Comparison of Dioxin Destruction in the Fly Ash and Froths under Microwave Irradiation

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ABSTRACT

The objective of this study was to check the feasibility to treat medical waste incinerator (MWI) fly ash directly through microwave irradiation. The destruction efficiency of dioxins in MWI fly ash and in its froth products after flotation was compared in the air/nitrogen (N₂) atmosphere. Results demonstrated that the dioxin destruction effect was better in a N₂ atmosphere than that in an air atmosphere. And the total dioxin mass destruction efficiency of fly ash and the froths were 55.4% and 95.6% in the air atmosphere, while their values were 65.0% and 98.4% in the N₂ atmosphere, respectively. The vaporisation ratio of dioxins in MWI fly ash was up to 10.2% after 9 min N₂ irradiation. Furthermore, dechlorinating reactions of dioxins would occur when MWI fly ash was treated in N₂ atmosphere. Therefore, microwave-absorbing additives should be used to improve the decomposition of dioxins because of MWI fly ash containing less carbon constituents than the froths.

Keywords: Fly ash; Microwave treatment; Dioxins; Destruction; Froths.

INTRODUCTION

Incineration has become one of the major methods for treatment of medical wastes, due to its advantages in terms of volume reduction, energy recovery, pathogen elimination and chemical-toxicity destruction (Hsieh *et al.*, 2018a). Organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCBs), and polybrominated diphenyl ethers (PBDEs), and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) were generated during incineration were controlled stringently due to their degradation resistance and hypertoxicity, especially for dioxins, which can cause a wide range of health effects in the immune, endocrine, nervous and reproductive systems of humans and animals. (Chao *et al.*, 2014; Tzanakos *et al.*, 2014; Cheruiyot *et al.*, 2015; Lee *et al.*, 2016; Hung *et al.*, 2018; Tsai *et al.*, 2018). Chlorine content in medical waste has reached 4.5%–7.5% due to the use of polyvinyl chloride plastic and NaCl in medical treatment, and it usually plays a major role in the formation of dioxins during medical waste incineration (MWI) process, leads to more dioxins be formed (Wang *et al.*, 2003; Xie *et al.*, 2013). The mean dioxin emission factor of the medical waste incinerator (MWI) (20.1 ng I-TEQ kg⁻¹

waste) was approximately 210 times of magnitude higher than that of municipal solid waste incinerators (MSWI) (0.0939 ng I-TEQ kg⁻¹ waste) (Chen *et al.*, 2014; Han *et al.*, 2017). 90% of the dioxins produced in incinerators were effectively captured by powder activated carbon (PAC), removed through bag filter and then transferred into MWI fly ash (Cheruiyot *et al.*, 2016; Zhan *et al.*, 2018). Researchers reported that MWI fly ash has a higher content of 2–3 orders for magnitude dioxins than that in MSWI fly ash (Hsieh *et al.*, 2018b). MWI fly ash has been identified as hazardous waste in many countries. MWI fly ash also contains carbon constituents including powder activated carbon (PACs) and unburned carbon, which was found to be a dioxin enrichment of source (Liu *et al.*, 2017a). In our previous study, a novel flotation technique was developed, which could separate the dioxins and carbon constituents from MWI fly ash simply and economically (Liu *et al.*, 2013). Most of the dioxins and carbon constituents were transferred into the froth product, and chlorides were simultaneously washed out from MWI fly ash (Liu *et al.*, 2017b). Thus, it is necessary to develop effective technology to thorough decompose the dioxins in the froths.

Thermal treatment is one of the most common methods to decompose the dioxins at approximately 300°C in inert gas conditions to dechlorination and hydrogenation promising, because dioxins are instability in the high temperature (Mizukoshi *et al.*, 2007; Zhu *et al.*, 2017). Wang *et al.* (2006) found that the detoxification efficiency of dioxins in MSWI fly ash was above 90% in nitrogen (N₂) atmosphere

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and 300°C for 2 h. Wu *et al.* (2011) reported that fly ash constituent is a crucial factor, which can influence or dominate the destruction efficiency of dioxins in fly ash. In addition, another effective method is thermal treatment at temperature exceeding 450°C in oxidative conditions (Hung *et al.*, 2013). Lundin *et al.* (2011) noted that the total dioxin content in fly ash was reduced significantly after treatment at 500°C in air because of degradation rather than dechlorination. However, in some cases, a high risk of de novo synthesis may be incurred, which leads to the reformation of dioxins (Lundin *et al.*, 2011). Wang *et al.* (2012) reported that the dioxin content in MWI fly ash increased from 6.2 to 401.0 ng I-TEQ g⁻¹ when fly ash was treated at 850°C in air atmosphere without adding CaO (I-TEQ is the international toxic equivalent quantity). Melting at over 1300°C is recommended to decompose dioxins in fly ash, the OCDD and OCDF in slag product was high (Kim *et al.*, 2005; Wang *et al.*, 2006; Lin *et al.*, 2011). The PCDD/Fs TEQ decomposition efficiency can exceed 99% after the plasma melting process, but it consumes considerable energy (Pan *et al.* 2013). Rafalp *et al.* (2001) treat fly ash by reburning treatment in the combustion chamber, more than 99% of the PCDD/Fs in the fly ash could be decomposed. In our previous study, the froths obtained after flotation were treated by reburning in the combustion chamber, the total dioxin mass destruction efficiency of which is more than 98% at temperatures higher than 1000°C (Wei *et al.*, 2017). However, if traditional heat treatment in air is used to treat the froths, resources will be wasted because large amounts of PAC in the froths are burnt instead of being reused.

Compared with conventional heating treatment, microwave heating is environmentally friendly and possesses additional advantages of high heating rates, selective heating, less treating time and lower energy consumption (Dehdashti *et al.*, 2011; Antonetti *et al.*, 2015; Rivas *et al.*, 2015). Researchers have found that organic pollutants can be decomposed by microwave heating (Liu *et al.*, 2008; Wu *et al.*, 2008; Lin *et al.*, 2010; Huang *et al.*, 2011; Lin *et al.*, 2013; Antonetti *et al.*, 2016). Meanwhile, activated carbon can adsorb and converse microwave energy into thermal energy due to its excellent dielectric properties (Jou *et al.*, 2009). Elimination of organic pollutants under microwave irradiation integrated with activated carbon addition was previously reported (Dehdashti *et al.*, 2011). “Hotspots” would be formed on the activated carbon surfaces during microwave irradiation, the temperature of these “hotspots” is particularly higher than that of other places. Thus, chemical reactions might occur easily at the high temperature, which could accelerate the elimination of organic pollutants (Zhang *et al.*, 2007, 2009). Dehdashti reported that the ‘temperature-rise’ phenomenon of activated carbon under microwave irradiation depended on microwave power and the nature of adsorbent in the sample (Dehdashti *et al.*, 2011). Redox atmosphere may also affect the organic pollutant decomposition because PAC is easily oxidised and combusted in suitable atmosphere (Amankwah *et al.*, 2005). Jou *et al.* (2009) concluded that organic pollutants that adsorbed on the surface of the PAC were degraded

under microwave irradiation because of microwave-assisted oxidation. Our previous study found that the total mass destruction efficiency of the PCDD/Fs in the froths could reached above 99 wt.% with a microwave incident power of 2100 W for 7 min in N₂ atmosphere, because PAC in the froths can work as microwave absorbent (Wei *et al.*, 2017).

Using microwave heating to treat incinerator fly ash is an innovative approach. In recent years, microwave sintering has been employed successfully on the stabilisation of heavy metals in MSWI fly ash. Chou *et al.* (2009) found that a long microwave sintering time of fly ash corresponded to a higher stabilisation efficiency of heavy metals. Besides, soluble chlorides in MSWI fly ash could affect the sintering effect (Lin *et al.*, 2018). However, MSWI fly ash treatment by microwave heating usually need microwave absorbent or microwave-absorbing crucible because of its low carbon content (Chou *et al.*, 2009; Chou *et al.*, 2013).

Comparing with MSWI fly ash, MWI fly ash contains higher content of carbon constituents (> 11%) due to PAC injection in the air pollution control devices (APCDs) (Liu *et al.*, 2013). However, few studies have questioned whether microwave sintering could directly detoxify the dioxins in MWI fly ash and whether its peculiar high carbon content might facilitate PCDD/F decomposition. Compared with the froths, relatively less carbon constituents and even more chlorides in the MWI fly ash might affect the detoxication of dioxins. The objective of this study was to investigate the feasibility to treat MWI fly ash directly by microwave. Meanwhile, the destruction effect of dioxins in raw fly ash and its froth products in different atmosphere were compared.

MATERIALS AND METHODS

Materials

25 kg of fly ash sample used in this study was obtained from a 20 t d⁻¹ gyration kiln incinerator at a MWI centre in northern China. The incinerator was equipped with a PAC sprayer device and bag filters as APCDs for dioxin management. The fresh and dry fly ash sample was collected from the hopper of a bag filter. The ash sample was collected over a 7-day period and homogenized and passed through a sieve of 20 meshes, and then was dried at 105°C for 24 h to further analyse.

15 kg of fly ash sample was treated by column flotation, the flotation experimental apparatus and operating conditions were the same as those of our previous study (Liu *et al.*, 2013). The suitable flotation conditions were 0.05 kg L⁻¹ of slurry concentration, 12 kg t⁻¹ of kerosene, 3 kg t⁻¹ of froths, and a 0.06 m³ h⁻¹ air flow rate. The froths were carefully vacuum-filtered, dried, weighed, and stored. Loss on ignition (LOI) analysis was used to determine the carbon content in the raw fly ash and froth product, respectively, as shown in Table 1. Chemical composition of fly ash was measured by MXF-2400 X-Ray Fluorescence Spectrometer. PAC sample that had been injected into the APCDs of the incinerator was obtained from the PAC storage tank at the waste incineration plant. The PAC is made from a coconut shell.

Table. 1. Chemical composition and LOI of raw fly ash and the froths (%).

Sample	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	SO ₃	Cl	P ₂ O ₅	TiO ₂	F	LOI
Raw fly ash	17.13	24.42	2.85	1.78	1.8	2.8	15.2	6.37	20.43	1.06	1.34	2.59	11.1
Froths	32.45	38.56	5.33	3.40	3.28	1.08	0.05	6.09	2.85	1.35	2.24	0.75	56.4

Methods

The raw fly ash, froths and PAC samples were pelleted for 5 s with a hydraulic press at a maximum pressure of 50 MPa. A water solution of 3 wt% polyvinyl alcohols was then added into the samples at a 5 wt% concentration to bind the pressed particles. Subsequently, pellets with a height of 15 mm and diameter of 10 mm were dried at 110°C for 3 h.

Then, these pellets were sintered in a high-temperature laboratory microwave oven (HAMilab-V3000, Synotherm Corporation, Changsha, China). A schematic diagram of the laboratory microwave oven is shown in Fig. 1. The power was varied from 0 to 3000 W and the magnetron operates at a frequency of 2450 MHz. The furnace was composed of a double-layer, water-cooled, vacuum-sealed, stainless steel chamber attached to vacuum and gas entrance systems. During this experiment, the pellets were placed in a microwave transparent quartz crucible with the following dimensions: the height of 45 mm, the diameter of 50 mm, and the thickness of 2 mm. During each experiment, eight pellets were placed inside the alumina crucible. The crucible and its contents were positioned in the center of the base of the microwave chamber, on a microwave transparent alumina platform that acted as an insulator. The alumina insulation board was a poor microwave absorber. During the experiment, radiation was continuous and uniformity was maintained to provide heat to each pellet under consideration.

Temperature measurement in microwave field is regarded crucial for microwave treatment. In view of that PAC

sample is relatively uniform; the infrared pyrometer was used to measure the surface temperature of PAC pellet on the top layer in a microwave field (Yuen *et al.*, 2009). Air or N₂ flowed through the microwave oven at a flow rate of 3 L min⁻¹ to provide an oxidation or inert atmosphere, respectively, and to evacuate any volatile products. According to the preliminary results, the processing time could influence the experiment. Initially, the microwave power was stabilized at 1800 W, and processing for 5, 7, and 9 min were used in N₂ atmosphere. When the atmosphere was changed, the microwave power and processing time were stabilised at 1800 W and 9 min, respectively. The specimens were then cooled in the furnace.

In each test run, the treated sample was also collected, grinded and thoroughly mixed after cooled. Samples collected were stored in a refrigerator before analysis. The exhaust gas generated from microwave treatment process was introduced into XAD-2 polymeric resin and a toluene absorber bottle to examine the evaporation of dioxins. After each test run, XAD-2, toluene and rinsed solvent (flushing the reactor and tube with toluene) was collected and mixed as one sample to follow the standard PCDD/F analysis procedures.

The content of 17 toxic dioxin congeners (2,3,7,8-substituted) were analysed using isotope dilution high-resolution gas chromatography/high-resolution mass spectrometry. The PCDD/F content analysis was performed following the method used in our previous report (Wei *et al.*, 2016). Analytical results for the 17 specific congeners used to calculate the I-TEQ are reported. The PCDD/F

1: Control system; 2: Rotameter; 3: Magnetron; 4: Air/Nitrogen; 5: Gas inlet; 6: Electric turntable; 7: Infrared pyrometer; 8: Gas outlet; 9: XAD -2 resin; 10: Toluene absorber bottle; 11: Silica gel bottle; 12: Vacuum pump; 13: Sample; 14: Graphite plate; 15: Alumina crucible; 16: Alumina platform.

Fig. 1. Schematic diagram of the microwave laboratory oven.

destruction efficiency was calculated for both gaseous dioxins vaporised or desorbed from the samples (raw fly ash or froths) during microwave treatment and adsorbed by XAD-2 resin, and for solid-phase dioxins that remained on the treated samples. The vaporisation ratio was defined as the percentage of gaseous dioxins that were vaporised off or desorbed from the untreated samples. The destruction efficiency and vaporisation ratio of dioxins in raw fly ash or the froths were calculated as follows, respectively.

Destruction efficiency =

$$[1 - ((\text{Dioxin amount adsorbed by XAD-2 resin}) + (\text{Dioxin amount in the treated sample})) / (\text{Dioxin amount in the untreated sample})] \times 100\% \quad (1)$$

Vaporisation ratio =

$$((\text{Amount of dioxins adsorbed by XAD-2 resin}) / (\text{Amount of dioxins in the untreated sample})) \times 100\% \quad (2)$$

RESULTS AND DISCUSSION

Surface Temperature of PAC in the Microwave Field

The behaviour of the PAC under microwave heating was evaluated by measuring the surface temperature of the PAC pellets in microwave field. Three replicates were made to obtain reliable data and the results were determined as the average of three measurement results. Fig. 2 illustrates the surface temperature of the PAC pellets in different atmospheres while being heated with microwaves incident power of 1800 W. The temperature increased with time in a N₂ atmosphere. After 5 min, the rate of the temperature rise decreased, which has previously been attributed to energy insufficiency (Dehdashti *et al.*, 2011). In an air atmosphere, the temperature increased again rapidly, and reached 860°C, which was relatively higher than that in the N₂ atmosphere. However, the sample temperature started to drop slowly after 7 min and dipped to a lower temperature than that when a N₂ atmosphere was used after 9 min. This may be related to the dielectric properties of PAC. The

dielectric loss factor of PAC initially increased sharply with the temperature rise. In an air atmosphere, the dielectric behaviour of PAC decreased because of partial oxidation or combustion. Most of the PAC was then consumed, which decreased its microwave coupling efficiency (Amankwah *et al.*, 2005). The vast difference of heating curves in the N₂ and air clearly suggested that the microwave absorption nature of PAC in air atmospheres was not identical after 9 min.

Influence of Processing Time on PCDD/F Destruction

The total PCDD/F content in the raw fly ash and froths were 78.8 and 403.8 ng g⁻¹, and the PCDD/Fs-I-TEQ were 5.6 and 29.0 ng I-TEQ g⁻¹, respectively (Fig. 3). The total PCDD/Fs-I-TEQ in the froths was more than 5 times of that in the raw fly ash. Our previous study demonstrated that the flotation process removed > 90% of dioxins during the transition from raw fly ash to froths (Liu *et al.*, 2013). The distribution of PCDD/F congeners in the froths was extremely similar to that in the raw fly ash. Most of the PCDDs came from HpCDDs and OCDDs, which are 7-Cl or 8-Cl PCDDs. Most of the PCDFs were TeCDFs, 1,2,3,4,7,8-HxCDFs, 2,3,4,6,7,8-HxCDFs, 1,2,3,4,6,7,8-HpCDFs, and OCDFs. Flotation did not substantially alter the congener fingerprint of PCDD/Fs.

Fig. 4 illustrates the total mass destruction efficiency of dioxins in the raw fly ash and froths when different processing times were used in a N₂ atmosphere. Fig. 5 shows the TEQ content of residual dioxins in the samples after microwave treatment. The destruction efficiency of both samples increased when the processing time was prolonged. For the raw fly ash, 34.6%, 47.7%, and 65.0% of total PCDD/F mass destruction efficiencies are achieved when processing for 5, 7, and 9 min, and the total TEQ content of dioxins decreased to 4.5, 3.5, and 1.6 ng g⁻¹, respectively. When the same experiment was performed using the froths, the total dioxin mass destruction efficiencies after 5, 7, and 9 min of processing were 76.9%, 91.9%, and 98.4%, and the total TEQ content of dioxins decreased from

Fig. 2. Effect of the atmosphere on the temperatures rising courses of the surface of PAC tables.

Fig. 3. Mass content of each dioxin congener for the raw fly ash and the froths.

Fig. 4. Effect of processing times on total mass destruction efficiency of dioxins in the samples.

Fig. 5. Residual PCDD/Fs-I-TEQ in the samples after microwave treatment at different processing time.

29.0 ng g⁻¹ to 6.7, 2.7, and 0.4 ng-TEQ g⁻¹, respectively. Therefore, a long processing time enhanced the destruction efficiency. Moreover, compared with the duration of traditional thermal treatment (more than 0.5 h) (Lundin *et al.*, 2011; Wu *et al.*, 2011; Hung *et al.*, 2013), microwave treatment took less time to achieve a similar decomposition efficiency, which indicated that microwave treatment of the froths is an efficient treatment technology.

Although the initial dioxin content in the froths was higher than that in raw fly ash, the dioxin mass destruction efficiencies in the froths were higher after equal processing time. The results explained by the higher amount of PAC in the froths than that in the raw fly ash. The thermal mechanism of microwave heating of the samples could be as follows: (i) the uneven surfaces of PAC firstly absorbed and transformed microwave energy into heat at room temperature and then formed numerous “hot spots” in the froths (Dehdashti *et al.*, 2011), leading to the adsorption of dioxins or rapid decomposition of the existed PAC; (ii) the local heating in the samples is not uniform, during which heat from the PAC raised the temperature of the pellets; (iii) the temperature of the pellets was high enough to allow chemical species such as Fe₃O₄, Fe₂O₃, MnO₂, MgO and TiO₂ to absorb and transform microwave energy into heat energy; and to remove the rest of dioxins in the samples (Chou *et al.*, 2013). The froths absorbed more energy than that of the same amount in the raw fly ash because the content of PAC in the froths was high, and more “hotspots” were formed in it during the microwave treatment. The whole temperature of the froths was also enhanced within a short period, and thus the dioxin destruction efficiency in the froths enhanced compared with that in the raw fly ash. Therefore, high carbon content in the froths contributed to high destruction of dioxins.

Fig. 6 shows the effect of processing time on the

distribution profiles of the 17 major dioxin congeners in MWI fly ash. The distributions of dioxin congeners in the treated samples were similar to those in raw fly ash. The initial contents of HpCDD, OCDD, TeCDF, 1,2,3,4,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, and OCDF were high, which lead to those remaining content in the treated samples were also high. The homologue distribution of dioxins did not change obviously when processing time was extended, which indicated the reductions of dioxin levels under microwave treatment are caused not by dechlorination but mainly by decomposition or vaporisation of dioxins. This result is not consistent with the study conducted by Chang using microwave peroxide oxidation (MPO) treatment methods (Chang *et al.*, 2013). They found the distribution of 17 major dioxin congeners shifted from highly chlorinated dioxins to low chlorinated dioxins after MPO treatment. The main reasons are intrinsic differences in molecular diffusion and reaction activity among dioxin congeners during MPO processing.

Influence of Processing Time on Dioxin Evaporation

Fig. 7 gives the vaporisation ratio of dioxins in the two samples on various processing times. Evaporation of dioxins from both raw fly ash and froths increased with the processing time increasing (up to a maximum of 9 min). The amount of dioxins in the exhaust gas after 9 min of raw fly ash treatment was 10.2 wt% of the original amount. By studying the evaporation of dioxins during the reburning process of fly ash, Kobylecki *et al.* (2011) reported that the amount of evaporated dioxins in fly ash did not exceed 3 wt% by conventional heating treatment. Wu *et al.* (2011) discovered that the amount of dioxins desorbed to the gas phase increased with the heating temperature from 300°C to 400°C.

The amount of dioxins in the exhaust gas after processing

Fig. 6. Distribution profiles of 17 major dioxin congeners in the samples under different processing time.

Fig. 7. Vaporisation ratio of dioxins in the samples at various processing times.

for 9 min was only 0.8 wt% of that in the untreated froths. Therefore, dioxins in the froths had mostly decomposed and just few evaporated into the exhaust gas. Compared with raw fly ash, the larger amount of PAC in the froths resulted in more effective microwave energy absorption, which initially caused a rapid increase of the overall temperature of the froths. Therefore, most of the dioxins in the froths were quickly decomposed, leaving few to be evaporated. Furthermore, PAC may have captured and decomposed gaseous phase dioxins and prolonged their escape time, making it possible for PCDD/F destruction. The content of PAC in raw fly ash is not enough to support the decomposition of dioxins in a short time, which is easy to lead to dioxin volatilizations. Thus, addition of appropriate amount of microwave-absorbing medium is necessary.

Effect of Atmosphere on Dioxin Destruction

Fig. 8 displays the residual content of each dioxin congener in the samples (the raw fly ash and froths) after microwave treatment for 9 min in air/N₂ atmospheres. The remaining content of each dioxin congener in the two residual samples was higher in an air atmosphere compared with that in a N₂ atmosphere. For the raw fly ash, the total mass dioxin destruction efficiency was 55.4% in an air atmosphere, 10% less than that in a N₂ atmosphere. This is also lower than that reported by other studies on low-temperature thermal treatment (Wu *et al.*, 2011; Hung *et al.*, 2013). For the froths, 95.6% and 98.4% of the dioxins were destroyed following treatment in air and N₂ atmosphere, respectively.

The redox atmosphere used affects not only the microwave absorption characteristics of PAC in the samples but also the dioxin removal mechanisms. PAC is a hyperactive material which may have interaction with microwaves. The permittivity of the PAC was extremely high even at room temperature and increased rapidly with the temperature rise, which facilitated microwave absorption. In a N₂ atmosphere, dioxins were desorbed, decomposed, and carbonised because of thermal effects. Not only the

simple chemical bonds such as C-Cl and C-C were destroyed, but also the benzene rings were degraded quickly (Zhang *et al.*, 2009). All these possible dioxin reactions (Eq. (3)) could occur. During microwave heating, PAC might serve as a catalyst of PCDD/Fs decomposition. And the catalytic action of the PAC might help the thermal decomposition of the PCDD/Fs in a relatively low temperature (Cha, 2001).

In an air atmosphere, however, PAC was easily oxidised and combusted and its permittivity would have thus decreased, which also limited its microwave absorption (Amankwah *et al.*, 2005). Therefore, the total destruction efficiency of dioxins was lower in an air atmosphere compared with that in a N₂ atmosphere. When oxygen was used, the process of dioxin removal was similar to the oxidation combustion of organic pollutants, for which decrease in decomposition also occurred (Zhang *et al.*, 2009). When dioxins experienced a carbon-carbon bond rupture and oxidation reactions under microwave irradiation, CO₂, H₂O, and simple inorganic ions were produced (Zhang *et al.*, 2009). The reaction of Eq. (4) is considered to have occurred.

Fig. 8. Effect of the atmospheres on residual mass content of each PCDD/F congener in the samples.

Effect of Atmosphere on Distribution of Dioxin Congeners in Exhaust Gas

Fig. 9 shows the distribution profiles of 17 major dioxin congeners in the exhaust adsorption traps for 9 min of microwave treatment of the raw fly ash and froths in air and N_2 atmospheres. As a whole, the distribution of dioxin congeners in four kinds of exhaust gas were similar to that in the raw material, HpCDDs, OCDDs, TeCDFs, 1,2,3,4,7,8-HxCDFs, 2,3,4,6,7,8-HxCDFs, 1,2,3,4,6,7,8-HpCDFs, and OCDFs still showed higher peak of fraction. For the raw fly ash, the fraction of low chlorinated congeners, such as 2,3,7,8-TeCDF and 1,2,3,7,8-PeCDF, were obviously higher in N_2 atmosphere than that in air atmosphere, and high chlorinated PCDD/Fs were relatively low. For froths, there was no obvious difference in the homologue distribution in gas phase of exhaust gas in air and N_2 atmosphere.

Dioxins in flue gases were susceptible to volatilization, dechlorination or de novo synthesis during microwave irradiation of the fly ash or the froths. Volatilization of dioxins might happen at the initial stage of microwave heating, during which the overall temperature of the two kinds of samples increased slowly. Thus, small amount of dioxins might evaporate into gaseous phase. Wang *et al.* (2006) reported that dechlorination of dioxins generally occur in an oxygen-deficient atmosphere during conventional low-temperature treatment. Similarly, raw fly ash contains less carbonaceous matter, its overall temperature is relatively low at initial stage after microwave heating, during which dechlorination reaction might happen in N_2 atmosphere. Fig. 10 shown that chlorination degree of dioxins in the gas phase of exhaust gas in N_2 atmosphere is 6.27, which is lower than that in raw fly ash (6.55). This also confirms the possibility of chlorination during this process. However, in air atmosphere, dioxin removal in raw fly ash might result in oxidation reactions rather than decomposition or

dechlorination process. For froths, chlorination degrees in products were found to have no significant change in air or N_2 atmosphere, which implies that contributors of dechlorination reactions were very litter during microwave heating. This is because that the froths contained with high content of PAC could quickly reached high temperature, which lead to more decomposition and less evaporation of dioxins.

The crucial elements of de novo synthesis are temperature, catalysis using carbon, chlorine, oxygen, and metals (especially Cu) (Wang *et al.*, 2012). Compared with the raw fly ash, the froths contained more carbon constituents, more copper and less chlorine. Residual carbon and PAC could provide basic organic material and the catalytic surface for dioxin formation (Kakuta *et al.*, 2005; Chang *et al.*, 2009). Cu is also essential for catalysing formation of dioxins. Therefore, high levels of Cu and carbon constituents in the froths might promote de novo synthesis of dioxins (Chin *et al.*, 2012). The lack of chlorine in the froths, however, inhibited this de novo synthesis during microwave heating. Furthermore, high PAC content in the froths effectively raised its ability to absorb microwave energy and made the froths quickly past the temperature range of de novo synthesis of dioxins (250–400°C) (Mizukoshi *et al.*, 2007). Therefore, for the froths, dioxins should hardly form via de novo synthesis under microwave irradiation. For the raw fly ash with high levels of chlorine, a certain amount of Cu, carbon constituents and the presence of oxygen easily led to the reformation of dioxins by de novo synthesis at the beginning of the microwave treatment. How the complex composition of the raw fly ash and froths precisely affect the de novo synthesis is unclear at present, given the discrepancies in the limited data available. Therefore, to judge whether de novo synthesis reactions occurs under microwave irradiation is difficult.

Fig. 9. Effect of the atmospheres on distribution of dioxin congeners in the exhaust gas after 9 min of microwave treatment.

Fig. 10. Chlorination degrees of PCDD/Fs in the raw fly ash and the froths under N₂/air atmosphere.

Certainly, decomposition, volatilization, dechlorination, and/or the de novo synthesis of dioxins in the sample during microwave heating are affected by the way of treatment and the treatment conditions. Influencing parameters including microwave incident power, volume and mass of sample, packing density, air flow rate, and particle size, all require more intensive study. Additionally, heavy metals present in the fly ash may be solidified during microwave treatment, and some volatile heavy metals, such as Pb, Zn, and Cd, may enter into the exhaust gas.

CONCLUSIONS

To explore the function of PAC in MWI fly ash during microwave heating, experiments were conducted using froths obtained after flotation and raw fly ash. The temperature changes of PAC surface under a microwave field were also recorded to assess “hotspot” effects of PAC. After treatment with a microwave incident power of 1800 W for 9 min in a N₂ atmosphere, above 98% of the dioxins in the froths were decomposed but 65.0% were decomposed in the raw

fly ash. The dioxin amounts evaporated from the raw fly ash were significantly higher than those from the froths. This is because large amounts of PAC presented in the froths may accelerate the elimination of dioxins during microwave irradiation. And carbon content in raw fly ash is insufficient to increase the decomposition of dioxins in a short time, thus addition of microwave-absorbing medium into the raw fly ash is necessary. Meanwhile, reaction atmosphere can affect the microwave absorption characteristics of PAC and the dioxin destruction mode. Therefore, dioxins were eliminated much more effectively in N₂ atmosphere than that in an air atmosphere. Besides, dechlorinating reactions of dioxins would occur when the raw fly ash was treated in N₂ atmosphere.

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