



Effect of Temperature and CaO Addition on the Removal of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Fly Ash from a Medical Waste Incinerator

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ABSTRACT

The effects of thermal treatment temperature and CaO addition on polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) content in the fly ashes from a medical waste incinerator with high chlorine content (7.5%) were investigated. Two kinds of batch mode were examined: without CaO addition under the temperature range of 50–850°C, and with CaO addition at various Ca/Cl molar ratios (CCR = 0.8–44.3) at 250°C.

The results show that the PCDD/F content in raw fly ash was 6.20 ng I-TEQ/g. When elevating the temperature from 50 to 400°C without CaO addition, the PCDD/F content dramatically increased from 5.38 to 575 ng I-TEQ/g. Even at 850°C, the PCDD/Fs were not destructed apparently and were still with a concentration of 401 ng I-TEQ/g. However, with the addition of CaO at CCR = 17.7 at only 250°C, the removal ratio of PCDD/Fs reached to 87.2% and the PCDD/F content was significantly reduced to 0.889 ng I-TEQ/g, which meets the soil pollution standard of Taiwan EPA (1 ng I-TEQ/g) and could be considered as backfill. CaO addition was proven efficiently to enhance the reduction rate of PCDD/Fs in fly ashes during the thermal treatment at a low temperature, as well as inhibit the formation of PCDD/Fs.

Keywords: PCDD/Fs; Fly ash; Thermal treatment; Calcium oxide.

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) have become a concern due to their adverse health effects (US EPA, 2000). Many studies have focused on PCDD/F emissions in thermal reaction facilities, including sinter plants, electric arc furnaces, secondary aluminum smelters, coal-fired power plants, and crematories (Rappe, 1992; Wang *et al.*, 2003a; Wang *et al.*, 2003c; Chen *et al.*, 2004; Lee *et al.*, 2004; Lee *et al.*, 2005; Lin *et al.*, 2007; Lin *et al.*, 2010; Chen *et al.*, 2011; Chiu *et al.*, 2011; Kuo *et al.*, 2011). Generally, the combustion temperature and chlorine content of raw materials plays an important role in

PCDD/F formation (Lee *et al.*, 2003; Wang *et al.*, 2003b; Li *et al.*, 2007; Wang *et al.*, 2010).

The typical chlorine level for municipal solid waste incinerators is between 0.2 and 0.8%, and that for medical waste is between 1.1 and 2.1% (Randall and Shoraka-Blair, 1994; Rigo *et al.*, 1995). Hence, high concentrations of PCDD/Fs were formed, deposited (Wang *et al.*, 2010; Huang *et al.*, 2011) and found in small fly ash particles with large amounts of chlorine (Cobo *et al.*, 2009).

There are two temperature windows in which PCDD/Fs are formed: the heterogeneous route (between 200°C and 400°C) and the homogeneous route (between 500°C and 800°C) (Stanmore, 2004). Three major mechanisms for PCDD/F emission from incinerators are: (1) high-temperature gas phase formation (300°C–600°C) (Everaert and Baeyens, 2002); (2) precursors transformation: such as chlorophenols, polychlorinated diphenyl ethers and chlorobenzenes (Lustenhouwer *et al.*, 1980; Hutzinger and Blumich, 1985); and, (3) production via de novo synthesis in the low-

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temperature post-combustion zone (250°C–450°C) through residue carbon or metal catalysts in the fly ash reaction (Dickson *et al.*, 1989; Everaert and Baeyens, 2002). For de novo synthesis, the important parameters are temperature, carbon, chlorine, oxygen and metal catalysis, especially copper, which act as a catalyst (Gullett *et al.*, 1992; Stieglitz *et al.*, 1989; Stanmore, 2004). De novo reaction shows that the PCDF/PCDD ratio is higher than one and the higher chlorinated congeners were dominant isomers (Everaert and Baeyens, 2002; Cunliffe and Williams, 2009). Additionally, the de novo reaction of PCDD/Fs was found in fly ash with a large change in PCDD/F concentration, but with a small change in temperature (Cunliffe and Williams, 2009). Therefore, the thermal treatment temperature is an important parameter related to the reduction rate of PCDD/Fs in fly ash treatment.

In order to reduce the PCDD/F emissions from incinerators, some additives, such as powder activated carbon, $(\text{NH}_4)_2\text{SO}_4$, urea, sulfur and calcium oxide (CaO) can be used. Adding $(\text{NH}_4)_2\text{SO}_4$ to fuel (3%) can reduce PCDD/F emissions by 90% (Pandelova *et al.*, 2005). The addition of urea resulted in the reduction of PCDD/F concentration by as much as 74% (Ruokojärvi *et al.*, 2001). Sulfur is a very strong inhibitor of PCDD formation; it converts into SO_2 and reduces Cl_2 to HCl (Gullett *et al.*, 1992).

Powder activated carbon injection is always used to reduce PCDD/F emission from MSWIs and can reach 92–99% removal efficiency of PCDD/Fs (Dong *et al.*, 2001). However, activated carbon only provides PCDD/Fs with an adsorption surface, not a decomposition reaction. In contrast, calcium-based sorbents are another choice, which are widely employed not only to remove SO_2 , but also to inhibit PCDD/F formation due to their removing HCl and Cl_2 from flue gas or fly ash and reduce the production opportunities of PCDD/Fs (Gullett *et al.*, 1994; Jozewicz and Gullett, 1995; Shemwell *et al.*, 2001). CaO addition can reduce the PCDD/Fs formation by catalysis of fly ash from pentachlorophenol (PCP) at 300°C (Naikwadi and Karasek, 1989). Furthermore, a clear PCDD/F inhibition effect was observed when reacting dioxin precursors, PCP, hexachlorobenzene (HCB), and 2,3,4,5-tetrachlorophenol (2,3,4,5- T_4CP) with CaO at temperatures of between 280°C and 450°C (Liu *et al.*, 2005). Thermal treatment also effectively removes PCDD/Fs from heavily contaminated soil, with removal efficiencies greater than 99.99% at primary furnace temperatures of 750°C and 850°C (Lee *et al.*, 2008; Lin *et al.*, 2011).

The literature is limited on investigating the effects of temperature gradient on the reformation or removal of PCDD/Fs in fly ashes from medical incinerators with/without the addition of CaO. In this study, experiments were designed to investigate the effect of the treatment temperature and inlet Ca/Cl molar ratio (CCR) by adding CaO on the variation of PCDD/F content. The results provide useful information for dealing with PCDD/F reduction in the treatment of high chlorine content of fly ashes.

EXPERIMENTAL METHOD

Composition Analysis

Fly ash samples were collected from a bag filter in a medical waste incinerator. An inductively coupled plasma atomic emission spectrometer (Jobin Yvon JY-38 Plus ICP-AES) was used to analyze the metal species. The processes are as follows. The fly ash was pulverized to a particle size that passed through a mesh 100 sieve to ensure a consistent digestion efficiency. 0.5 g samples were digested with an acid mixture (1 mL HBF_4 + 5 mL HNO_3 + 5 mL HClO_4) in a hermetically sealed Teflon tube by a microwave digester. The heating program was: 20–180°C at 10 °C/min and held isothermally for 30 min. The digestion solution was diluted to 25 mL with deionized water, filtrated by a cellulose ester filter, and then analyzed. The relative composition of Si and Ca was determined using scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) (Jeol JXA-840). The chlorine contents of fly ashes were determined by an energy-dispersive X-ray fluorescence spectrometer (EDXRF) (SPECTRO, XEPOS). Thermal gravimetric analysis (TGA) (TA, SDT Q600) was performed at a heating rate of 10 °C/min in a nitrogen atmosphere from room temperature to 1200°C.

Thermal Treatment Experiments

The experiments were divided into two parts: (1) 10 g of raw fly ash was treated at various temperatures (50°C–850°C); and (2) 10 g of raw fly ash was added various amounts of CaO (1, 5.25, 21, and 52.5 g of CaO, equal to Ca/Cl molar ratio (CCR) = 0.8, 4.4, 17.7 and 44.3, respectively) and treated at 250°C. All samples were put in a graphite crucible and placed in the furnace at atmospheric environment. The experiments were performed by increasing the furnace temperature by 6 °C/min from room temperature and maintaining it at 50, 100, 150, 200, 250, 300, 400, 500, 600, 750, and 850°C, respectively, for 1 h. Then, the samples were cooled by natural cooling process in the furnace.

Analysis of PCDD/Fs

Two PCDD/F samples were analyzed and averaged for each fly ash sample in this study. Fly ash samples were analyzed using the US EPA Method 1613B (US EPA, 1994). Samples were extracted with toluene for 24 hr followed by a series of sample cleanup procedures. The extract was transferred to a vial, and further concentrated using a N_2 stream.

High-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) was used for PCDD/F analysis. The HRGC (Hewlett-Packard 6970 Series gas, CA) system was equipped with a DB-5 fused silica capillary column (L = 60 m, ID = 0.25 mm, film thickness = 0.25 μm) (J&W Scientific, CA) with splitless injection. The HRMS (Micromass Autospec Ultima, Manchester, UK) system used a positive electron impact (EI+) source. The analyzer mode of the selected ion monitoring was used with a resolving power of 10,000. The electron energy and source temperature were specified at 35 eV and 250°C, respectively. The oven temperature program was set as follows: the temperature was initially 150°C (held for 1 min), then increased by 30 °C/min to 220°C (held for 12 min), and finally increased by 1.5 °C/min to 310°C (held for 20 min). Helium was used as

the carrier gas.

EPA Method 5050 followed by EPA Method 9056 was used for the analysis of chlorine content in the fly ash. The fly ash is oxidized by combustion in a bomb containing oxygen under pressure. The liberated chlorinated compounds are adsorbed in a sodium carbonate/sodium bicarbonate solution. A small volume of combustate collection solution, 1.5 mL/min, was injected into an ion chromatograph to flush and fill a constant volume sample loop. The sample is then injected into a stream of carbonate-bicarbonate eluent of the same strength as the collection solution. Chlorine content was identified based on their retention times compared to standards. Quantitation is accomplished by measuring the peak area and comparing it to the calibration curve.

RESULTS AND DISCUSSION

Composition and PCDD/F Content in Medical Waste and Raw Fly Ash

The compositions of medical waste showed that the contents of moisture, ash, and volatile matter with fixed carbon were 9.3%, 17.3%, and 73.4%, respectively, indicating this type of ash contained high amount of unburned organic-matter. The element analysis of medical waste shows that the major metals were Ca, Na, Fe, Si, and Al, reaching 9619, 7497, 5872, 5658, and 1914 ppm, respectively (Table 1).

From the thermal gravimetric analysis (Fig. 1), the patterns indicate the weight loss of fly ashes are apparently found at the intervals of room temperature-100°C, and 400–550°C, indicating the water and volatile matter are the major compositions in the fly ashes. In addition, the metal analysis of fly ash shows that high amount of catalysts for forming PCDD/Fs via de nova synthesis process, including Fe and Cu was found, reaching 48282 and 554 ppm, respectively (Table 1). Moreover, a large amount of Na was also measured

Table 1. The element analysis of medical waste and fly ashes (mg/kg)

Species (mg/kg)	Medical waste	Fly ash
Ag	6.4	19.0
Al	1914	123
As	72.0	73.9
Ba	95.2	10.3
Ca	9619	3481
Cd	2.4	11.2
Cr	141	9550
Cu	63.1	554
Fe	5872	48282
Hg	18.3	8.9
K	426	2571
Mg	678	610
Mn	55.7	1454
Na	7497	73152
Ni	88.2	9235
Pb	23.8	39.9
Se	30.6	1419
Si	5658	1850
Zn	348.9	571

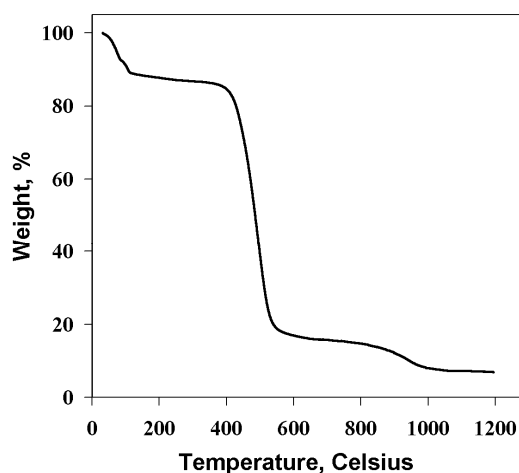


Fig. 1. The pattern of thermal gravimetric analysis of raw fly ashes.

(73152 ppm) and is relative with the high concentration of chlorine content 7.5% which is close the value (8.1%) (Zhao *et al.*, 2010). The high quantity of Cl was presented perhaps because the usage of polyvinyl chloride disposable infusion devices and NaCl that was used frequently in medical treatment. However, high Cr content (9550 ppm) will conduct to the fly ash being belong to hazardous waste.

The PCDD/F content in raw fly ash is shown in Table 2. The mean PCDD/Fs and I-TEQ were 58.6 ng/g and 6.20 ng I-TEQ/g, respectively, which exceeds the regulatory standard of the Taiwan EPA (the limit of 1 ng I-TEQ/g) (Taiwan EPA, 2008). The PCDD/F content in the fly ash is close to that in Mininni's study (1.7–147 ng I-TEQ/g), which investigated PCDD/F formation in fly ash collected from a hospital incinerator (Mininni *et al.*, 2007). The ratio of PCDD/PCDF was 0.251, indicating that the dominant congeners were PCDFs.

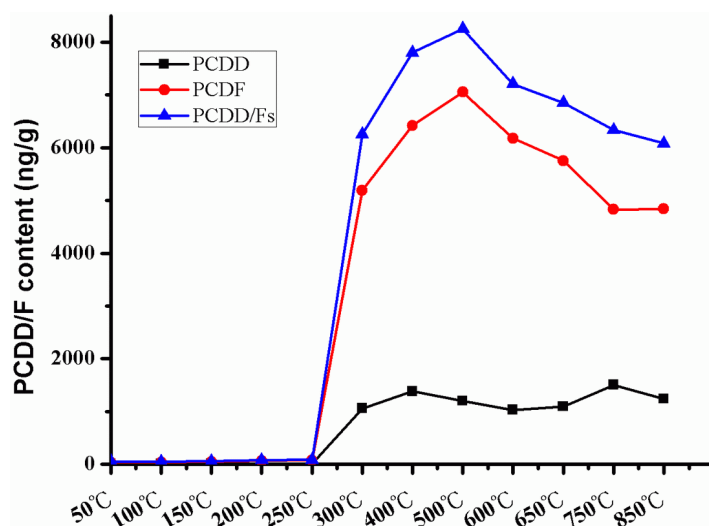
PCDD/F Content in Thermally Treated Fly Ash under Various Temperatures without CaO Addition

The PCDD/F content in thermally treated fly ash under various temperatures is shown in Table 2. The PCDD/F content in thermally treated fly ash was between 50.5–57.8 ng/g under low temperatures (50–150°C), which was close to that of raw fly ash (58.6 ng/g). There was a dramatic increase in PCDD/F content in thermally treated fly ash under middle temperatures (200–400°C) when the temperature reached 300°C (Fig. 2). The total PCDD/F content and total I-TEQ content reached 6252 ng/g and 381 ng I-TEQ/g at 300°C, respectively, which are 107 and 62 times higher than those for the raw fly ash. Furthermore, the highest PCDD/F content in thermally treated fly ash was 8251 ng/g, with a corresponding I-TEQ of 621 ng I-TEQ/g at 500°C, which is 100 times larger than that for raw fly ash. The PCDD/F content in thermally treated fly ash ranged from 401 to 544 ng I-TEQ/g under high temperatures (600°C–850°C), which is over 60 times higher than that for the raw fly ash.

Fig. 3 showed that the pattern of the PCDFs/PCDDs ratio and PCDFs/PCDDs I-TEQ ratio was similar for

Table 2. PCDD/F content in raw fly ash and treated fly ash at various temperatures without CaO addition.

PCDD/Fs (ng/g)	Raw fly ash	50°C	100°C	150°C	200°C	250°C	300°C	400°C	500°C	600°C	650°C	750°C	850°C
2,3,7,8-TeCDD	0.52	0.62	0.56	0.63	0.55	0.38	5.60	9.26	8.35	6.14	7.07	6.19	5.52
1,2,3,7,8-PeCDD	1.15	1.23	1.06	1.26	1.43	0.90	33.3	59.7	61.4	48.0	52.2	47.4	43.6
1,2,3,4,7,8-HxCDD	0.52	0.41	0.36	0.55	0.58	0.55	45.4	67.6	67.5	60.5	65.2	67.1	59.0
1,2,3,6,7,8-HxCDD	0.68	0.86	0.71	0.79	0.96	0.54	53.8	80.7	79.2	66.1	73.9	84.8	69.5
1,2,3,7,8,9-HxCDD	0.64	0.69	0.68	0.64	1.10	0.69	48.3	95.4	80.9	71.8	74.4	84.1	76.0
1,2,3,4,6,7,8-HpCDD	3.04	2.72	3.15	2.97	4.30	2.69	402	554	495	425	472	690	521
OCDD	5.21	4.02	3.47	4.95	4.81	3.77	472	515	407	354	353	524	463
2,3,7,8-TeCDF	4.40	4.05	3.69	3.90	4.10	2.76	82.5	125	125	111	118	89.3	65.3
1,2,3,7,8-PeCDF	5.59	4.95	5.12	4.96	6.06	4.64	180	312	301	258	277	218	180
2,3,4,7,8-PeCDF	5.06	4.02	4.02	4.35	6.33	4.17	294	458	507	440	452	352	302
1,2,3,4,7,8-HxCDF	5.35	5.11	4.90	5.36	7.83	5.94	485	664	705	639	638	508	472
1,2,3,6,7,8-HxCDF	5.90	5.79	4.88	5.62	8.54	6.04	511	753	792	692	690	565	529
1,2,3,7,8,9-HxCDF	3.47	3.49	3.19	3.35	6.29	3.54	494	778	908	822	740	601	582
2,3,4,6,7,8-HxCDF	0.31	0.28	0.31	0.31	0.41	0.21	26.2	22.6	26.6	26.8	24.4	19.4	15.7
1,2,3,4,6,7,8-HpCDF	11.2	10.1	9.21	12.3	19.7	15.0	1986	2207	2503	2299	2088	1746	1810
1,2,3,4,7,8,9-HpCDF	1.32	1.53	1.72	1.20	2.49	1.92	312	356	374	276	256	242	267
OCDF	4.29	3.79	3.42	4.69	6.04	33.21	822	743	811	612	468	490	617
PCDDs	11.8	10.6	9.99	11.8	13.7	9.52	1060	1382	1199	1031	1098	1504	1238
PCDFs	46.9	43.1	40.5	46.0	67.8	77.4	5192	6417	7053	6177	5751	4832	4840
PCDDs/PCDFs ratio	0.25	0.24	0.25	0.26	0.20	0.12	0.20	0.22	0.17	0.17	0.19	0.31	0.26
Total PCDD/Fs	58.6	53.7	50.5	57.8	81.6	86.9	6252	7799	8251	7208	6849	6336	6078
PCDDs I-TEQ	1.32	1.46	1.30	1.49	1.58	1.04	41.5	69.5	67.2	54.6	59.6	60.9	53.5
PCDFs I-TEQ	4.88	4.25	4.08	4.41	6.41	4.37	340	505	554	489	485	386	348
PCDDs/PCDFs I-TEQ ratio	0.27	0.34	0.32	0.34	0.25	0.24	0.12	0.14	0.12	0.11	0.12	0.16	0.15
Total PCDD/Fs I-TEQ	6.20	5.71	5.38	5.91	7.99	5.41	381	575	621	543	544	447	401

**Fig. 2.** PCDD/F content in medical fly ash by thermal treatment at 50–850°C without CaO addition.

temperatures from 50 to 200°C. This illustrates that the variations between concentration and I-TEQ were consistent when the temperature was less than 250°C. However, the de novo reaction was the dominant mechanism when the temperature was greater than 250°C and led to more PCDF formation. This resulted in an obvious increase in the PCDFs/PCDDs ratio and PCDFs/PCDDs I-TEQ ratio, which implies that the de novo reaction was probably the dominant mechanism (Huang and Buekens, 1995).

The de novo synthesis reaction temperature ranged from 250 to 400°C. Stanmore (2004) indicated PCDD/F congeners are effectively destroyed at temperatures over 500°C. Dechlorination, desorption or destruction might be responsible for the reduction of PCDD/F content in the fly ash during heating (Cunliffe and Williams, 2007). However, the PCDD/F content reached its highest at 500°C and then decreased by only around 26% at 850°C in this study. This was probably because the de novo synthesis led to PCDD/F being formed

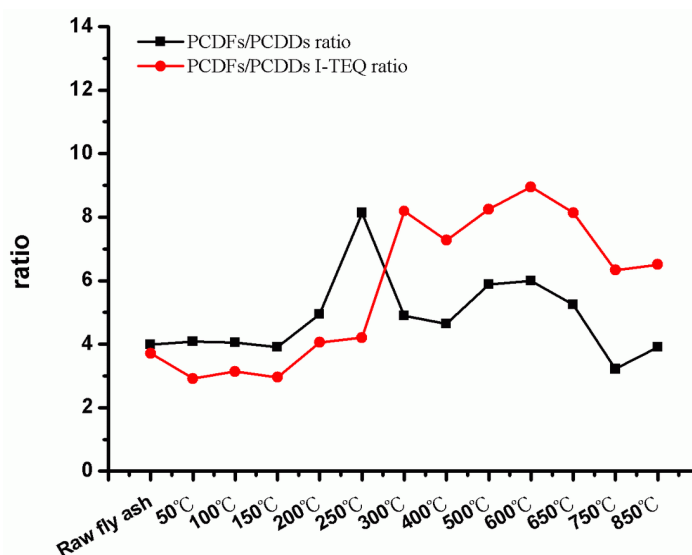


Fig. 3. Relationship among PCDFs/PCDDs ratio and PCDFs/PCDDs I-TEQ ratio without CaO addition at various thermal treatment temperatures.

again during the natural cooling process in the furnace. Lee's study (Lee *et al.*, 2008) indicated that the reduction rate of PCDD/Fs in contaminated soil reached 99.99% at the temperatures of 750°C and 850°C. This may be due to the different properties between soil and medical fly ash. Stieglitz's study reported that in municipal waste incineration particulate organic carbon is the primary source for PCDD/PCDF formation (Stieglitz *et al.*, 1989). The medical fly ash contained much Fe and unburned carbon, which acted as a catalyst to promote the reactions of adsorbed organic compounds, resulting in the formation of high amounts of PCDD/Fs.

PCDD/F Content in Fly Ash for Various Amounts of CaO Addition at 250°C

Due to a dramatic increase in PCDD/F content in thermally treated fly ash was found when the temperature was greater than 250°C (Fig. 2), a low temperature of 250°C was set by adding CaO for removing PCDD/Fs. After adding 0, 1, 5.25, 21, and 52.5 g of CaO (CCR = 0, 0.8, 4.4, 17.7 and 44.3, respectively) into 10 g of fly ash and heating at 250°C for 1 hr, the total PCDD/F content values in the fly ash were 86.9, 31.0, 24.3, 7.53, and 4.47 ng/g, with corresponding total PCDD/F I-TEQ content values of 5.41, 3.88, 3.08, 0.889, and 0.535 ng I-TEQ/g, respectively (Table 3 and Fig. 4). The results showed that the PCDD/F content in the fly ash could be decreased to lower than the soil pollution standard of Taiwan EPA (1 ng I-TEQ/g) when enough CaO was added.

The removal efficiencies (compared with raw fly ash) of total PCDD/Fs increased from 58.5% to 92.4% with corresponding I-TEQ values of 50.3% to 91.4% when the CCR elevated from 0.8 to 44.3. However, when the CCR was set at 17.7, the PCDD/F content in the fly ash decreased to 0.889 ng I-TEQ/g, which meets the soil pollution standard of Taiwan EPA (1 ng I-TEQ/g) and could be considered as backfill. Furthermore, the removal ratio (compared with

non-CaO addition at 250°C) of total PCDD/Fs ranged from 64.4% to 94.9% with corresponding I-TEQ values of 28.3% to 90.1%. Increasing CCR increased the removal ratio and CaO addition was shown to reduce the formation of PCDD/Fs.

CaO is often used as a good absorber of HCl and SO₂. Results show that CaO inhibits PCDD/F formation for capturing HCl or Cl₂ during the thermal treatment process. It has been reported that CaO inhibits PCDD/F formation from PCP, HCB, and 2,3,4,5-T₄CP at temperatures in the range of 280°C to 450°C (Liu *et al.*, 2005). Chlorophenols (CPs) and chlorobenzene (CBs) play decisive roles in PCDD/F formation (Altwicker, 1996). Liu indicated CaO absorbed PCP, then decomposed it and inhibited the PCDD/F formation (Liu *et al.*, 2005). Accordingly, we inferred that the high chlorine content (7.5%) and volatile matter (17.3%) in the fly ash from a medical incinerator apparently increased the possibility to form precursors, such as CPs or CBs. However, the CaO addition may have increased the reaction or absorption rate between CaO and chlorine, decreased the formation of precursors, and then inhibited the PCDD/F formation.

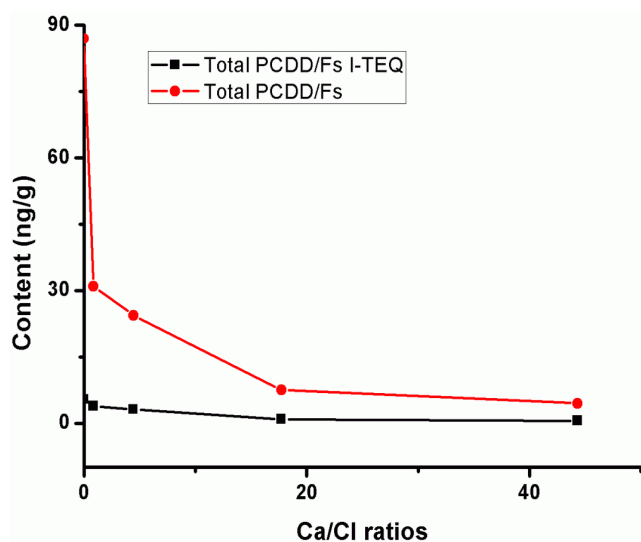
Congener Profiles of PCDD/F Content in Fly Ash

Fig 5 shows the congener profiles of the seventeen PCDD/Fs. Each congener was normalized by the sum of the seventeen PCDD/Fs. The most prevalent congeners in the raw fly ash were 1,2,3,4,6,7,8-HpCDF (19.1%), 1,2,3,6,7,8-HxCDF (10.1%), and 1,2,3,7,8-PeCDF (9.53%) (Fig 5(a)). After 50–250°C thermal treatment, the dominant congeners in the fly ash were similar to those in the raw fly ash, with the first two dominant congeners being 1,2,3,4,6,7,8-HpCDF (17.2–24.2%) and 1,2,3,6,7,8-HxCDF (6.95–10.8%) (Fig. 5(b)). The results showed that PCDD/Fs can not be desorbed at 50–250°C.

After 300–850°C thermal treatment, the dominant congeners in the fly ash were 1,2,3,4,6,7,8-HpCDF (27.6–31.8%), OCDF (6.84–13.2%), and 1,2,3,7,8,9-HxCDF (7.91–

Table 3. PCDD/F content in fly ash treated at various Ca/Cl ratios and at 250°C.

PCDD/Fs (ng/g)	Ca/Cl = 0	Ca/Cl = 0.8	Ca/Cl = 4.4	Ca/Cl = 17.7	Ca/Cl = 44.3
2,3,7,8-TeCDD	0.38	0.380	0.293	0.084	0.050
1,2,3,7,8-PeCDD	0.90	0.729	0.615	0.139	0.095
1,2,3,4,7,8-HxCDD	0.55	0.257	0.209	0.061	0.037
1,2,3,6,7,8-HxCDD	0.54	0.377	0.302	0.092	0.055
1,2,3,7,8,9-HxCDD	0.69	0.414	0.331	0.110	0.064
1,2,3,4,6,7,8-HpCDD	2.69	1.64	1.25	0.407	0.249
OCDD	3.77	1.82	1.30	0.454	0.287
2,3,7,8-TeCDF	2.76	3.13	2.32	0.679	0.384
1,2,3,7,8-PeCDF	4.64	3.67	2.97	0.839	0.482
2,3,4,7,8-PeCDF	4.17	3.49	2.74	0.768	0.463
1,2,3,4,7,8-HxCDF	5.94	3.17	2.44	0.715	0.429
1,2,3,6,7,8-HxCDF	6.04	3.13	2.64	0.756	0.426
1,2,3,7,8,9-HxCDF	3.54	0.265	0.258	0.073	0.049
2,3,4,6,7,8-HxCDF	0.21	0.510	0.450	0.410	0.262
1,2,3,4,6,7,8-HpCDF	15.0	5.63	4.47	1.39	0.814
1,2,3,4,7,8,9-HpCDF	1.92	0.590	0.461	0.142	0.084
OCDF	33.21	1.74	1.29	0.409	0.238
PCDDs	9.52	5.62	4.29	1.35	0.836
PCDFs	77.4	25.3	20.0	6.18	3.63
PCDDs/PCDFs ratio	0.12	0.222	0.214	0.218	0.230
Total PCDD/Fs	86.9	31.0	24.3	7.53	4.47
PCDDs I-TEQ	1.04	0.867	0.699	0.184	0.115
PCDFs I-TEQ	4.37	3.01	2.38	0.705	0.420
PCDDs/PCDFs I-TEQ ratio	0.24	0.288	0.294	0.262	0.275
Total PCDD/Fs I-TEQ	5.41	3.88	3.08	0.889	0.535

**Fig. 4.** PCDD/F content in medical fly ash treated with CaO addition at various Ca/Cl ratios and at 250°C.

11.4%), and were different with the raw fly ashes (Fig. 5(c)). The fractions of low-chlorine compounds, such as TeCDD, PeCDD, TeCDF and PeCDF obviously decreased when the treatment temperature was greater than 300°C. High PCDD/F content in thermally treated fly ash was attributed to 1,2,3,4,7,8,9-HpCDF, OCDF, and 1,2,3,7,8,9-HxCDF and resulted in the increasing PCDFs/PCDDs I-TEQ ratio.

The comparison of seventeen PCDD/F congeners at various CCRs is shown in Fig. 5(d). Changing the CCR didn't change the distribution of individual congeners much. Moreover, the addition of CaO at 250°C did not change the PCDD/F congener profiles compared with raw fly ash.

Based on Stanmore's study, PCDD/F congeners should be effectively destroyed when the temperature is over 500°C (Stanmore, 2004); however, the PCDD/F content (> 500°C) in this study was higher than 6,000 ng/g and 400 ng I-TEQ/g. It is probable that the thermally treated fly ash passed the de novo synthesis window when the system cooled down naturally and a lot of PCDD/F congeners formed again. Adding CaO apparently inhibited the PCDD/F formation, especially when the CCR was greater than 17.7, then the resultant PCDD/F content in fly ash could be less than the standard of the Taiwan EPA (1.0 ng I-TEQ/g) at low treatment temperature as 250°C

CONCLUSION

The mean total PCDD/F I-TEQ in raw fly ash from a medical incinerator was 6.20 ng I-TEQ/g. After thermal treatment (50–250°C), the total PCDD/F content in treated fly ash was 5.38–7.99 ng I-TEQ/g. However, after high-temperature treatment (300–850°C), the total PCDD/F content in thermally treated fly ash elevated and reached 401–621 ng I-TEQ/g. It is probable that the thermally treated fly ash passed the de novo synthesis window when the system

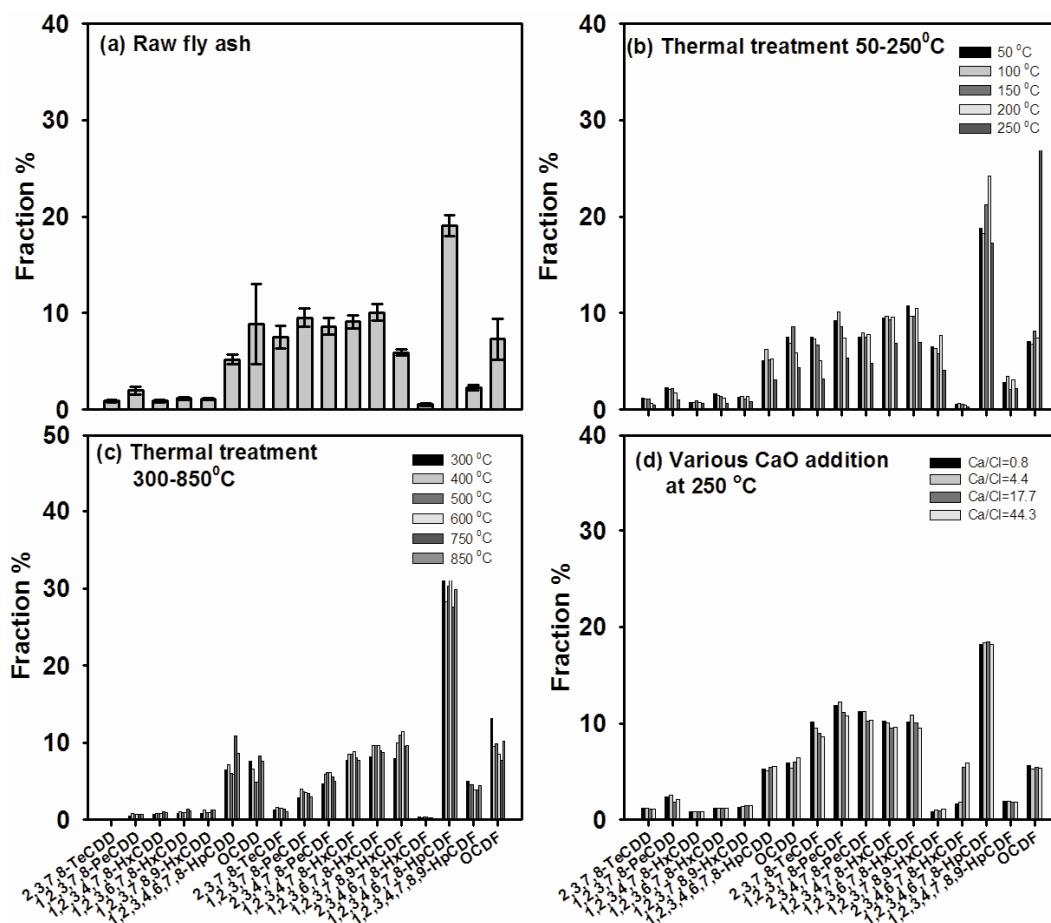


Fig. 5. Congener profiles of PCDD/Fs. (a) raw fly ash (b) thermally treated at 50–250°C without CaO addition (c) thermally treated at 300–850°C without CaO addition (d) with CaO addition for various Ca/Cl ratios at 250°C.

cooled down naturally and a lot of PCDD/F congeners formed again. At low treatment temperature as 250°C with CaO addition, the removal fraction of PCDD/Fs in fly ashes increased from 58.5% to 92.4% with CCRs = 0.8, 4.4, 17.7, and 44.3. When the CCR was at 17.7, the PCDD/F content in the fly ashes decreased to 0.889 ng I-TEQ/g, which meets the Taiwan EPA standard (1.0 ng I-TEQ/g). Accordingly, CaO addition with thermal treatment at low temperature (250°C) could be taken into consideration as an alternative to reduce the PCDD/F content in fly ashes with high chlorine levels.

NOMENCLATURE

CCR Ca/Cl molar ratio
APCD air pollution control devices

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