PCDD/F Formation Catalyzed by the Metal Chlorides and Chlorinated Aromatic Compounds in Fly Ash

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ABSTRACT

The entrained fine fly ash particles carried into the post-combustion region and collected by air pollution control devices were capable of such surface-mediated dibenzo-*p*-dioxin and dibenzofurans (PCDD/Fs) formation. The secondary formation of PCDD/Fs in the flue gas and ash from the municipal solid waste incinerator (MSWI) systems has attracted considerable public concern. The objective of this study was to examine reactions in fly ash from an municipal solid waste incinerator (MSWI) operated with metal chlorides and chlorinated aromatic precursors. When 10 wt% $FeCl_2$, $ZnCl_2$ and $CuCl_2$ were added onto the fly ash medium, the PCDD/Fs concentration is 8.8, 25.5 and 369.5 ng/g, respectively. This indicates that the formation of PCDD/Fs was significantly increased by $CuCl_2$. In the case of $CaCl_2$ addition, the results showed that it acts in a minor role as a catalyst to promote the formation of PCDD/Fs. In addition, the results of adding $HgCl_2$ has no transformation effect on the formation of PCDD/Fs in the residue and gas phases. Moreover, in an experiment using chlorinated aromatic precursors, the formation of PCDD/Fs was significantly increased by pentachlorophenol (PCP). This study suggests that the filter cake ash treatment should be studied extensively to control dioxin yields on the fly ash matrix.

Keywords: Fly ash; PCDD/Fs; Metal chloride; Chlorinated aromatic compounds; Catalysis.

INTRODUCTION

The mixture of refuse, hazardous household waste (plastic bags, paints, solvents, metal-containing substances, discarded electronic waste), and discarded tires can be problematic when combined with poor combustion conditions, resulting in significant levels of trace pollutant formation (Hu *et al.*, 2009; Wang *et al.*, 2010; Lin *et al.*, 2010). Pollution issues of incineration process have drawn much more attention even the products have been reduced and stabilized. Unfortunately, the incineration is an indispensable method for waste disposal in the city today. Exhaust fume emissions from the incineration process include heavy metals, suspended solids, SO_x, NO_x and organic contaminants such as dibenzo-*p*-dioxin and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), all of which can have serious effects on humans and the wider environment (Fujimori *et al.*, 2009; Lin *et al.*, 2009; Chuang *et al.*, 2010; Wang *et al.*, 2010). However, solidification of fly ashes after incineration is one potential way to trap a high concentration of heavy metals and PCDD/Fs in order to ensure their safe disposal (Wang *et al.*, 2009; Wu *et al.*, 2010; Chen *et al.*, 2011; Chiu *et al.*, 2011).

The precursor substances in similar chemical structures are chlorophenols (CPs), chlorobenzenes (CBs), and PAHs (Tuppurainen *et al.*, 2003; Briois *et al.*, 2007; Aracil *et al.*, 2010). The fly ash surface bonding forms surface-active material to adsorb precursor materials, and the complicated precursor condensation reaction is formed by catalyzing metals to form PCDD/Fs. (Zheng *et al.*, 2004; Ryu, 2008; Liu *et al.*, 2011). The degradation of carbon structures forms small molecule substances, and then the interaction forms PCDD/Fs (Lundin and Marklund, 2007). Luijk and Kishi found that 2,4,6-trichlorophenol formed PCDD/Fs, with the main product based on PCDDs, and two forms of 2,4,6-trichlorophenol with a similar structures release OH and Cl on chlorophenol and integrate as 1,3,6,8-TCDD or 1,3,7,9-TCDD (Luijk *et al.*, 1994; Kishi *et al.*, 2009). However, flue gas and ash from incinerators tend to contain unburned carbon, heavy metals, and organic toxic substances, including

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dioxins. These dioxins can exist in a gas phase due to reactions between aromatic rings that contain chlorine (such as CBs and CPs), by heterogeneous reactions between chlorinated organic precursors and fly ash-based catalysts (Gullett *et al.*, 1992; Kuzuhara *et al.*, 2003), and by de novo synthesis (complex reactions between unburned carbon and chlorine sources with metallic catalysts, such as Cu, Fe, and Mn) (Stieglitz *et al.*, 1989; Hinton *et al.*, 1991; Gullett *et al.*, 1992; Chin *et al.*, 2011).

Metal elements cab bed divided into those that are volatile, semi-volatile and low-volatile (Ito and Shooter, 2002; Pavageau *et al.*, 2002). Volatile metals in the downstream of combustion chambers and air pollution control devices (APCDs) exist in a gas phase under high vapor pressure, and highly volatile metals, such as Hg, are mainly distributed in flue gas, while semi-volatile metals such as Pb, Cd, Zn and Cu are adsorbed on the surface of particles, and low-volatile metals such as Sb, As Be and Cr exist in bottom ash (Hiserod *et al.*, 1997; Abanades *et al.*, 2002). However, fly ash is an extremely complex material, and there are many types of metal in municipal solid waste. Although the mass and volume of wastes can be significantly reduced by incineration, heavy metals condensed or adsorbed in ash or vapor may be present in flue gas or residues (Chang and Wey, 2006; Chang *et al.*, 2009). Ferreira *et al.*, indicate that metal concentrations in fly ash are: 6.2 g/kg for Zn, 2.4 g/kg for Pb, 1.7 g/kg for Fe, and 7.9 g/kg for Mg. Cu, Mn, Cr, and Cd are also present with 546, 338, 104 and 91 mg/kg of fly ash, respectively (Ferreira *et al.*, 2003).

The objective of this study was to conduct by adding the inorganic (metal chlorides) and organic chloride sources (chlorinated aromatic compounds) into fly ashes in a packed bed reactor under real flue gas conditions to simulate the formation of PCDD/Fs in the filter cake zone. The contributions of toxicities and the phases transformation were the focuses of this study. The final goal of this research is to develop a cost-effective and safe approach for treating the fly ash matrix.

MATERIALS AND METHODS

Test Facility and Experimental Parameters

The experiment in this study was performed precursors experiments took place in a laboratory scales packed-bed reactor, which is shown in Fig. 1 The packed bed comprised a quartz tube 130 (length) × 5.5 cm (diameter) that absorbed PCDD/Fs in the outlet from the gas phase. Fly ash was collected from an MSWI in southern Taiwan. After the continuous extraction of fly ash, the residue concentration of PCDD/Fs was 3.68 ± 0.43 ng/g or 0.10 ± 0.03ng I-TEQ/g. Numerous investigators have conducted laboratory experiments to assess the formation mechanisms of PCDD/F. Experimental temperatures and the solids residence time were mostly in the range 250–500°C and at 10–60 min (Luijk *et al.*, 1994; Everaert and Baeyens, 2002; Ryu, 2008). Therefore, Experiments were conducted at 300°C and 60 min to investigate the catalytic formation of PCDD/Fs in fly ash with various metal chlorides. In addition, Experiments were conducted at about 160°C to simulate the bag house conditions (160−180°C) (lin *et al.*, 2008) and the residence time of the flue gas pass through reactor was 10 minutes to simulate the rapping cycle of bag filter. Table 1 shows the complete experimental matrix and control parameters for the PCDD/Fs experiments in our study.
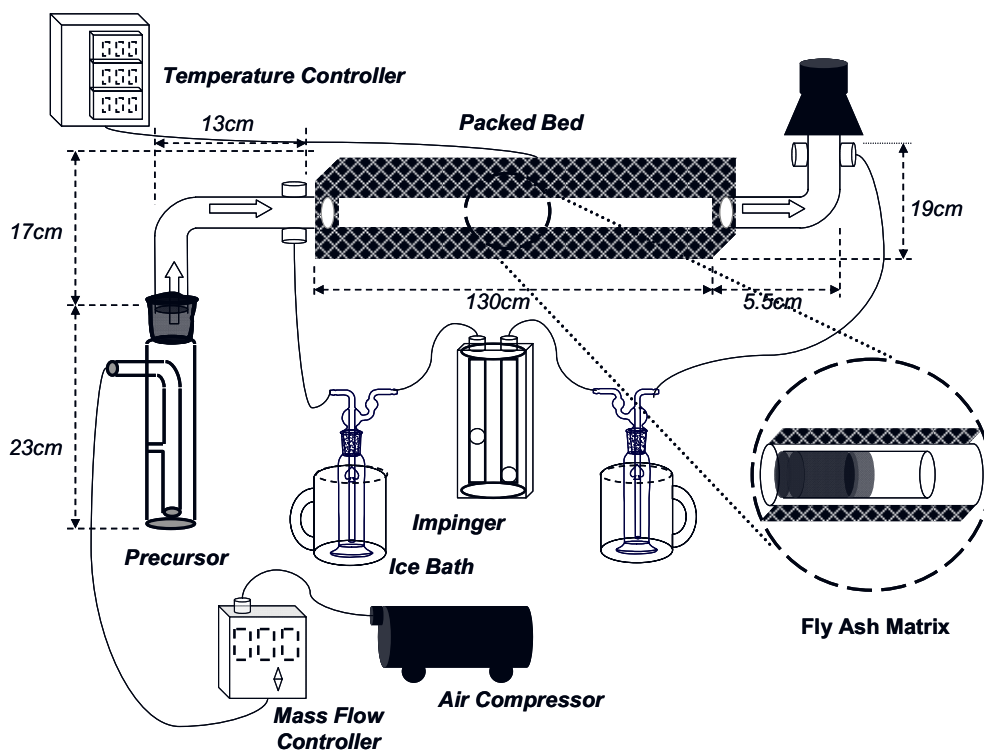

Fig. 1. Schematic of Experimental System.

Table 1. Experimental Operation Parameters.

Matrix Type	Gas phase Feeding	Formation Temperature (°C)	Retention Time (min)	Concentration weight ratio (w/w)
FA + FeCl₂	Air	300	60	FeCl₂/FA = 10%
FA + ZnCl₂	Air	300	60	ZnCl₂/FA = 10%
FA + CuCl₂	Air	300	60	CuCl₂/FA = 10%
FA + CaCl₂	Air	160	10	CaCl₂/FA = 10%
FA +HgCl₂	Air	160	10	HgCl₂/FA = 0.1%
FA +HgCl₂	Air	160	10	HgCl₂/FA = 0..01%
FA + TCP	Air	160	10	PCP/FA=0.2%
FA + PCP	Air	160	10	PCP/FA=0.1%
FA + PCP	Air	160	10	PCP/FA=0.2%

FA: Fly Ash,

Laboratory Analyses

All chemical analyses were conducted at the Super Micro Mass Research and Technology Center, Cheng-Shiu University, an accredited laboratory in Taiwan.

The analyses were performed according to the US EPA Modified Methods 23 and 1613. Prior to analysis, each sample collected in the extraction thimble was spiked with a known amount of the $^{13}C_{12}$-labeled internal standard. After 24 h of extraction in a Soxhlet extractor, the extract was concentrated and then treated with concentrated sulfuric acid. A series of sample cleanup and fractionation procedures were then conducted. The eluate was concentrated to around 1 mL and transferred to a vial. The concentrate was almost completely dried in a stream of nitrogen. Prior to analysis, the standard solution for recovery checking was added to the sample.

A high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS) was used for the PCDD/Fs analyses. The HRGC (Hewlett Packard 6970 Series gas, CA, USA) was equipped with a DB-5MS fused silica capillary column (L = 60m, ID = 0.25 mm, film thickness = 0.25 μm) (J & W Scientific, CA, USA) with splitless injection. The HRMS (Micromass Autospec Ultima, Manchester, UK) was equipped with a positive electron impact (EI⁺) source. Selected ion monitoring (SIM) was performed in analyzer mode with a resolving power of 10,000, as described in detail in Wang and Chang-Chien (Wang and Chang-Chien, 2007). The method detection limits (MDLs) for the 17 individual PCDD/Fs were determined from the standard deviations determined from the analyses of the matrix-spiked samples. The MDLs of the PCDD/Fs in the samples were 0.202–6.271 pg.

RESULTS AND DISCUSSION

Comparison of FeCl₂, ZnCl₂ and CuCl₂

Certain metals act as catalysts for PCDD/Fs formation, providing a surface upon which PCDD/Fss can readily form. This generally occurs during and after combustion processes on the fly ash in boilers and incinerators. Therefore, in this phase, the fly ash medium is mixed with 10% (w/w) precursors with chlorine of divalent metals to simulate the formation of PCDD/Fs, as shown in Table 2. The results show that when the fly ash medium are mixed with FeCl₂, ZnCl₂ and CuCl₂, the PCDD/Fs concentration is 8.8, 25.5

and 369.5 ng/g, respectively. As for the catalytic effect, the Cu^{2+} is predominant, and the catalytic effect of Fe^{2+} and Zn^{2+} on formation of PCDD/Fs is lower than that of Cu^{2+}. As for the formation mechanism, the PCDD/PCDF ratios of CuCl₂ and FeCl₂ present the de novo synthesis, but the ZnCl₂ presents a powerful precursor mechanism. (Everaert and Baeyens, 2002) indicated that the PCDD/PCDF ratio << 1 is the de novo synthesis. Besides, the PCDD/PCDF ratio >> 1 is the precursor mechanism. In Taiwan, twenty-four incinerators have been built and can be operated to burn 24,650 tons of MSW daily (Chang *et al*., 2007). Zn and Al are the main sources of fly ash in bag house, Fe and Pb are secondary sources, and Cu, Cd, and Hg are minor sources. The amounts of Cu, Fe and Zn in bag house fly ashes are about 1, 17 and 30%, respectively. There are large differences in the contribution of the catalytic effect of different metal chlorides to the formation of PCDD/Fs. This indicates that although the content of Cu in fly ash is low, a small amount of Cu^{2+} can produce a large amount of PCDD/Fs. De novo synthesis is the key mechanism in the formation of PCDD/Fs during combustion. Cu is thought to be the key catalyst of the de novo synthesis in both modeled and real fly ash (Ryu, 2008; Chin *et al*., 2011). CuCl₂, in particular, has been identified as an important catalyst in the formation of PCDD/Fs and other related compounds in experiments that involve the heating of modeled fly ash (Stieglitz *et al*., 1989; Luijk *et al*., 1994; Addink and Olie, 1995; Schoonenboom *et al*., 1995). The catalytic power of three metal chlorides is CuCl₂ >> ZnCl₂ > FeCl₂, and the ratio among CuCl₂, ZnCl₂ and FeCl₂ is 42:3:1. As for the toxic equivalent (TEQ), the toxicity of PCDD/Fs catalyzed by CuCl₂ is much higher than that of FeCl₂ and ZnCl₂, and the toxicity of CuCl₂ is 34 times that of FeCl₂ and ZnCl₂.

As for species distribution, the first three dominant species of CuCl₂ and FeCl₂ are mainly of PeCDF and HxCDF. Hatanaka *et al*. (2002) indicated that the route of metastasis of PCDFs with and without CuCl₂·H₂O is from low chlorine (T4~P5-CDF) to high chlorine (H6~O8-CDF) species. The primary cause for the formation of PCDFs is that CuCl₂ can promote catalytic reactions, and then form chloric species related to the deacon reaction. The catalytic reaction between Cu compounds and carbon molecules promotes CuCl₂ to form PCDFs. However, the ZnCl₂ is not only the main component of PeCDF, but also has effect on PeCDD and HxCDD

Table 2. Concentrations of PCDD/Fs in the fly ash with $FeCl_2$, $ZnCl_2$ and $CuCl_2$.

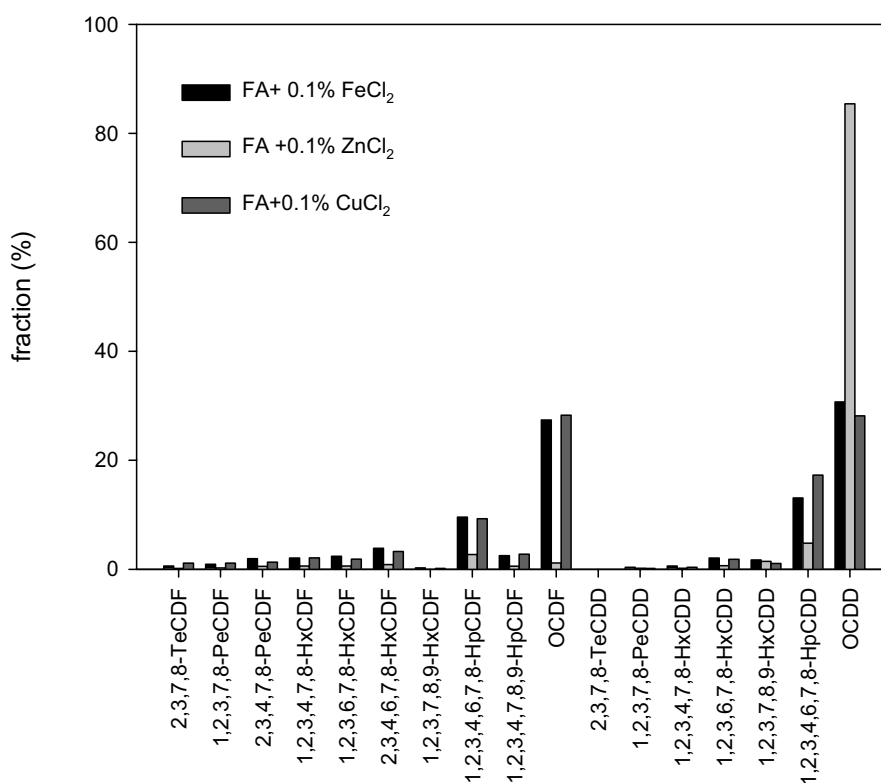| Compound	FA+ 10% $FeCl_2$	FA +10% $ZnCl_2$	FA +10% $CuCl_2$
(ng/g)			
2,3,7,8-TeCDF	0.05	0.04	4.08
1,2,3,7,8-PeCDF	0.08	0.06	4.15
2,3,4,7,8-PeCDF	0.17	0.13	4.7
1,2,3,4,7,8-HxCDF	0.18	0.15	7.71
1,2,3,6,7,8-HxCDF	0.21	0.15	6.81
2,3,4,6,7,8-HxCDF	0.34	0.22	12.08
1,2,3,7,8,9-HxCDF	0.02	0.01	0.55
1,2,3,4,6,7,8-HpCDF	0.84	0.69	34.3
1,2,3,4,7,8,9-HpCDF	0.22	0.14	10.2
OCDF	2.41	0.29	104.45
2,3,7,8-TeCDD	0.01	0.01	0.04
1,2,3,7,8-PeCDD	0.03	0.05	0.6
1,2,3,4,7,8-HxCDD	0.05	0.05	1.33
1,2,3,6,7,8-HxCDD	0.18	0.16	6.7
1,2,3,7,8,9-HxCDD	0.15	0.37	3.89
1,2,3,4,6,7,8-HpCDD	1.15	1.22	63.87
OCDD	2.7	21.78	104.05
Total PCDD/Fs	8.8	25.5	369.5
Total PCDDs	4.3	23.6	180.5
Total PCDFs	4.5	1.9	189
PCDDs/PCDFs	0.9	12.6	0.9
(ng I-TEQ/g)			
Total PCDD/Fs	0.3	0.3	8.5
Total PCDDs	0.1	0.1	2.3
Total PCDFs	0.2	0.1	6.2
PCDDs/PCDFs	0.4	1.0	0.4

species, as they are mainly composed of 2,3,4,7,8-PeCDF. In the formation of PCDD/Fs, the Cu is very activating, the amount of PCDD/Fs formed from other metal chlorides such as $MgCl_2$, $ZnCl_2$, $FeCl_2$, $MnCl_2$, $HgCl_2$, $CdCl_2$, $NiCl_2$, $SnCl_2$ and $PbCl_2$ is lower than that formed from $CuCl_2$ (Stieglitz *et al.*, 1989). This shows that Cu has strong catalytic power. The formation trends of the three metal chlorides added in fly ash are shown in Fig. 2. It can be seen, that $CuCl_2$ and $FeCl_2$ are coincident for PCDDs and PCDFs, and their dominant species (OCDD, OCDF) are both saturated chlorine. When $ZnCl_2$ is added to fly ash for formation of PCDD/Fs, the distribution of PCDDs and PCDFs is changed, with the former accounting for about 90% of the whole. In addition, OCDDs is the main dominant species. It is supposed that the original Zn element in fly ash and the additional Zn^{2+} increase the PCDDs content sharply, but at the same time decrease the content of PCDFs. (Qian *et al.*, 2005) reported that the ZnO has certain promotion effects on PCDD/Fs formation from PCP and the primary product is PCDDs.

Comparison of $CaCl_2$ and $HgCl_2$

There are two chlorine sources for the synthesis of PCDD/Fs (Rghei and Eiceman, 1985; Lenoir *et al.*, 1991): (1) chlorides of alkaline metals and alkaline earths, such as $CaCl_2$, $MgCl_2$, NaCl, KCl, and $CuCl_2$; and (2) HCl. The CaO and CaOH are often used in general waste incineration processes, which neutralize acidic materials in exhaust gas (e.g. HCl,

Cl_2, SO_2, HF), and reduce the discharge of acidic materials. As for the formation of PCDD/Fs mechanism, HCl forms Cl_2 through deacon reaction, the chlorination reaction can be reduced when the alkaline matter neutralizes chlorine, and the byproduct is $CaCl_2$. In addition, as $HgCl_2$ accounts for 60–95% of total mercury in general waste incineration processes, and mercury is a highly-volatile metal element (Clarke and Stoss, 1992; Young, 2004), so $HgCl_2$ is used as a chlorine source. Therefore, in this phase, the temperature is 160°C, and 0.1% $CaCl_2$, 0.1% $HgCl_2$ and 0.01% $HgCl_2$ are added to explore the formation of PCDD/Fs in the bag filter area. The results are shown in Table 3, and it can be seen that the concentrations of PCDD/Fs with 0.1% $CaCl_2$ and 0.1% $HgCl_2$ added to the formation of the fly ash medium is 95.4 ng/g and 198 ng/g, respectively. As for the TEQ concentration, it is 0.7 when 0.1% $CaCl_2$ is added. This shows the $CaCl_2$ has a slight influence on the formation of PCDD/Fs.

The PCDD/Fs concentration of fly ash with 0.01% $HgCl_2$(s) and 0.1% $HgCl_2$(s) is 53.34 ng/g and 198.01 ng/g, respectively. It is obvious that the PCDD/Fs concentration increases by about 3.7 times when $HgCl_2$(s) is increased by 10 times. As for the PCDDs/PCDFs ratio, with the addition of 0.01% and 0.1 % $HgCl_2$(s) this is greater than 1, which shows that the precursor mechanism is dominant, and the primary product is PCDDs. The gas and residue phase distributions are also compared. For the residue phase, the formation percentage of PCDD/Fs is 96.01% and 97.81%,

Fig. 2. The homologue profiles of PCDD/Fs from $FeCl_2$, $ZnCl_2$ and $CuCl_2$.

Table 3. Concentrations of PCDD/Fs in the fly ash with $CaCl_2$ and $HgCl_2$.

Compound	FA +10% $CaCl_2$	FA +0.1% $HgCl_2$	FA +0.01% $HgCl_2$
(ng/g)			
2,3,7,8-TeCDF	0.06	0.21	0.06
1,2,3,7,8-PeCDF	0.15	0.46	0.15
2,3,4,7,8-PeCDF	0.25	0.77	0.24
1,2,3,4,7,8-HxCDF	0.30	0.89	0.30
1,2,3,6,7,8-HxCDF	0.39	1.21	0.41
2,3,4,6,7,8-HxCDF	0.75	2.18	0.74
1,2,3,7,8,9-HxCDF	0.07	0.19	0.06
1,2,3,4,6,7,8-HpCDF	2.05	5.77	1.87
1,2,3,4,7,8,9-HpCDF	0.50	1.52	0.52
OCDF	2.22	5.88	2.53
2,3,7,8-TeCDD	0.01	0.04	0.01
1,2,3,7,8-PeCDD	0.06	0.17	0.06
1,2,3,4,7,8-HxCDD	0.14	0.36	0.11
1,2,3,6,7,8-HxCDD	0.81	2.09	0.69
1,2,3,7,8,9-HxCDD	0.29	0.76	0.23
1,2,3,4,6,7,8-HpCDD	13.13	30.03	9.40
OCDD	74.28	145.49	35.96
Total PCDD/Fs	95.4	198.0	53.3
Total PCDDs	88.7	178.9	46.5
Total PCDFs	6.7	19.1	6.9
PCDDs/PCDFs	13.2	9.4	6.8
(ng I-TEQ/g)			
Total PCDD/Fs	0.7	1.8	0.6
Total PCDDs	0.4	0.9	0.3
Total PCDFs	0.3	1.0	0.3
PCDDs/PCDFs	1.2	0.9	0.9

respectively, while for the gas phase, the formation percentage of PCDD/Fs is 3.99% and 2.19%, respectively. It is clear that the distribution ratios are similar between 0.01% $HgCl_2(s)$ and 0.1% $HgCl_2$ in both gas and solid phases. This indicates that the increase in $HgCl_2$ has no s transformation effect on the formation of PCDD/Fs in the residue and gas phases. As for the species distribution, the formation trend is shown in Fig. 3, the overall PCDD/Fs species distribution trend is consistent, and the main dominant species are OCDD and 1,2,3,4,6,7,8-HpCDD.

Comparison of Different Chlorinated Aromatic Precursors

Ghoristi and Hell indicated that when phenol and 2-PCP, 2,4,6-trichlorophenol are used, a large amount of PCDD/Fs are formed (Ghorishi and Altwicker, 1996; Hell *et al.*, 1997). CPs are considered as important precursors for PCDD/Fs formation (Qian *et al.*, 2005; Liu *et al.*, 2011). Therefore, this phase adds pentachlorophenol (PCP) and 2,4,6-trichlorophenol (TCP) to simulate the conversion effect of precursor substances in similar structures on the PCDD/Fs in fly ash medium.

The PCDD/Fs concentration of fly ash with 0.1% PCP, 0.2% PCP and 0.2% TCP is 4710.7 ng/g, 5329.3 ng/g and 130.9 ng/g, respectively (Table 4). This indicates that the formation of PCDD/Fs was significantly increased by PCP. Cains *et al.* (1997) found that PCPs only forms a large amount of PCDDs instead of contributing to the formation of PCDFs, meaning that the PCDFs do not replace phenol molecules for a condensation reaction. The PCDDs/PCDFs ratio is greater than 1, indicating that the precursor mechanism is dominant, and the primary product is PCDDs. Dickson *et al.* (1992) indicated that the precursor heterogeneous catalytic

reaction in the post-combustion zone of an incinerator is more likely to form PCDD/Fs than the de novo synthetic reaction. The CP of different bonding condenses into different PCDDs. The CP with high chlorine content is likely to form a high chlorine PCDD species distribution. The formation of PCDD/Fs trend is shown in Fig. 4, and it can be seen that the overall PCDD/Fs species distribution trend is similar, while the main dominant species are OCDD and OCDF.

CONCLUSIONS

The combustion treatment process of a MSWI may have a significant level adverse environmental impact. This study explores the catalytic and inhibiting effects between PCDD/Fs and chlorinated metals or aromatic precursors in order to better understand the relationship between the transformation characteristics and multiple transfer characteristics. When 10 wt% $FeCl_2$, $ZnCl_2$ and $CuCl_2$ were added onto the fly ash medium, the experimental results showed that the formation of PCDD/Fs was significantly increased by $CuCl_2$. In the case of $CaCl_2$ addition, the results showed that the $CaCl_2$ has slight influence on the formation of PCDD/Fs. Experiments were conducted adding $HgCl_2$ to the bag house fly ashes in a packed bed reactor under real flue gas conditions to simulate the filter cake zone. The results showed that the $HgCl_2$ clearly changed the PCDD/Fs distribution in the residue phase. Moreover, in an experiment examining the aromatic precursors, the formation of PCDD/Fs was significantly increased by the addition of PCP. The PCDD:PCDF ratio is consistently greater than 1, so PCDDs predominate over PCDFs. This suggests that the filter cake ash treatment
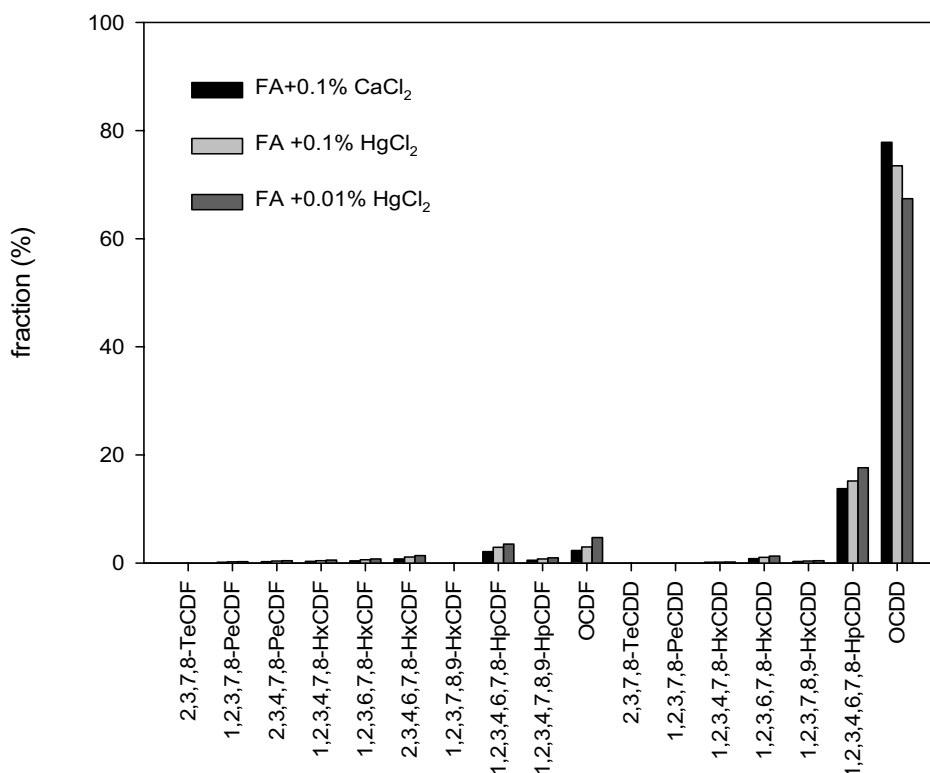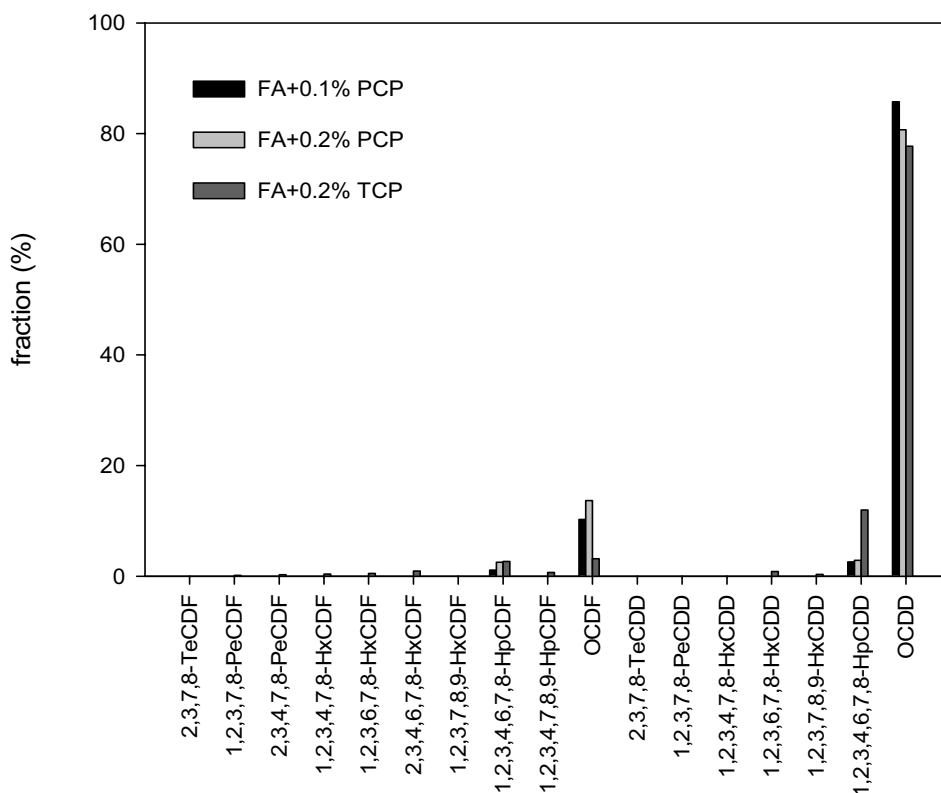

Fig. 3. The homologue profiles of PCDD/Fs from $CaCl_2$ and $HgCl_2$.

Table 4. Concentrations of PCDD/Fs in the fly ash with PCP and TCP.

Compound	FA +0.1% PCP	FA+ 0.2% PCP	FA+ 0.2% TCP
(ng/g)			
2,3,7,8-TeCDF	0.15	0.09	0.10
1,2,3,7,8-PeCDF	0.32	0.17	0.21
2,3,4,7,8-PeCDF	0.58	0.30	0.36
1,2,3,4,7,8-HxCDF	0.96	0.75	0.50
1,2,3,6,7,8-HxCDF	1.12	0.93	0.70
2,3,4,6,7,8-HxCDF	2.10	1.47	1.24
1,2,3,7,8,9-HxCDF	0.08	0.06	0.06
1,2,3,4,6,7,8-HpCDF	53.14	134.29	3.48
1,2,3,4,7,8,9-HpCDF	3.10	3.45	0.92
OCDF	483.45	729.03	4.14
2,3,7,8-TeCDD	0.03	0.02	0.02
1,2,3,7,8-PeCDD	0.10	0.07	0.08
1,2,3,4,7,8-HxCDD	0.28	0.18	0.18
1,2,3,6,7,8-HxCDD	2.82	2.58	1.11
1,2,3,7,8,9-HxCDD	0.74	0.49	0.41
1,2,3,4,6,7,8-HpCDD	122.19	154.12	15.67
OCDD	4039.53	4301.34	101.73
Total PCDD/Fs	4710.7	5329.3	130.9
Total PCDDs	4165.7	4458.8	119.2
Total PCDFs	545.0	870.5	11.7
PCDDs/PCDFs	7.6	5.1	10.2
(ng I-TEQ/g)			
Total PCDD/Fs	7.5	8.8	1.0
Total PCDDs	5.7	6.2	0.5
Total PCDFs	1.8	2.6	0.5
PCDDs/PCDFs	3.2	2.4	1.0

Fig. 4. The homologue profiles of PCDD/Fs from different chlorinated aromatic precursors.

should be studied extensively to control dioxin yields on the fly ash matrix. Future research will report on efforts to undertake simulation experiments for the determination of the relative emission factors from fly ash and stack flue gas.

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