



# Thermochemical formation of polychlorinated dibenzo-p-dioxins and dibenzofurans on the fly ash matrix from metal smelting sources



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## HIGHLIGHTS

- PCDD/F formation on different metal smelting fly ash is compared for the first time.
- Contents of TOC, metal and chlorine were important to PCDD/F formation.
- Activation energies of congener formation explained PCDD/F profiles.

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## ABSTRACT

Metal smelting processes are important sources of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). The present work aims to clarify the formation characteristics of PCDD/Fs by heterogeneous mechanisms on fly ash from typical multiple secondary aluminum (SAI), secondary lead (SPb) smelting, and iron ore sintering (SNT) sources in China. The formation characteristics of PCDD/Fs on fly ash were studied in the temperature range 250–450 °C for 10–150 min. Substantial thermochemical formation of PCDD/Fs on SAI and SNT ash was observed. The maximum increase of PCDD/F concentrations under 350 °C for 30 min was 604 times greater than the initial concentration in SAI ash. The concentration of PCDD/Fs was 77 times greater than that of SNT fly ash under 350 °C for 30 min. However, the maximum increase of PCDD/F concentrations was less than 8 times that in raw SPb ash under 350 °C. Contents of total organic carbon (TOC), Cu, Al, Zn and Cl, which are widely recognized as important elements for promoting PCDD/F formation, were obviously higher in SAI and SNT ash than in SPb ash. This may explain the greater observed formation times of PCDD/Fs on SAI and SNT ash than that on SPb ash. It was found that several congeners tended to form at higher temperatures than those for SAI ash. Activation energy calculation according to the Arrhenius equations could explain the dominant formation of those congeners at much higher temperatures on SAI ash.

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## 1. Introduction

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) have received much public concern worldwide owing to their persistence, toxicity, bioaccumulation and long-range transport (Altarawneh et al., 2009; Liu et al., 2015).

In terms of the emission inventory for PCDD/Fs, secondary non-ferrous metal smelters and iron ore sintering, as typical industrial thermal processes, have been considered important sources of PCDD/Fs in China (Hanari et al., 2004; Bocio and Domingo, 2005; Ba et al., 2009; Chin et al., 2011; Jiang et al., 2015; Li et al., 2017; Sun et al., 2017). Prevention or reduction of human exposure to PCDD/Fs is best done via source-directed measures, i.e., strict control of industrial processes to reduce PCDD/F formation. Therefore, the most basic means of achieving this objective is to make the generation mechanism clear.

Heterogeneous reactions on fly ash surfaces are widely

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recognized as the most important pathway for the unintentional formation of PCDD/Fs. This is a more important pathway than gas phase formation of PCDD/Fs at high temperatures (Takasuga et al., 2000). With residual carbon, chlorine, oxygen, and metals such as Cu, Zn, Al, and Fe contained in the fly ash, it is easier to form PCDD/Fs in the post combustion zone by heterogeneously catalyzed reaction on fly ash surfaces (Liu et al., 2015; Zhou et al., 2015; Zhan et al., 2016). Therefore, fly ash has been widely used to simulate thermochemical reaction processes in studies of PCDD/F mechanisms (Jiang et al., 2015). Some studies have indicated that fly ash of secondary copper and municipal solid waste incinerators can strongly promote PCDD/F formation by heterogeneous reactions during industrial thermal processes (Ba et al., 2009; Chin et al., 2011; Tang et al., 2013; Wang et al., 2016). At a given temperature and time, the fly ash of secondary copper produces hundreds of times more PCDD/Fs than those of original fly ash (Olie et al., 1998; Chin et al., 2011). However, thermochemical experiments about whether fly ashes from multiple metal smelters other than secondary copper smelting plants can enhance PCDD/F formations so strongly have not been evaluated. In addition, it is necessary to analyze and compare how different fly ashes have various effects on PCDD/F formation. This would increase understanding of potential mechanisms of PCDD/F formation mediated by fly ash.

The metal smelting industry has been developing rapidly over the last 30 years. China has been one of the world's largest producers of copper, steel, aluminum and lead for 15 consecutive years. In 2016, 10 types of non-ferrous metal production reached 52.83 million tons, with interannual growth of >2.5%. The same year, the production of iron and steel in China was ~800 million tons. Iron accounts for at least 90% of metal production (Hanari et al., 2004). With metal smelters widely established in recent years, PCDD/Fs control regulation has been strictly observed (Ba et al., 2009). Secondary non-ferrous metal smelters and steelmaking are important industries of PCDD/Fs emission in China, so they have greater potential to abate such emissions.

There have been studies of PCDD/F formation on fly ash from secondary copper smelting processes (Chin et al., 2011). However, few studies compared the congener profiles and distribution characteristics of PCDD/F formations on different fly ash matrixes from typical secondary aluminum, secondary lead and iron ore sintering, which are important sources of PCDD/Fs. In the present study, formation characteristics of PCDD/Fs on fly ash collected from typical and representative secondary aluminum, lead smelting and iron ore sintering in China were studied using a tube furnace in the temperature range 250–450 °C. The primary goals of this research were to: 1) compare the formation characteristics of PCDD/Fs from different metal smelting sources, which could verify the influence of the fly ash on PCDD/Fs generation; 2) comprehensively evaluate the distribution characteristics in congener profiles of PCDD/Fs from fly ash-mediated formation in the metal smelting industry and the mechanisms involved, which may enhance understanding of PCDD/F patterns and potential mechanisms involved; 3) investigate the main factors and their influences on PCDD/F emissions, which would be useful for understanding PCDD/F mechanisms, and developing an effective way to reduce PCDD/Fs in smelting process.

## 2. Materials and methods

### 2.1. Design of thermochemical experiments

A series of laboratory experiments using secondary aluminum, secondary lead and iron ore sintering fly ash as a matrix were performed in a tube furnace under controlled temperature and time to simulate thermochemical reactions of PCDD/Fs. The fly ash

samples were collected from typical multiple industry sources in China. The chemical composition of the fly ash samples was stable. The samples comprised a mixture of fly ash captured by air pollution control devices and were collected from outlets at the bottom of those devices for gathering and storing fly ash. This fly ash was used to simulate as closely as possible the active surfaces of fly ash produced during thermochemical processes.

The tube furnace equipped with a temperature control sensor and time switch was used to conduct the experiment. Cylindrical quartz tubes were used for the reaction chamber. The tubes were ~600 mm long and had a diameter of 45 mm, and were installed on the horizontal laboratory furnace. The pre-weighed fly ash (0.5 g SAl fly ash, 0.5 g SNT fly ash and 1 g SPb fly ash) was put in a porcelain boat and placed in the furnace, respectively. Synthetic air released from a compressed air tank passed through the furnace at a constant flow rate of 50 mL/min to simulate conditions in an open smelter system. Tube furnace apparatus used for the thermochemical reaction experiments has been shown and detail described in our previous study (Wang et al., 2015).

The widely recognized temperature for PCDD/F generation in the post-combustion zone is 250–450 °C. PCDD/Fs form in the cooling zone (from several minutes to hours) of a real plant. Various fly ashes were heated at 250, 350, and 450 °C for 30 min to examine the effect of the fly ash matrix and temperature on PCDD/F formation. The fly ashes were controlled at 350 °C for 10, 30, 120 and 150 min to determine the effect of reaction time on PCDD/F patterns.

Two absorption impingers containing toluene with ice condensation were connected in tandem, which could strongly absorb PCDD/Fs. After the end of the reaction, the absorption liquid was restored for the subsequent experiment. The quartz tube and the absorption bottles were rinsed three times with toluene to collect residues of the target compounds. Gaseous products of the simulation experiments had two parts, the cleaning solution (toluene used to rinse the apparatus) and absorption solution (toluene in the impingers). The toluene solutions and fly ash residue after each thermochemical experiment were stored at ~4 °C until they were analyzed.

### 2.2. Characterization of fly ash by X-Ray fluorescence, scanning electron microscopy and total organic carbon

X-ray fluorescence (XRF) technology (Arl Perform'X, designed by Thermo Fisher Scientific, USA) was used to determine the elemental composition of fly ash from secondary aluminum (SAl), secondary lead (SPb), and iron ore sintering (SNT). The elemental compositions and contents in the fly ash samples were determined by using XRF. Scanning electron microscopy (using a S-3000 N instrument; Hitachi, Tokyo, Japan) was used to evaluate structure and composition. High-resolution images of surface topography, with excellent depth of field, are produced using a highly focused, scanning (primary) electron beam. Analyses of total organic carbon (TOC) in fly ash samples were conducted using TC-IC methods. Fly ash powder was transferred to the sample boat and then weighed using an electronic balance. The sample boat together with the sample was placed in the above system, in which TOC was then measured.

### 2.3. Analytical procedure

PCDD/Fs was analyzed using isotope dilution high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS) (Ba et al., 2009; Liu et al., 2015). Toluene from the traps and residues was spiked with a mixture of 1 ng <sup>13</sup>C<sub>12</sub>-labeled PCDD/Fs internal standards (EPA-1613 LCS, Wellington

Laboratories, Guelph, Canada) according to U.S. Environmental Protection Agency (EPA) method 1613. The burned fly ash samples were acidified with 1 mol/L HCl, shaken well, and washed with deionized water to neutral. The fly ash samples were dried using vacuum-freezing drying equipment for ~48 h. Then, the samples were extracted by Soxhlet extraction with 250 mL of toluene for 24 h. Each residue extract and gas absorption extraction solution were evaporated to a small volume using a rotary evaporator. After concentration, the vaporized sample components passed through a series of chromatographic columns (acidified silica gel, a multilayer silica gel, and activated-charcoal columns) for purification and obtaining the PCDD/Fs. Finally, the liquid samples were concentrated to ~5  $\mu\text{L}$  by nitrogen gas. Before HRGC/HRMS analysis, the samples were spiked with  $^{13}\text{C}_{12}$ -labeled PCDD/Fs recovery standards (EPA-1613 IS). HRGC/HRMS instruments were used with an Agilent 6890 gas chromatograph coupled with an AutoSpec Ultima mass spectrometer (Waters, USA). For PCDD/Fs analysis, a DB-5 capillary column (60-m length, 0.25 mm i. d, 0.25- $\mu\text{m}$ -thick film; Agilent J&W, USA) was used to separate the analytes. The MS was operated at high resolution, around 10,000 in selected ion monitoring mode. The recoveries of  $^{13}\text{C}_{12}$ -labeled PCDD/F standards ranged from 32% to 145%, meeting analytical method requirements. The signal-to-noise ratio was >3:1. The ratio of the two monitored ions for the analyte had to be within 15% of the theoretical value.

### 3. Results and discussion

#### 3.1. PCDD/F formation on fly ash matrix from secondary aluminum, lead smelting and iron ore sintering sources

Under temperatures of 250–450 °C for 30 min, most total PCDD/Fs concentrations were in the vapor phase instead of solid residue, as described previously (Jiang et al., 2015; Wang et al., 2015, 2016). Thus, PCDD/Fs trapped in impingers were determined and compared instead of the sum of PCDD/Fs in solid residue and gas phases trapped in the impingers.

The effects of SAI, SNT and SPb fly ash on promoting PCDD/F formations in the temperature range 250–450 °C for 30 min were shown in Fig. 1A, B and C, respectively. Initial PCDD and PCDF concentrations in the secondary aluminum fly ash were 1.62 and 37.67 ng/g, respectively. As seen in Fig. 1A, large amounts of PCDD/Fs were produced when the secondary aluminum fly ash was heated from 250 to 450 °C. The result of this experiment was consistent with the optimal temperature for PCDD/F formation between 250 and 450 °C. The PCDD/F concentration only increased about 8 times to 297 ng/g when the SAI fly ash was heated for 30 min at 250 °C. However, large amounts of PCDD/F were found, with maximum concentration 23.7  $\mu\text{g}/\text{g}$  when the SAI fly ash was heated at 350 °C for 30 min, 604 times the initial concentration in that fly ash. Such vigorous increase of PCDD/F concentration was unexpected.

The unexpectedly large amounts of PCDD/Fs were formed after the heating of fly ash at 350 °C for several minutes, which indicating that SAI fly ash can greatly enhance PCDD/Fs formation. The original concentrations of PCDFs and PCDDs in the fly ash were ~37.67 ng/g and 1.62 ng/g, respectively. The concentrations of PCDD/Fs peaked at 350 °C, with a 2250-fold increase in PCDDs and 533-fold in PCDFs. The ratios of PCDFs to PCDDs formed on the SAI fly ash matrix from 250 to 450 °C for 30 min were 5–14, indicating that larger amounts of PCDFs than PCDDs formed during the thermochemical reaction.

In the original iron ore sintering fly ash, the concentrations of PCDDs and PCDFs were 108 and 180 pg/g, respectively. Simulation experiments between 250 and 450 °C for 30 min were carried out to study PCDD/F formation in the iron ore sintering fly ash. The

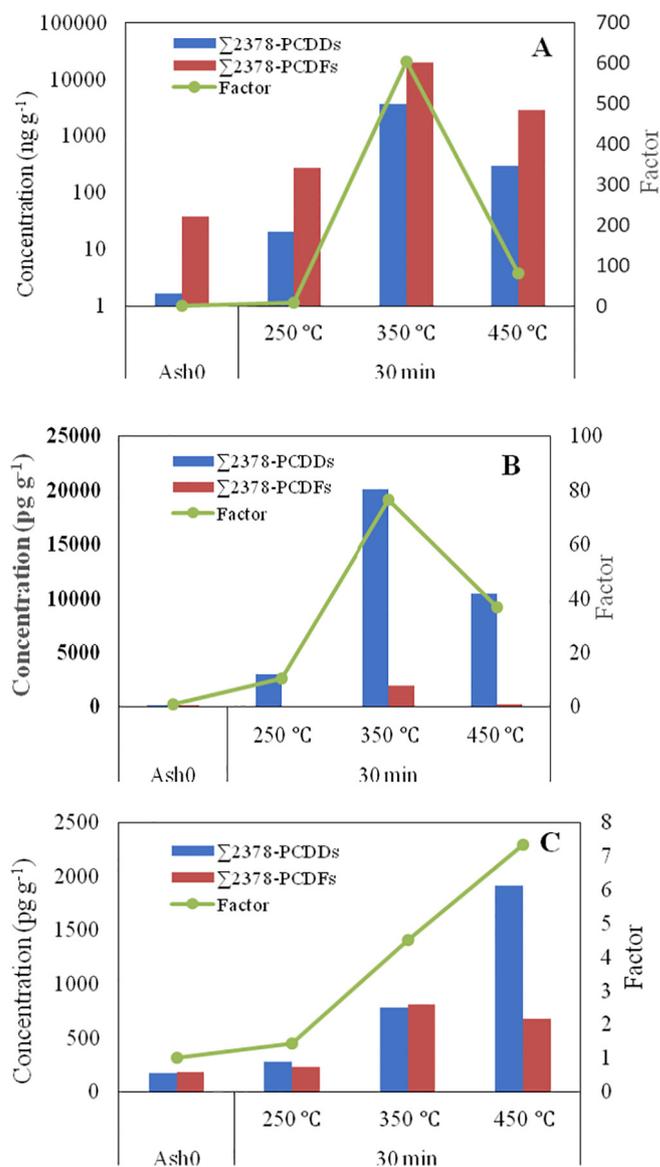


Fig. 1. Polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) concentrations (bars and left y-axis) formed during thermochemical reactions on SAI (A), SNT (B) and SPb (C) fly ash matrix at temperatures 250–450 °C for 30 min, and number of times greater than concentration in original fly ash (Ash0) ("factor"; points and right y-axis).

concentration of PCDFs was much less than PCDDs when the fly ash was heated at 250–450 °C for 30 min. The PCDD/F profile has traits different from those of the secondary copper and aluminum metallurgies fly ash. The dominant compounds are PCDDs. Fig. 1B demonstrates that the SNT fly ash amplified PCDDs 27–185 fold and PCDFs were consistent with the temperature increase. Therefore, the SNT fly ash strongly promoted PCDD formation greater than that of PCDFs. The maximum PCDD/Fs formed at 350 °C for 30 min was 22.1 ng/g, 77 times greater than that in the original SNT fly ash. The discrepancies between PCDD to PCDF ratios were between 10 and 43. The vast majority formed were PCDDs. The analysis shows that the SNT fly ash could substantially elevate the risk of toxic effects.

We also tracked the secondary lead fly ash to examine the effect of temperatures from 250 to 450 °C on PCDD/F formation over a fixed time of 30 min. The results are shown in Fig. 1C.

Concentrations of PCDDs and PCDFs in the original SPb fly ash were 171 and 183 pg/g, respectively. PCDD/Fs formed on the SPb fly ash was obviously less than that on SAI and SNT fly ash. Even at 450 °C, maximum formation of PCDD/Fs on the SPb fly ash was only ~8 times that in the raw SPb fly ash.

### 3.2. Underlying mechanism contributing to different PCDD/F formation amounts on multiple metal smelting fly ash samples

The carbon source, catalytically metal elements, and chlorine source are widely recognized as important promoters of PCDD/F formation. Therefore, the contents of TOC, elemental composition and chlorine in the fly ash from the three smelting sources were determined to explore the underlying mechanism of the variable PCDD/F formation amounts on different metal smelting fly ash (Ruud Addink and Altwicker, 1998; Kakuta et al., 2007; Vallejo et al., 2013; Vehlow et al., 2016). The elemental contents in the fly ash samples collected from different metal smelting sources determined by the XRF were shown in Table 1.

The results indicate that the chemical composition of the three metal smelting fly ashes varied considerably. The major elements in SAI fly ash were Al (12.75%), Na (5.19%), Cl (4.53%), Si (1.77%) and Mg (1.28%). Contents of Zn and Cu were 0.37% and 0.11%, respectively. As in SNT fly ash, Fe (26.14%), Al (2.22%) and Mg (1.65%) were the dominant elements. Pb was ~14.67% in the SPb fly ash. However, the contents of Cu, Fe and Mg in SPb fly ash were much lower than those in SAI and SNT fly ashes. Many studies have indicated that Cu, Al, Zn, Fe are important metal elements for promoting PCDD/F formation (Halonen Ismo and Ruuskanen, 1997; Chin et al., 2011; Heeb et al., 2013; Potter et al., 2016). Thus, the much lower contents of these metal elements might contribute less PCDD/F formation on SPb fly ash than those on SAI and SNT fly ashes.

The chlorine contents are widely considered as the important influencing factors of PCDD/F formations. Many studies (Halonen and Tarhanen, 1995; Takeshi Hatanaka and Takeuchi, 2000; S. Kuzuhara et al., 2003) have suggested that chlorine contents are significantly correlated with PCDD/F levels. Chlorine contents in the SAI, SNT and SPb fly ashes were 4.53%, 2.36% and 0.01%, respectively. Corresponding trends of those contents were consistent with PCDD/F formation levels in our study, indicating the powerful influence of chlorine contents in the various fly ashes on PCDD/F formation.

Organic carbon is an important carbon source for PCDD/F formation. TOC contents were determined to be 14.91% in SAI ash, 1.32% in SNT ash, and 0.27% in SPb ash. The much greater TOC content in SAI ash than in SNT and SPb ashes was identified an important reason for the substantially greater PCDD/F formation on SAI ash than on SNT and SPb ashes.

Generally, the much greater contents of TOC as a carbon source, chlorine source, Cu, Al, Zn, Fe as catalytically metal elements,

combined in the SAI fly ash as compared with SNT and SPb ashes might be the reason for the much greater PCDD/F formation on SAI ash than on SNT and SPb ashes.

### 3.3. Variation of PCDD/F congener profiles during thermochemical reactions

The influence of temperature on the congener profiles of PCDD/Fs in the secondary aluminum fly ash is presented in Fig. 2. As described in Fig. 2, the congener concentrations increased considerably with temperature increase from 250 to 450 °C. The congener patterns of the PCDD/Fs during secondary aluminum fly ash-mediated thermochemical reactions varied with temperature. Under reaction temperatures 250–450 °C,  $\sum$ 2378-PCDFs were dominant, greater than 85% of  $\sum$ 2378-PCDD/Fs. The PCDD/F congener profiles formed on the secondary aluminum fly ash at different temperatures are shown in Fig. 2.

As seen from the congener patterns of PCDDs in the second aluminum fly ash, fractions of 123789-HxCDD, 1234678-HpCDD and OCDD was obviously elevated after thermochemical reactions. 2378-TCDD decreased as the temperature rose. The hexachlorinated furan congeners (123478-HxCDF, 123678-HxCDF and 234678-HxCDF) to total PCDD/F concentration in the original secondary aluminum fly ash were 3.4%, 3.4% and 3.2%, respectively. As temperature rose from 250 to 450 °C, the proportions of the corresponding hexa-chlorinated furan congeners increased to 9.3%, 11%, 12.7%, respectively. These results indicate that these congeners easily formed at elevated temperature. The Arrhenius equation was used to calculate activation energy of the formation of PCDD/Fs congeners.

$$K = A \exp(-E_a/RT),$$

where A is the pre-exponential factor,  $E_a$  (kJ/mol) is the apparent activation energy, R is the ideal gas constant, and T (in K) is the absolute temperature. Strong linearity in plotting the logarithm of the reaction rate for the formation of PCDD/Fs and 1/T for the reaction time was achieved according to the Arrhenius equation. The value of  $E_a$  is calculated from the slope. Calculated values of activation energy are given in Table 2.

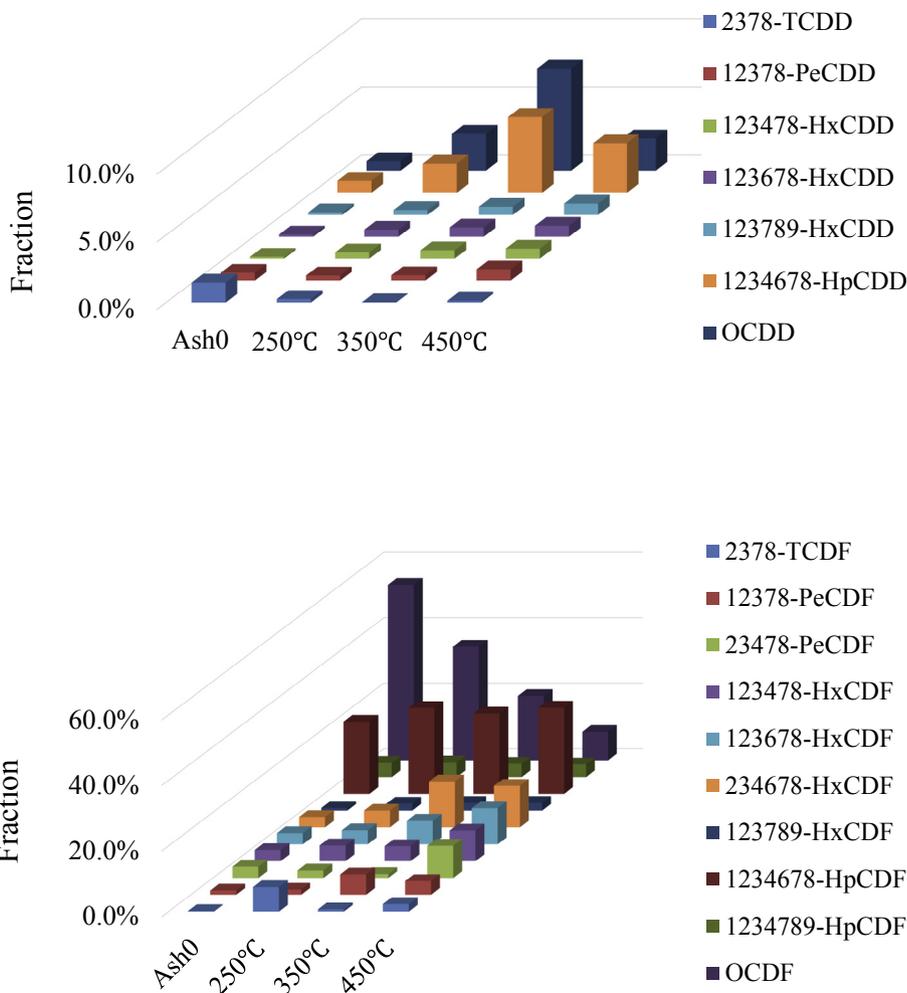
$E_a$  of 123789-HxCDD and 1234678-HpCDD were relatively high. The calculated activated energies of 123478-HxCDF, 123678-HxCDF and 234678-HxCDF were also greater than most of other PCDF congeners. The calculated data coincided with experimental results, which explains why these congeners can readily form at higher temperatures. Reaction with high activation energy requires high temperature. For PCDD/Fs formation, high activation energy means that the reaction requires more energy.

By using SNT metallurgies fly ash as the matrix, the effect of temperature change on the congener profiles of PCDD/Fs was investigated, which have traits different from those of the secondary copper and secondary aluminum metallurgy fly ash. The effect of reaction temperature was investigated for a fixed residence time of 30 min (Fig. 3). In the original SNT fly ash, 37.6% of the PCDD/Fs was PCDDs, and PCDFs made up 62.4%. However, when the SNT fly ash was heated, the fraction of PCDFs was much less than that of PCDDs, and the dominant compounds were highly chlorinated PCDD congeners. Hexa- and hepta-chlorinated PCDD congeners showed the largest increase with temperature. The fractions of PCDFs were estimated to be <10% during the thermochemical process. Thus, the iron ore sintering fly ash appeared to have only substantially different effects in the formation of highly chlorinated PCDD/Fs during the thermochemical process. This result is different from the SAI fly ash, which could increase both PCDD and PCDF congeners as temperature increased.

**Table 1**  
Elemental composition of fly ash (wt%).

Element	SAI	SNT	SPb
Al	12.75	2.22	ND*
Cl	4.53	0.19	0.01
Cu	0.11	ND	ND
Ca	0.49	6.36	ND
Fe	0.41	26.14	0.02
Mg	1.28	1.65	0.04
Na	5.19	0.07	1.49
Pb	0.02	ND	14.67
Si	1.77	2.36	0.01
Zn	0.37	0.02	0.03

\* <0.01 (wt%).



**Fig. 2.** Fraction of polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) congener patterns in original SAI fly ash (Ash0) and SAI fly ashes that were heated at 250 °C, 350 °C and 450 °C for 30 min.

**Table 2**

Arrhenius formulae for thermochemical reactions involved in formation of PCDD/Fs on secondary aluminum fly ash between 423 and 723 K over 30 min.

congener	Arrhenius formula
2378-TCDD	$k = 0.00098 \times \exp(-49.59/RT)$
12378-PeCDD	$k = 0.036 \times \exp(-57.61/RT)$
123478-HxCDD	$k = 0.038 \times \exp(-57.10/RT)$
123678-HxCDD	$k = 0.012 \times \exp(-50.36/RT)$
123789-HxCDD	$k = 0.017 \times \exp(-52.80/RT)$
1234678-HpCDD	$k = 0.50 \times \exp(-61.17/RT)$
OCDD	$k = 0.091 \times \exp(-52.33/RT)$
2378-TCDF	$k = 0.0017 \times \exp(-34.45/RT)$
12378-PeCDF	$k = 0.10 \times \exp(-52.72/RT)$
23478-PeCDF	$k = 0.82 \times \exp(-60.03/RT)$
123478-HxCDF	$k = 0.35 \times \exp(-56.54/RT)$
123678-HxCDF	$k = 0.82 \times \exp(-60.03/RT)$
234678-HxCDF	$k = 0.15 \times \exp(-63.30/RT)$
123789-HxCDF	$k = 0.084 \times \exp(-54.31/RT)$
1234678-HpCDF	$k = 0.13 \times \exp(-43.90/RT)$
1234789-HpCDF	$k = 0.014 \times \exp(-41.75/RT)$
OCDF	$k = 0.0015 \times \exp(-23.37/RT)$

In contrast with the secondary aluminum metallurgy fly ash and SNT metallurgy fly ash, for which either PCDDs or PCDFs constituted the majority of PCDD/Fs quantities, concentrations of PCDDs and PCDFs did not vary much after the secondary lead fly ash was heated. In addition, even when the heat treatment temperature was

450 °C, the secondary lead fly ash produced only modest improvement (<8 times) in the concentration of PCDD/Fs. The clear differences in congener fractions between the original fly ash and tempered fly ash treated by the tube furnace under variable temperature are shown in Fig. 4.

Results show that for 2,3,7,8-substituted PCDD congeners, with the increase of temperature, fractions of 123678-HxCDD and 123789-HxCDD increased and 12378-PeCDD decreased. However, change in fractions of hexachlorinated PCDFs as affected by temperature was not obvious.

Among four metal smelting processes, concentrations of PCDDs and PCDFs were compared during the simulated thermal experiments. The concentration of PCDFs was much higher than PCDDs when the secondary aluminum and the secondary copper fly ashes were heated to different temperatures. In contrast, PCDDs had greater concentration in the SNT metallurgy fly ash matrix than PCDFs during the heat treatment. Interestingly, in the secondary lead fly ash, concentrations of PCDDs and PCDFs produced during heat treatment showed little difference.

**4. Conclusions**

We studied PCDD/F formation by heterogeneous reactions on fly ashes from typical and representative secondary aluminum, secondary lead smelting and iron ore sintering fly ash in China. We

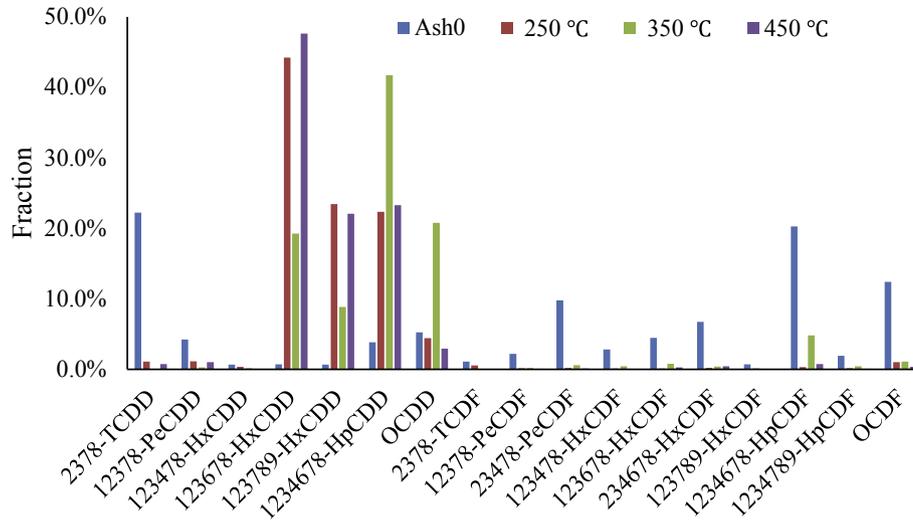


Fig. 3. Congener profiles of PCDD/Fs in original iron ore sintering fly ash and after fly ash was heated from 250 to 450 °C over 30 min.

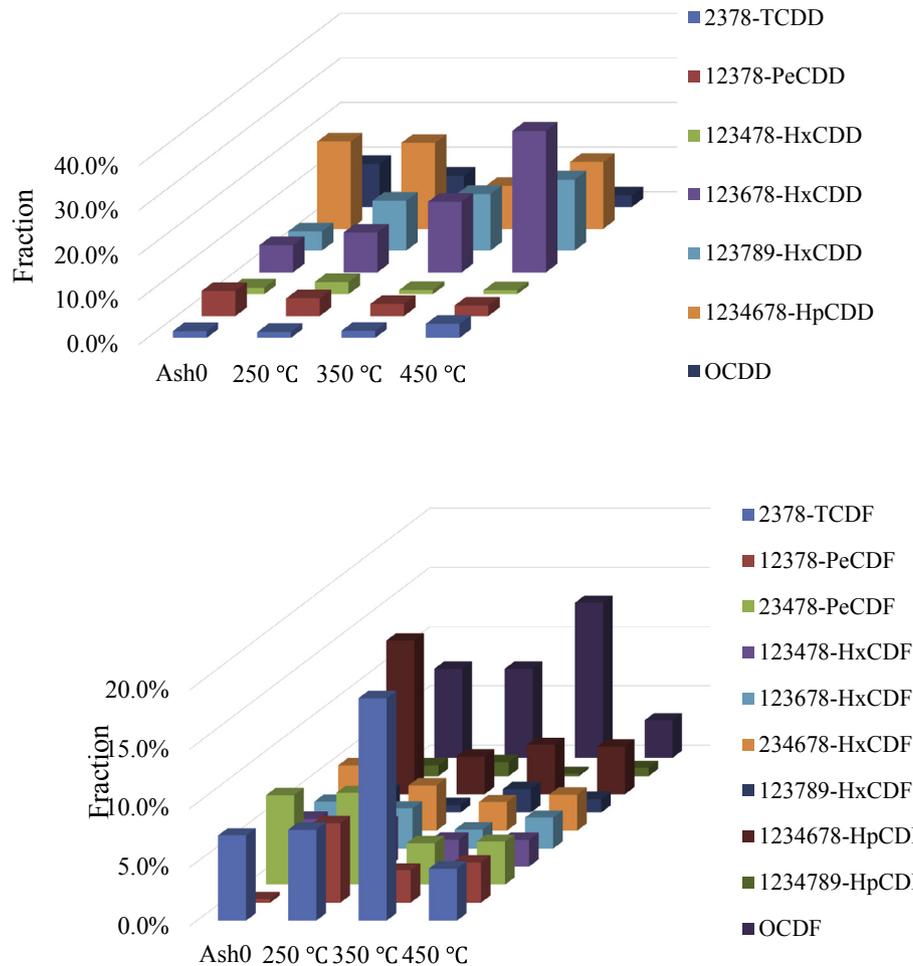


Fig. 4. Percentage concentration of polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) congener patterns in original secondary lead ash and after fly ash heating from 250 to 450 °C over 30 min.

quantified formation potentials of PCDD/Fs on real fly ash collected from typical metal smelting plants. It was found that substantial PCDD/Fs formed on the secondary aluminum smelting fly ash. PCDD/F formation on SPb fly ash was much less than that on SAI

and SNT fly ash. Increased PCDD/F formation was correlated with temperature and fly ash characteristics, such as the contents of TOC, chlorine and catalytic metals. The results suggest that fly ash with high loads of TOC, chlorine and catalytic metal actively promote

PCDD/F formation in the post-flame zones of combustion systems or metal smelting industries. Because of great concern for PCDD/F emissions in industrial stack gas and solid residues, control standards were further improved and many end-of-pipe measures applied to pollution control of stack gas. This resulted in further transformation of PCDD/Fs into fly ash. Many techniques including high-temperature treatment have been used for the disposal of fly ash. The present study suggests that much more attention should be paid to the potential regeneration of PCDD/Fs catalyzed by fly ash during high-temperature disposal.

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