pb, and Cd was higher in the particle size fraction of –75 μm than in the particle size fraction of +75 μm (Fig. 7). Moreover, HCl present in flue gases at combustion chamber outlets may have affected the speciation of Pb, Zn, and Cd by forming heavy metal chlorides that generated smaller particles through the volatilization–condensation processes (Gilardoni *et al*., 2004). Cd associated with Fe–Mn oxide, and organic and residual speciation among different particle size fractions was not remarkable. These results were inconsistent with those reported by Sukandar *et al*. (2006) that Fe–Mn oxide-associated Cd was the highest in the particle size fraction of –150 + 106 μm.

The residual speciation of Cu in all particle size fractions was the most dominant. Compared with other speciation, exchangeable and associated Cu was relatively less. Carbonate-associated Cu was the lowest (6.7%) in the particle size fraction of –25 μm. The behavior of Cr was similar to that of Cu, which mainly existed as a residual fraction (> 71.3%); however, some Cr existed as an exchangeable and carbonate-associated fraction. The exchangeable form of Cr was not observed in the particle size fraction of –106 + 75 μm and +106 μm. Therefore, additional studies investigating the relationship between particle size distribution and heavy metal speciation are warranted.

Leaching Concentration of Heavy Metals in Different Particle Size Fractions

Table 3 lists the leaching concentration of heavy metals in different particle size fractions. If the leaching concentration of heavy metals is under the permitted limits, fly ash can be deposited in the landfill site of municipal solid waste (GB16889–2008). The leaching concentrations of Zn, Pb, and Cd were higher than those of Cu and Cr. With regard to the particle size, the minimum leaching concentration of Pb and Cd was observed in the particle size fraction of –106 + 75 μm. The leaching concentration of Zn, Pb, and Cd was higher in the particle size fraction of –75 μm than in the particle size fraction of +75 μm. These results were in accordance with high exchangeable and carbonate fractions observed in the small particle size of Zn, Pb, and Cd (Fig. 7). No significant variations in the leaching concentration of Cu and Cr were observed for different particle size fractions. According to the landfill standard, the leaching concentration of Pb and Cd was 7–14 and 5–10 times, respectively, higher than the permitted limits. Therefore, fly ash should be treated prior to deposition in the landfill site of municipal solid waste in China.

From the viewpoint of resource recovery, the concentration of Pb and Zn and their carbonate speciation in fly ash was high; it is necessary to consider the recovery of Pb and Zn before depositing tailings in the landfill site. Pb, Zn, and Cd have high release and are converted into liquids at a low pH value. However, decarbonization flotation can only successfully remove carbon constituents and PCDD/Fs from HSWI fly ash under neutral or slightly acidic conditions (Huang *et al*., 2007; Liu *et al*., 2013; Liu *et al*., 2014). After decarbonization flotation, most heavy metals would be enriched into the residual slurry. Therefore, the treatment of the residual slurry by using the acid leaching-sulfide precipitation-flotation method should be considered to recover Pb and Zn from fly ash (Kuchar *et al.*, 2007).

CONCLUSIONS

A high amount of injected PAC in HSWI fly ash made

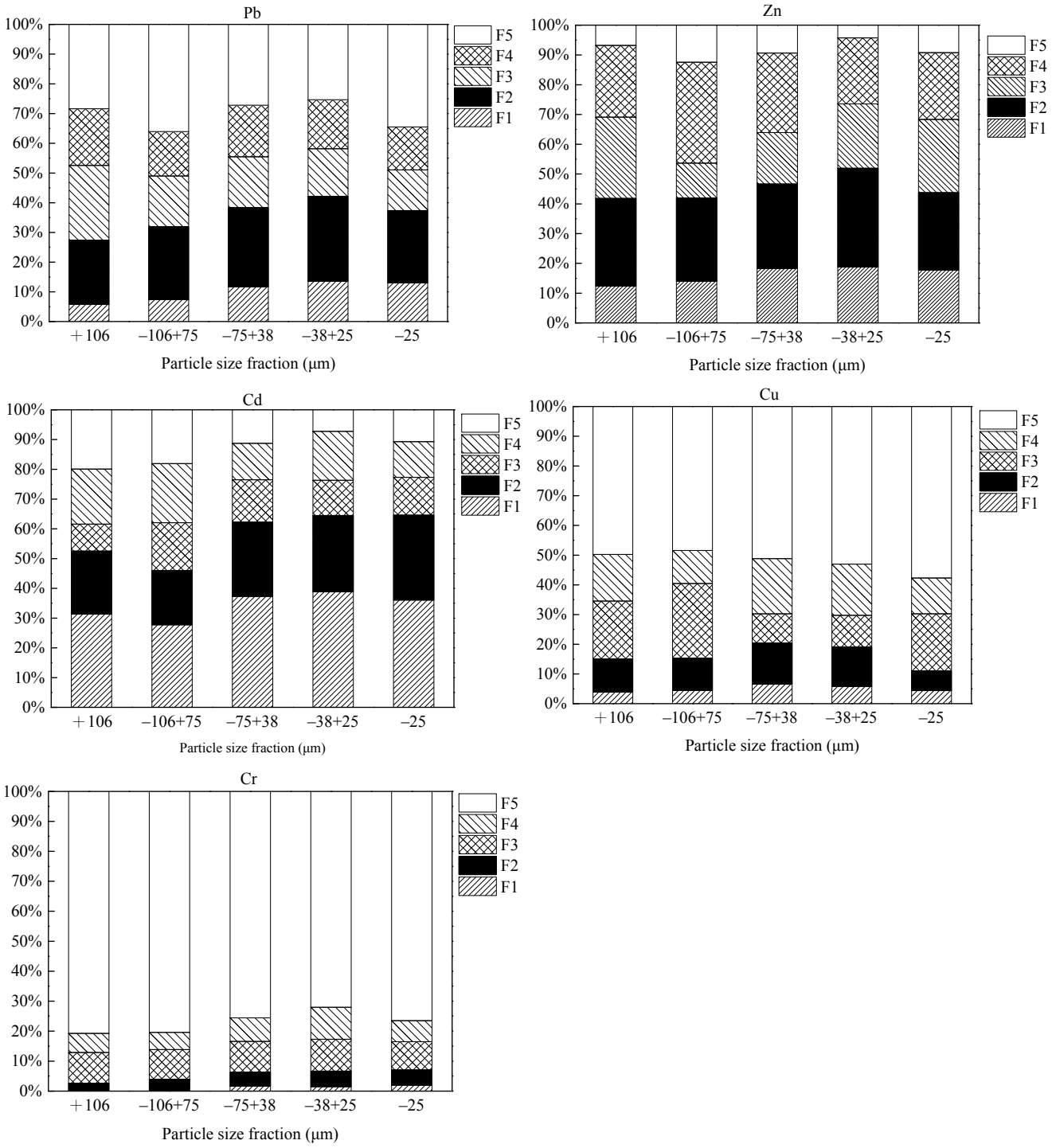

Fig. 7. Speciation distributions of heavy metals in different particle size fractions.

the physical and chemical properties of fly ash extremely complex. We investigated the relationship between the particle size and chemical composition of fly ash. We observed that 89.3% of fly ash particles had a diameter of –75 μm because of the presence of a high amount of PAC. LOI in the fraction of –25 μm was higher than that in the fractions of other sizes. The particle size of fly ash was highly suitable for flotation treatment without the grinding pretreatment. Because PAC adsorbed a higher amount of low-chlorinated PCDD/Fs in the gaseous phase, the concentration of each PCDD/F congener, particularly of low-chlorinated PCDD/Fs, increased with a decrease in particle size. The TEQ value of the particle size fraction of +75 μm satisfied the landfill site standard (3 ng-TEQ g^{-1}) but the particle size fraction of –75 μm did not. The fraction of –38 + 25 μm had the highest concentration of Pb, Zn, and Cd. The exchangeable speciation of Zn, Pb, and Cd was relatively high in the particle size fraction of +75 μm.

Table 3. Leaching concentration of heavy metals in different particle size fractions (mg L^{-1}).

Heavy metals	+106	–106 + 75	–75 + 38	–38 + 25	–25	Permitted limit of the landfill site
Pb	3.1	2.1	3.7	3.6	3.8	0.3
Zn	11.0	18.8	26.6	32.5	24.1	100.0
Cu	1.4	1.2	1.6	1.6	1.2	40.0
Cd	2.5	2.3	2.8	3.0	2.5	0.2
Cr	0.1	0.2	0.2	0.1	0.2	4.5

The carbonate speciation of Pb and Zn was the highest in the particle size fraction of –38 + 25 μm. The leaching concentration of Pb and Cd in all particle size fractions surpassed the permitted limits of the landfill site of municipal solid waste in China. Additional studies should be conducted to better understand processes underlying the partitioning of heavy metals in the particle size fractions of fly ash.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the National Natural Science Foundation of China under grant under the project number NSFC 51378332 and Tianjin science and technology correspondent project number 15JCTPJC63600.

REFFERENCES

Abkhoshk, E., Kor, M. and Rezai, B. (2010). A study on the effect of particle size on coal flotation kinetics using fuzzy logic. *Expert Syst. Appl.* 37: 5201–5207.

Anjum, F., Shahid, M., Bukhari, S.A. and Potgieter, J.H., (2014). Combined ultrasonic and bioleaching treatment of hospital waste (HW) incinerator bottom ash with simultaneous recovery of selected metals. *Environ. Technol.* 35: 262–270.

Atkinson, J.D., Huang, P.C., Zhang, Z., Chang, M.B., Yan, Z. and Road, M.J. (2015). Adsorption and destruction of PCDDFs using surface-functionalized activated carbons. *Chemosphere* 118: 136–142.

Bakkali, M.E., Bahri, M., Gmouh, S., Jaddi, H., Bakkali, M., Laglaoui, A. and Mzibri, M.E. (2013). Characterization of bottom ash from two hospital waste incinerators in Rabat, Morocco. *Waste Manage. Res.* 31: 1228–1236.

Buekens, A. and Cen, K.F. (2011). Waste incineration, PVC, and dioxins. *J. Mater. Cycles Waste Manage.* 13: 190–197.

Chang, Y.M., Hung, C.Y., Chen, J.H., Chang, C.T. and Chen, C.H. (2009). Minimum feeding rate of activated carbon to control dioxin emissions from a large-scale municipal solid waste. *J. Hazard. Mater*. 161: 1436–1443.

Chang, Y.M., Dai, W.C., Tsai, K.S., Chen, S.S., Chen, J.H. and Kao, J.C.M. (2013). Reduction of PCDDs/ PCDFs in MSWI fly ash using microwave peroxide oxidation in H_2SO_4/HNO_3 solution. *Chemosphere* 91: 864–868.

Chen, Y., Zhao, R.Z., Xue, Jun. and Li, J.H (2013). Generation and distribution of PAHs in the process of medical waste incineration. *Waste Manage.* 33: 1165–1173

Chen, M.W., Lin, T.C., Wang, T.C., Guo, P. and Chien, C. (2014). The PCDD/F removal efficiency of a medical waste incinerator dual-bag filter system. *Aerosol Air Qual. Res.* 14: 1223–1231.

Dahl, O., Nurmesniem, Hi., Risto, P. and Watkins, G. (2010). Heavy metal concentrations in bottom ash and fly ash fractions from a large-sized (246 MW) fluidized bed boiler with respect to their Finnish forest fertilizerlimit values. *Fuel Process. Technol.* 91: 1634–1639.

Dermont, G., Bergeron, M., Richer-Laflèche, M. and Mercier, G. (2010). Remediation of metal-contaminated urban soil using flotation technique. *Sci. Total Environ*. 408: 1199–1211.

Du, Y.Z., Jin, Y.Q., Lu, S.Y., Peng, Z., Li, X.D. and Yan, J.H. (2013). Study of PCDD/Fs distribution in fly ash, ash deposits, and bottom ash from a medical waste incinerator in China. *J. Air Waste Manage. Assoc.* 63: 230–236.

Gilardoni, S., Fermo, P., Ciati, F., Gianelle, V., Pitea, D., Collina, E. and Lasagni, M. (2004). MSWI fly ash particle analysis by scanning electron microscopy-energy dispersive X-ray spectroscopy. *Environ. Sci. Technol*. 38: 6669–6675.

Huang, Y., Takaoka, M., Takeda, N. and Oshita, K. (2007). Partial removal of PCDD/Fs, coplanar PCBs, and PCBs from municipal solid waste incineration fly ash by a column flotation process. *Environ. Sci. Technol*. 41: 257–262.

Javied, S., Tufail, M. and Sofia, K. (2008). Heavy metal pollution from medical waste incineration at Islamabad and Rawalpindi, Pakistan. *Microchem. J.* 90: 77–81.

Ji, S.S., Ren, Y., Buekens, A., Chen, T., Lu, S.Y., Cen, K.F. and Li, X.D. (2013). Treating PCDDFs by combined catalysis and activated carbon adsorption. *Chemosphere* 102: 31–36.

Jorjani, E., Esmaeili, S. and Tayebi Khorami, M. (2013). The effect of particle size on coal maceral group's separation using flotation. *Fuel* 114: 10–15.

Kakuta, Y., Matsuto, T., Tojo, Y. and Tomikawa, H., (2009). Characterization of residual carbon influencing on de novo synthesis of PCDDFs in MSWI fly ash. *Chemosphere* 68: 880–886.

Kim, W.S. and Lee, D.W. (2002). Size characterization of incinerator fly ash using sedimentation/steric field-flow fractionation. *Anal. Chem*. 74: 848–855.

Kuchar, D., Fukuta, T., Onyango, M.S. and Matsuda, H. (2007). Sulfidation treatment of molten incineration fly ashes with Na_2S for zinc, lead and copper resource recovery. *Chemosphere* 67: 1518–1525.

Liu, H.Q., Wei, G.X. and Zhang, R. (2013). Removal of carbon constituents from hospital solid waste incinerator fly ash by column flotation. *Waste Manage.* 33: 168–174.

Liu, H.Q., Wei, G.X., Zhang, R. and Liu, F.G. (2014). Simultaneous removal of heavy metals and PCDD/Fs from hospital waste incinerator fly ash by flotation assisted. *Sep. Sci. Technol.* 49: 1–10.

Lombardi, F., Mangialardi, T., Piga, L. and Sirini, P. (1998). Mechanical and leaching properties of cement solidied hospital solid waste incinerator fly ash. *Waste Manage.* 18: 99–106.

Lu, S.Y., Yan, J.H., Li X.D., Ni, M.J., Cen, K.F. and Dai, H.F. (2007). Effects of inorganic chlorine source on dioxin formation using fly ash from a fluidized bed incinerator. *J. Environ. Sci.-China* 19: 756–761.

Lu, S.Y., Du, Y.Z., Yan, J.H., Li, X.D., Ni M.J. and Cen, K.F. (2012). Dioxins and their fingerprint in size-classified fly ash fractions from municipal solid waste incinerators in China Mechanical grate and fluidized bed units. *J. Air Waste Manage. Assoc.* 62: 717–724.

Pan, Y., Yang, L.B., Zhou, J.Z., Liu, J.Y., Qian, G.R., Ohtsuka, N., Motegi, M., Oh, K. and Hosono, S. (2013). Characteristics of dioxins content in fly ash from municipal solid waste incinerators in China. *Chemosphere* 92: 765–771.

Sukandar, S., Yasuda, K., Tanaka, M. and Aoyama, I., (2006). Metals leachability from medical waste incinerator fly ash: A case study on particle size comparison. *Environ. Pollut*. 144: 726–735.

Gidarakos, E., Petrantonaki, M., Anastasiadou, K. and Schramm, K.W. (2009). Characterization and hazard evaluation of bottom ash produced from incinerated hospital waste. *J. Hazard. Mater.* 172: 935–942.

Thipse, S.S., Schoenitz, M. and Dreizin, E.L. (2002). Morphology and composition of the fly ash particles produced in incineration of municipal solid waste. *Fuel Process. Technol*. 75: 173–184.

Wang, L.C., Lee, W.J., Lee, W.S., Chang-Chien, G.P. and Tsai, P.J. (2003). Effect of chlorine content in feeding wastes of incineration on the emission of polychlorinated dibenzo-*p*-dioxins/dibenzofurans. *Sci*. *Total Environ*. 302: 185–198.

Wang, Y.H., Lin, C., Chien, C. and Guo, P. (2009). Characteristics of PCDD/Fs in a particles filtration device with activated carbon injection. *Aerosol Air Qual. Res*. 9: 317–322.

Xie, R., Li, W.J., Li, J., Wu, B.L. and Yi, J.Q. (2009). Emissions investigation for a novel medical waste incinerator. *J. Hazard. Mater*. 166: 365–371.

Xiong, Y.Q., Zhu, F.F., Zhao, L.Y., Jiang, H.M. and Zhang, Z.L. (2014). Heavy metal speciation in various types of fly ash from municipal solid waste incinerator. *J. Mater. Cycles Waste Manage.* 16: 608–615

Yan, M., Li, X.D., Lu, S.Y., Chen, T., Chi, Y. and Yan, J.H. (2011). Persistent organic pollutant emissions from medical waste incinerators in China. *J. Mater. Cycles Waste Manage.* 13: 213–218.

Zhang, H.J., Liu, J.T., Cao, Y.J. and Wang Y.T. (2013). Effects of particle size on lignite reverse flotation kinetics in the presence of sodium chloride. *Powder Technol*. 246: 658–663.

Zhao, L.J., Zhang, F.S., Hao, Z.P. and Wang, H.L. (2008). Levels of polycyclic aromatic hydrocarbons in different types of hospital waste incinerator ashes. *Sci. Total Environ*. 397: 24–30.

Zhao, L., Zhang, F.S., Wang, K. and Zhu, J. (2008). Chemical properties of heavy metals in typical hospital waste incinerator ashes in China. *Waste Manage.* 29: 1114–1121.

Zou, D.A., Chi, Y., Fu, C., Dong, J., Wang, F. and Ni, M.J. (2013). Co-destruction of organic pollutants in municipal solid waste leachate and dioxins in fly ash under supercritical water using H_2O_2 as oxidant. *J. Hazard. Mater*. 248–249: 177–184.

Received for review, February 4, 2016
Revised, April 28, 2016
Accepted, May 2, 2016