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Effects of Sulfur and Calcium Compounds on Dioxin Reduction in a Fluidized Bed Combustor

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ABSTRACT

The focus of this study is the effects of sulfur and calcium compounds on reducing dioxins in fly ash collected from the baghouse of a pilot-scale fluidized bed combustor. Pelletized sawdust with various amounts of polyvinyl chloride (PVC), pyrite, and calcium hydroxide was used as the feeding material. The experimental results indicated an extremely low concentration of dioxin in the fly ash from the cyclone (0.025 to 0.284 ng g^{-1}), and the concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in the fly ash collected from the baghouse increased by 27.4% as the chlorine content increased from 0.568 to 1.136 wt%. The inhibition of PCDD/Fs by sulfur is not clear and can be attributed to the low content of copper (average 387 ppm), which serves as the catalyst for the Deacon reaction. Octa-chlorinated dibenzofuran (OCDF) was the major congener of the PCDD/Fs. The highest toxicity-equivalent (I-TEQ) of 2,3,7,8-substituted congeners was 2,3,4,7,8-PeCDF, which accounted for 37% of the total congeners (average value). The correlation between the I-TEQ values and 2,3,4,7,8-PeCDF concentration of fly ash is also discussed.

Keywords: Dioxin; Fly ash; Sulfur compound; Calcium compound; Fluidized bed combustor.

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and dibenzofuran (PCDD/Fs) emissions from incineration processes were first reported by Olie *et al.* (1977). The main cause of dioxin generation is the chlorine content of the feeding material used in the incineration process (Hatanaka *et al.*, 2000; Wang *et al.*, 2003; Stanmore, 2004). Mattila *et al.* (1992) found that a large amount of PCDD/Fs was generated when the chlorine content of the feeding material was increased from 0.4% to 1.2%. Some studies (Lenoir *et al.*, 1991; Frankenhaeuser *et al.*, 1993; Halonen *et al.*, 1993; Ruuskanen *et al.*, 1994) found that when the chlorine content in the fuel is below 1%, the levels of PCDD/Fs in the flue are approximately the same. However, the formation of dioxin increases significantly when the chlorine content of the feeding material exceeds 1% (Wikström *et al.*, 1996).

Numerous studies have been conducted to determine effective methods of inhibiting or reducing dioxin formation during the combustion process. Griffin (1986) presented a mechanism involving sulfur as an inhibitor of dioxin formation, and similar methods have also been proposed by other researchers (Stieglitz *et al.*, 1990; Stieglitz *et al.*, 1991; Gullett *et al.*, 1992a, b; Lindbauer *et al.*, 1992, 1993; Ogawa *et al.*, 1996; Raghunathan and Gullett, 1996; Preto *et al.*, 2005). Gullett *et al.* (1992b) suggested that the reaction of Cu(II) with SO_2 to form $CuSO_4$ renders the catalyst less active, thus decreasing PCDD formation. This finding was supported by the results obtained by Ryan *et al.* (2006) and Ke *et al.* (2010). Lin *et al.* (2015) found that the amount of PCDD/Fs can be reduced by 94% with the addition of pyrite (FeS_2).

Ogawa *et al.* (1996) found that the inhibitory effect was increased when the S/Cl ratio ranged from 0.1 to 0.65, and Anthony *et al.* (2001) stated that the sulfur contained in fuel can be used to reduce dioxin formation, which is considered to depend on the S/Cl ratio. Their results showed that the addition of sulfur at a higher ratio (S/Cl > 1) appeared to reduce the emission of PCDD/Fs; however, no benefit was derived from addition of higher amounts of sulfur (S/Cl > 2). Chang *et al.* (2006) found that PCDD/Fs formation can be decreased to 54.1% by adding sulfur at a S/Cl ratio of approximately 2 in a laboratory-scale system. As mentioned above, the efficiency of reducing PCDD/Fs formation by adding sulfur is strongly influenced by the S/Cl molar ratio, and no benefit was derived from further increasing the sulfur levels (S/Cl > 2). However, the absolute

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quantities of sulfur and chlorine have not been indicated. The levels of PCDD/Fs produced by the combustion of fuel flue are similar when the chlorine content of the fuel is lower than 1%, and dioxin formation significantly increases when the chlorine content exceeds 1%. The effect of the S/Cl ratio on dioxin formation may also depend on the absolute quantity of sulfur or chlorine.

Calcium oxide can effectively control the emissions of dioxin and acid gas from municipal waste incineration systems (Liu *et al.*, 2000). Bie *et al.* (2005) observed the highest conversion rate for the chlorination of calcium oxide in fluidized bed combustion at 600°C. Lawrence and Bu (2000) stated that the calcium oxide entrained into the freeboard at 650°C has a better hydrogen chloride removal efficiency. Kobyashi *et al.* (2005) stated that Ca-based substances can be used to remove hydrogen chloride in a fluidized bed, even at temperatures exceeding 1000 K. The results of recent research indicate that the simultaneous desulfurization and dechlorination are possible at high temperatures in a furnace (Lin and Chyang, 2016).

Hung *et al.* (2018) indicated that total PCDD/Fs concentrations ranging from 45.5% to 73.8% were partitioned in the solid phase. Activated carbon (AC) injections have been used to reduce the dioxin in flue gas for a long time. Buekens and Huang (1998) demonstrated that a dioxin removal efficiency of 95% can be achieved by using an AC moving bed, while that from using a fixed bed was approximately 80%. Chiang *et al.* (2000) indicated that a fluidized bed activated carbon adsorber has a high removal efficiency of polycyclic aromatic hydrocarbons (PAHs). Wang *et al.* (2009) found that the concentrations of PCDD congeners at the stack and PCDFs decreased from 117.00 to 0.32 ng Nm^{-3} and 94.84 to 0.19 ng Nm^{-3} when the injection of AC increased from 10 to 17 kg h^{-1} at a mean flue gas rate of 1600 Nm^3 min^{-1}, respectively. A multilayer AC-adsorption system (MAS) was developed to improve the control of PCDD/Fs emissions (Chi *et al.*, 2008; Lin *et al.*, 2008; Hung *et al.*, 2011; Cui *et al.*, 2017).

Recently, several studies focused on the effects of sulfur or calcium compounds on dioxin emissions in flue gas (Chyang *et al.*, 2010; Li *et al.*, 2015; Lin *et al.*, 2015; Ma *et al.*, 2018). Few studies have discussed the effects of sulfur and calcium compounds on the dioxin content of fly ash (Hajizadeh *et al.*, 2012), and the effects of calcium oxide, sulfur, and dioxin emission control have been discussed separately (Chyang *et al.*, 2010). However, comprehensive studies are minimal. Calcium can simultaneously desulfurize and dechlorinate substances at high temperatures (Lin and Chyang, 2016), but experimental data regarding the effects of dioxin formation are still required. The purpose of this study is to investigate the relationship between sulfide, calcium, and the dioxin in fly ash. The inhibitory effects of adding calcium/sulfur on dioxin in fly ash are also investigated. To remove the influence of activated carbon on the dioxin in fly ash, activated carbon injection is not used in this study.

METHODS

Material

Pelletized wood sawdust with various additives (PVC, pyrite, and calcium hydroxide) and varied amounts of chlorine, sulfur, and calcium were used as the feeding material. In the granulation process, a small amount of composite-modified starch was added to increase the cohesive force and shape the sawdust into pellets. Each pellet was 6 mm in diameter with a mean length of 15 mm. The results of the proximate and ultimate analyses of the pelletized wood sawdust are provided in Table 1, while the composition of each feeding material is shown in Table 2. Only PVC was added to group B. PVC and pyrite were added to group C, with a S/Cl ratio below 1, and PVC was added to group S, with a S/Cl ratio exceeding 1. Under the criterion of Ca/(S + 0.5Cl) = 1.98, calcium hydroxide was added to feeding materials C2, C4, S2, and S4. Silica sand (99.5% SiO_2) with a mean diameter of 0.506 mm and apparent density of 2600 kg m^{-3} was used as the inert bed material in this study.

Experimental Apparatus

All of the experiments were conducted in a bubbling fluidized-bed combustion (BFBC) system, as shown in Fig. 1, and the configuration of the bubbling fluidized-bed combustor is shown in Fig. 2. The combustor was divided into four parts, i.e., the wind box, distributor, combustion chamber, and freeboard. The combustion chamber had a cross-section of 0.8 × 0.4 m and was constructed from 6-mm carbon steel lined with a 150-mm refractory to reduce heat

Table 1. Proximate and ultimate analyses of the feeding materials.

Proximately analysis (wt.% as-received)					Ultimate analysis (wt% Dry and ash free)					
feeding material	Moisture	Volatile	Fixed carbon	Ash	C	H	O	N	S	Cl
B1	9.86	75.03	14.09	1.03	49.87	6.65	42.58	0.26	0.06	0.57
B2	10.24	74.54	13.87	1.36	49.71	6.71	42.16	0.23	0.04	1.15
C1	10.65	73.58	14.26	1.52	50.00	6.62	42.11	0.29	0.40	0.57
C2	9.38	74.31	14.39	1.93	49.22	6.70	42.84	0.24	0.41	0.58
C3	10.88	74.03	13.51	1.58	49.08	6.29	42.39	0.29	0.80	1.14
C4	10.52	73.46	13.11	2.90	47.07	6.42	44.29	0.23	0.82	1.17
S1	10.72	72.73	13.90	2.65	48.94	6.54	42.89	0.25	0.80	0.57
S2	11.85	72.66	13.05	2.44	47.58	6.47	44.29	0.25	0.82	0.58
S3	10.55	74.23	13.41	1.82	47.53	6.35	43.05	0.31	1.61	1.15
S4	9.88	73.25	13.55	3.32	46.55	6.23	44.04	0.27	1.70	1.21

Table 2. Composition of the feeding materials.

Additives	Chlorine		Sulfur < Chlorine				Sulfur > Chlorine			
	Low	High	High		High		Low		High	
	(B1)	(B2)	(C1)	(C2)	(C3)	(C4)	(S1)	(S2)	(S3)	(S4)
FeS_2 (wt%)	–	–	0.750	0.750	1.500	1.500	1.500	1.500	3.000	3.000
S (wt%)	–	–	0.400	0.400	0.800	0.800	0.800	0.800	1.599	1.599
PVC (wt%)	1.000	2.000	1.000	1.000	2.000	2.000	1.000	1.000	2.000	2.000
Cl (wt%)	0.568	1.136	0.568	0.568	1.136	1.136	0.568	0.568	1.136	1.136
$Ca(OH)_2$ (wt%)	–	–	–	3.000	–	6.000	–	4.830	–	9.660
Ca (wt%)	–	–	–	1.623	–	3.246	–	2.613	–	5.226
S/Cl (-)	–	–	0.781	0.781	0.781	0.781	1.562	1.562	1.562	1.562
Ca/(S + 0.5Cl)	–	–	–	1.980	–	1.980	–	1.981	–	1.981
HHV(WB)	4000.5	3629.3	3916.4	3939.3	4079.3	3929.4	4100.4	3858.3	4014.5	3830.9
LHV(WB)	4048.2	3676.4	3550.9	3571.2	3728.2	3578.4	3737.1	3508.9	3660.5	3495.8

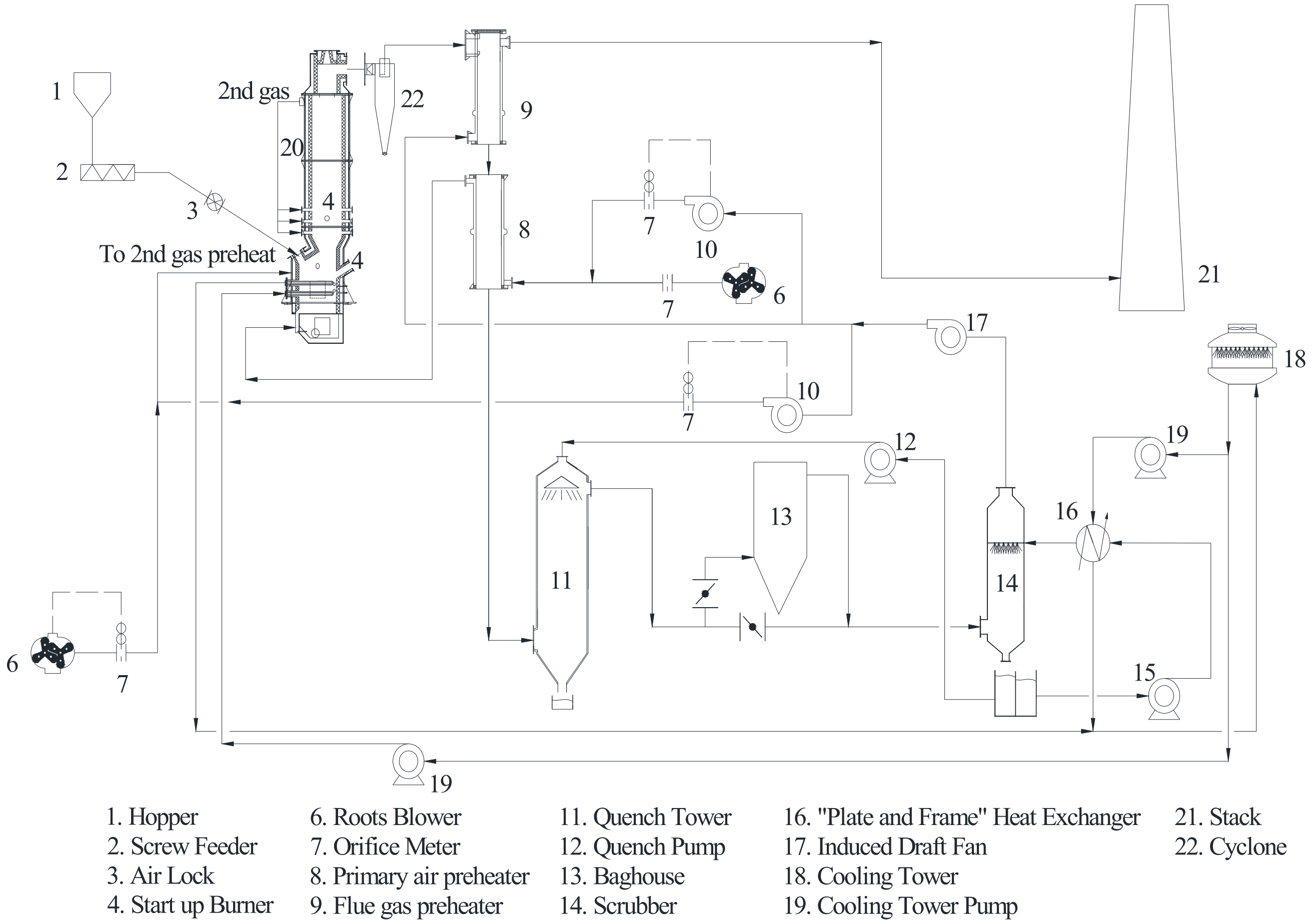

Fig. 1. Flow chart of the fluidized-bed combustion system.

loss. The freeboard with a diameter and height of 0.64 and 2.55 m, respectively, was located above the combustion chamber. A total of 27 tuyeres with 5 and 3-mm orifices and an open-area ratio of 0.52% were mounted on a 6-mm stainless-steel plate and used as the gas distributor. The total height of the combustor, from the distributor to the outlet, was 4.75 m.

The over-bed feeding system was employed here. The feeding material stored in a hopper fell directly through the screw feeder and airlock and then through a water-cooled chute into the fluidized bed chamber 0.45 m above the distributor. The fluidizing and primary combustion air were supplied by an 11.2 kW Roots blower, and the secondary air was supplied by a 5.6 kW Roots blower. Four equally spaced secondary gas injection nozzles with diameters of 30 mm were installed tangentially 2.05 m above the distributor to generate the swirling flow in the freeboard.

The APCD is mainly used to remove particulate matter and pollutants. The flue gas from the combustor at first was introduced into heat convection sections and then input

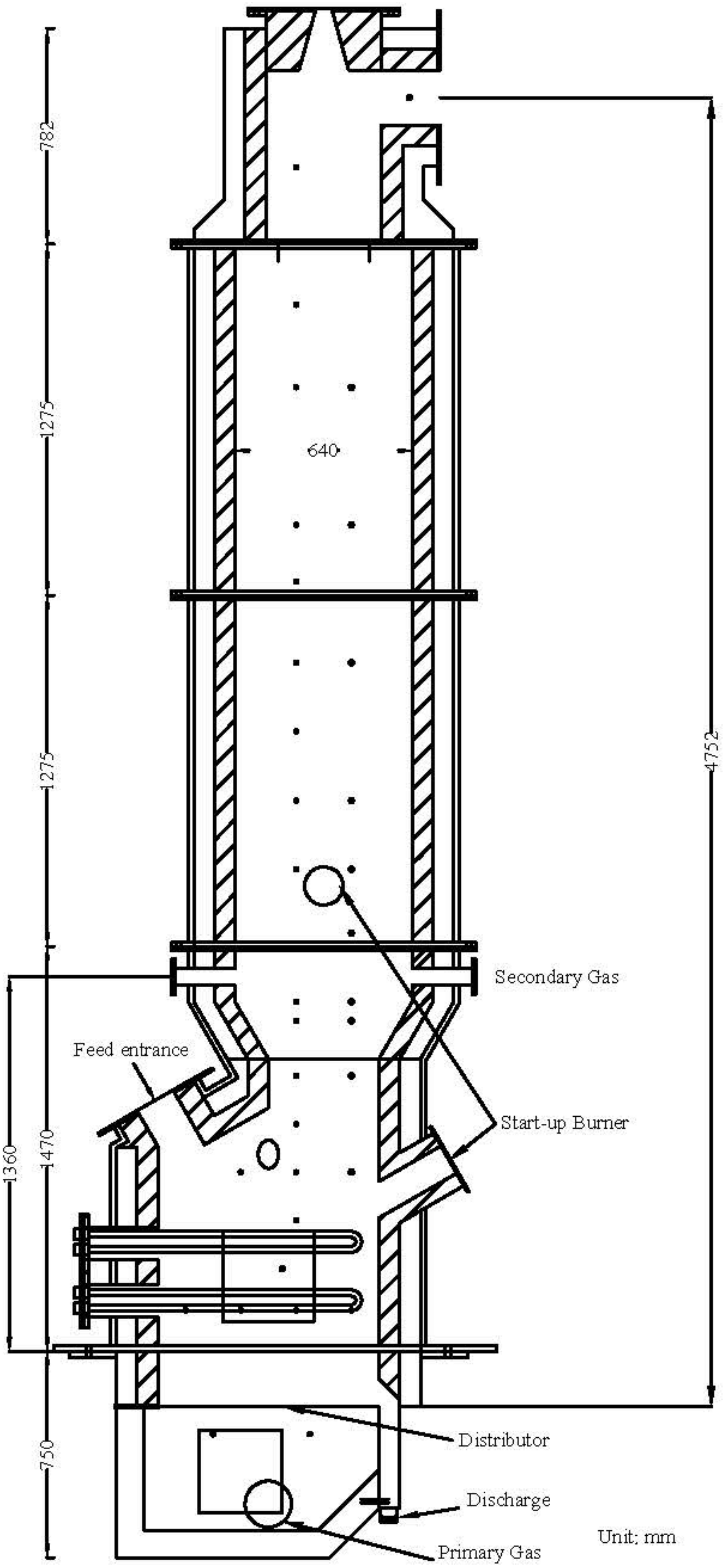

Fig. 2. Configuration of the bubbling fluidized-bed combustor.

into a flue gas treatment system including quench tower, baghouse and scrubber. The high-temperature flue gas flows firstly through the quench tower which enables the flue gas to lower the temperature to 150°C for an instant. Then most of particulate matters in the low-temperature flue gas were removed after the flue gas flows through the baghouse. Subsequently the flue gas was fed into the scrubber where water was atomized into drops and sprayed with a water flow rate of 50 L min^{-1}. Acid gases, such as SO_2 and HCl, were washed out from the flue gas. Then the flue gas was heated up to 120°C after flowing through a reheater and finally emitted into the atmosphere.

Data Acquisition

The PCDD/Fs content of the fly ash collected from the bottom of cyclone and the bottom of baghouse were sent to the ITRI (Industrial Technology Research Institute of Taiwan) for analysis, which was conducted using a high-resolution gas chromatography/high-resolution mass spectrometry/data system (HRGC/HRMS) (EPA Method 8290A). The HRGC and HRMS equipment were an Agilent 6890N and Thermo Finnigan MAT 95XL, respectively. The components of the flue gas, including CO, O_2, and NO_x, were analyzed using HORIBA-PG250 gas analyzers. Specifically, NO_x was analyzed following the chemiluminescence detection method, with full-scale repeatability and linearity of ±0.5% and ±2.0%, respectively. To reduce the influence of the memory effect, the sand was replaced in each experiment, and the amount of air used to blow away the fly ash in the system was increased.

Experimental Conditions

To characterize the combustion of the feeding material in the combustor, a combustion fraction model based on oxygen consumption was developed. The combustion fraction can be calculated using the following equation:

$$Y_i = \frac{Q_{in,O_2} - Q_{out,O_2}}{Q_t} \times 100\%, \tag{1}$$

where $Q_{in,O2}$ and $Q_{out,O2}$ are the oxygen flow rate of the inlet and outlet in each zone ($\text{Nm}^3\ \text{min}^{-1}$), respectively, and Q_{TO} is the total amount of oxygen consumed by the combustor ($\text{Nm}^3\ \text{min}^{-1}$).

The experimental conditions for all tests are shown in Table 3. The bed temperature was fixed at 750°C, and the feeding rate was 35 kg h^{-1}. The freeboard wall temperatures were fixed at 800 and 900°C using an on-off controlled diesel burner. To minimize the cross effects of the operating parameters, all experiments were conducted at fixed primary and secondary gas flow rates of 3 and 1 $\text{Nm}^3\ \text{min}^{-1}$, respectively.

RESULTS AND DISCUSSION

The experimental data for the PCDD/Fs concentration of fly ash obtained from the combustion of various feeding materials in this study are shown in Table 4. The concentration of PCDD/Fs in the fly ash collected from the baghouse ranged from 21.937 to 48.722 ng g^{-1}, while that of the fly ash collected from the cyclone ranged from 0.025 to 0.284 ng g^{-1}. The I-TEQ values of fly ash collected from the baghouse and cyclone ranged from 2.13 to 3.42 and 0.0012 to 0.0193 ng I-TEQ g^{-1}, respectively.

The experimental data shown in Table 4 indicate that the dioxin content of the fly ash from the cyclone was extremely low, which is similar to the results obtained by Lundin and Marklund (2007). The results of Chang and Huang (1999) also indicated that the dioxin concentration of fly ash from a baghouse is higher than that from a cyclone, and they found the PCDD/PCDF ratio of ash collected from the cyclone to be higher than that of the fly ash collected from the boiler and baghouse. This can be attributed to the dioxin formation mechanism. The condensation of a heterogeneous precursor yields more PCDDs than PCDFs (Huang and Buekens, 1995), whereas *de novo* synthesis yields more PCDFs than PCDDs. It is believed that the *de novo* synthesis of PCDD/Fs occurs in the presence of oxygen at temperatures of approximately 250–400°C (Vogg *et al.*, 1987; Milligan and Altwicker, 1993; Cunliffe and Williams, 2009). High-temperature flue gas and particles are separated by a cyclone, resulting in fly ash with a very low concentration of dioxins, and *de novo* synthesis is reduced due to the environment without flue gas. Song *et al.* (2008) found that under an anoxic or inert atmosphere at 300–600°C, the dioxin content decreases through de-chlorination and destruction. In this study, the ash collected at the bottom of the cyclone was located in a gas flow stagnation zone that received no downward flue gas flow. Owing to the extremely

Table 3. Experimental conditions.

Operating parameter	Conditions
Feeding material	Pelletized sawdust
Feeding rate (kg hr^{-1})	35
Excess oxygen ratio (%)	60
Bed temperature (°C)	750
Freeboard temperature (°C)	800, 900
Primary air flow rate ($\text{Nm}^3\ \text{min}^{-1}$)	3
Secondary air flow rate ($\text{Nm}^3\ \text{min}^{-1}$)	1
Bed material	Silica sand
Apparent density (kg m^{-3})	2600
Average particle size of the bed material (μm)	506

Table 4. PCDD/Fs concentrations and I-TEQ values of the fly ash.

Fly ash	concentration	B1	B2	C1	C2	C3	C4	S1	S2	S3	S4
cyclone (800°C)	PCDD/Fs (ng I-TEQ g^{-1})	0.0037	0.0012	0.0019	0.0015	0.0021	0.0018	0.0040	0.0193	0.0028	0.0032
	PCDD (ng g^{-1})	0.087	0.035	0.111	0.020	0.254	0.017	0.020	0.022	0.100	0.025
	PCDF (ng g^{-1})	0.050	0.028	0.058	0.032	0.030	0.023	0.033	0.087	0.064	0.029
	PCDD/Fs (ng g^{-1})	0.137	0.063	0.169	0.052	0.284	0.04	0.053	0.109	0.164	0.054
	PCDF/PCDD	0.6	0.8	0.5	1.6	0.1	1.3	1.6	3.9	0.6	1.2
cyclone (900°C)	PCDD/Fs (ng I-TEQ g^{-1})	0.0015	0.0015	0.0013	0.0017	0.0073	0.0026	0.0014	0.0049	0.0028	0.0062
	PCDD (ng g^{-1})	0.012	0.012	0.011	0.018	0.014	0.007	0.013	0.032	0.021	0.025
	PCDF (ng g^{-1})	0.013	0.013	0.014	0.016	0.046	0.018	0.017	0.039	0.019	0.050
	PCDD/Fs (ng g^{-1})	0.025	0.025	0.025	0.034	0.06	0.025	0.03	0.071	0.04	0.075
	PCDF/PCDD	1.0	1.0	1.3	0.9	3.4	2.4	1.3	1.2	0.9	2.0
bag house (800°C)	PCDD/Fs (ng I-TEQ g^{-1})	2.13	2.41	2.46	2.72	3.08	2.41	3.00	3.11	2.75	2.61
	PCDD (ng g^{-1})	6.998	8.810	10.879	12.938	13.077	10.194	10.236	11.464	11.433	10.408
	PCDF (ng g^{-1})	15.600	19.600	24.284	27.731	31.697	23.582	24.643	27.234	25.997	24.583
	PCDD/Fs (ng g^{-1})	22.598	28.41	35.163	40.669	44.774	33.776	34.879	38.698	37.43	34.991
	PCDF/PCDD	2.2	2.2	2.2	2.1	2.4	2.3	2.4	2.4	2.3	2.4
bag house (900°C)	PCDD/Fs (ng I-TEQ g^{-1})	2.03	2.98	2.44	3.42	2.89	2.80	2.74	3.38	2.48	2.79
	PCDD (ng g^{-1})	6.991	12.463	10.422	13.623	13.059	11.519	9.754	12.837	10.446	10.813
	PCDF (ng g^{-1})	14.946	27.100	23.072	35.099	30.973	23.862	21.414	30.372	22.871	25.449
	PCDD/Fs (ng g^{-1})	21.937	39.563	33.494	48.722	44.032	35.381	31.168	43.209	33.317	36.262
	PCDF/PCDD	2.1	2.2	2.2	2.6	2.4	2.1	2.2	2.4	2.2	2.4

low dioxin and PCDD content of the ash, we can state that no *de novo* synthesis occurred in this area, and the combustion in the combustor was highly efficient. Chang and Huang (1999) found the dioxin concentration of cyclone ash to be lower than that of baghouse ash, and the PCDD > PCDF indicated that most of the dioxin concentration originated from a precursor reaction. In this study, the results obtained at 800°C were similar to those obtained by Chang and Huang (1999). When the freeboard temperature increased from 800 to 900°C, which was caused by the enhanced Deacon reaction of chlorine with a content exceeding 1% (Wikström *et al.*, 1996), the I-TEQ values of the fly ash collected from the baghouse for the combustion of B2 increased from 2.41 to 2.98 ng I-TEQ g^{-1}. This finding was consistent with the results obtained by Griffin (1986).

When the freeboard temperature increased from 800 to 900°C, the PCDD/Fs concentration of fly ash from the cyclone decreased from 0.136 to 0.025 ng g^{-1} (0.0037–0.0015 ng I-TEQ g^{-1}) for the combustion of B1, and from 0.063–0.025 ng g^{-1} (0.0012–0.0015 ng I-TEQ g^{-1}) for the combustion of B2. The ratio of PCDD to PCDF was approximately 1, as shown in Table 4. This result was also consistent with our expected observations. No *de novo* synthesis occurred at the bottom of the cyclone, and the increase in temperature resulted in more complete combustion, thus decreasing the PCDD/Fs concentration.

Effect of Chlorine Content on PCDD/Fs in the Fly Ash Collected from the Baghouse

Because the dioxin concentration of the fly ash from the cyclone was extremely low, our discussion focuses on the fly ash baghouse. The concentrations of PCDD/Fs in the fly ash collected from the baghouse were 22.60 ng g^{-1} and 2.13 ng I-TEQ g^{-1} after the combustion of B1, while those after the combustion of B2 were 28.41 ng g^{-1} and 2.41 ng I-TEQ g^{-1}. The results indicate that the formation of PCDD/Fs increased with the chlorine content, which was consistent with our expectations.

Table 5 shows that the copper content of B1 and B2 was 265 and 324 ppm, respectively. The production of chlorine gas was low since the catalyst was insufficient, as shown in formula (2). Even with the combustion of a feeding material with high chlorine content, such as B2, there was no significant difference in the dioxin production in the case of either B1 or B2. To evaluate the role of particulate organic carbon in the formation of PCDD/PCDF in fly ash, Stieglitz *et al.* (1989) investigated the correlation between PCDD/Fs and Cu(II) by adding copper content of 0, 0.08, 0.24, and 0.4%, and their results showed that only small concentrations of PCDD (4.5 ng g^{-1}) and PCDF (22.6 ng g^{-1}) were produced without copper. The addition of 0.08% Cu(II) promoted the formation of PCDD at 100 ng g^{-1}, and PCDF at 760 ng g^{-1}. An increase in the copper concentrations to 0.24% and 0.4% caused a significant increase in the PCDD/F content. Mattila *et al.* (1992) found the addition of copper to lead to an increase in the formation of PCDD/Fs, especially PCDFs. According to the experimental data obtained from this study, the formation of dioxin is dependent not only on the chlorine content, but also on the copper content. A study conducted by Liu *et al.* (2019) had similar results. However, further study is required.

As the freeboard temperature increased from 800 to 900°C, the PCDD/Fs concentration of fly ash decreased from 22.60 to 21.94 ng g^{-1} (2.13 to 2.03 ng I-TEQ g^{-1}) for the combustion of B1 and increased from 28.41 ng g^{-1} to 39.56 ng g^{-1} (2.41 ng I-TEQ/g to 2.98 ng I-TEQ g^{-1}) for the combustion of B2. The PCDD/Fs concentration in the fly ash decreased with an increase in the freeboard temperature for the combustion of B1, but it increased with an increase in the freeboard temperature for combustion of B2.

Typically, an increase in temperature makes the combustion more complete and decreases the formation of dioxin. As the freeboard temperature is increased, the products of incomplete combustion (PICs) are reduced, resulting in a decline in the carbon source required for PCDD/Fs formation. The results of this test showed that the dioxin concentration in the fly ash from B2 increased as the freeboard temperature increased, which can be attributed to the release of the large amount of hydrogen chloride released into the furnace to increase the chlorine content beyond 1%. As the temperature increases, the Deacon reaction also increases (Liu *et al.*, 2000),

$$2\mathrm{HCl} + 1/2\,\mathrm{O}_2 \xrightarrow{\mathrm{Cu}} \mathrm{Cl}_2 + \mathrm{H}_2\mathrm{O}, \qquad (2)$$

Table 5. Copper content of the fly and bottom ash.

feeding material	Cu (ppm) in bottom ash	Cu (ppm) in fly ash (at 800°C)	Cu (ppm) in fly ash (at 900°C)
B1 (Cl = 0.568%)	ND	265	323
B2 (Cl = 1.136%)	ND	324	346
C1 (Cl = 0.568% S = 0.4%)	ND	359	366
C2 (Cl = 0.568% S = 0.4% Ca = 1.62%)	61	400	371
C3 (Cl = 1.136% S = 0.8%)	10	647	430
C4 (Cl = 1.136% S = 0.8% Ca = 3.25%)	3	405	418
S1 (Cl = 0.568% S = 0.8%)	17	415	424
S2 (Cl = 0.568% S = 0.8% Ca = 2.61%)	20	374	395
S3 (Cl = 1.136% S = 1.6%)	33	360	380
S4 (Cl = 1.136% S = 1.6% Ca= 5.23%)	22	338	395

ND: non-detected.

and the enhancement of *de novo* synthesis caused by the increase in chlorine results in a significant increase in the production of PCDD/Fs. Liu *et al.* (2000) suggested that the optimum combustion condition for controlling molecular chlorine formation is to maintain the combustion temperatures in the freeboard at 650°C. However, the temperature of the secondary combustion chamber in the incinerator is 850°C, according to the regulations set forth by the Taiwan EPA.

Effect of Sulfur Content on PCDD/Fs in the Fly Ash Collected from the Baghouse

Table 2 shows that the S/Cl ratios were 0.781 for C1 and C3, and 1.562 for S1 and S3, respectively. Table 4 shows that the I-TEQ values of the fly ash for the combustion of C1 and C3 at a freeboard temperature of 800°C were 2.46 and 3.08 ng I-TEQ g^{-1}, respectively. The I-TEQ values in the fly ash obtained from the combustion of S1 and S3 at a freeboard temperature of 800°C were 3.00 and 2.75 ng I-TEQ g^{-1}, respectively, and the experimental data obtained from this test show that the effect of the S/Cl ratio on the reduction of PCDD/Fs was not obvious.

Ogawa *et al.* (1996) indicated that SO_2 reacts with Cu(II) to reduce the ability of copper to catalyze the production of Cl_2 while inhibiting the formation of PCDD/Fs.

$$CuO + SO_2 + 1/2\ O_2 \rightarrow CuSO_4 \qquad (3)$$

It is believed that pyrite may react with copper compounds, such as copper chloride and oxide, to form copper sulfate (Takaoka *et al.*, 2005; Pekarek *et al.*, 2007). The reduction in the number of copper ions also reduces the Deacon reaction, and the decrease in chlorine production reduces the formation of dioxin. The research by Goldin *et al.* (1992) demonstrated that the copper content in the fly ash from incinerating municipal solid waste can be as high as 0.17%. In this study, we found that the inhibitory effect of sulfur was not as expected, which may be attributed to the low copper content in the feeding material. Further study is required to verify this.

As the freeboard temperature was increased from 800 to 900°C, the I-TEQ values of the fly ash collected from the baghouse after the combustion of C1, C3, S1, and S3 decreased from 2.46 to 2.44, 3.08 to 2.89, 3.00 to 2.74, and 2.75 to 2.48 ng I-TEQ g^{-1}, respectively. The I-TEQ values of the fly ash collected from the baghouse decreased with increases in the freeboard temperature. Griffin (1986) proposed a mechanism involving sulfur as an inhibitor of dioxin formation and suggested that SO_2 is attacked by Cl_2 to form SO_3 and HCl in the presence of H_2O. Similar results were also obtained by Liu *et al.* (2000).

$$Cl_2 + H_2O + SO_2 \rightarrow SO_3 + 2HCl \qquad (4)$$

Fig. 3 shows the measured SO_2 emissions and theoretical maximum SO_2 values calculated using the data presented in Table 1. According to Fig. 3, the theoretical maximum SO_2 concentration was much higher than the observed concentration. As the sulfur content increased, the theoretical calculated and experimental values of SO_2 increased. The chlorine content of C3 was higher than that of S1, and the SO_2 concentration of the flue gas from the combustion of C3 was lower than that of S1. This can be attributed to the consumption of SO_2 as it reacted with chlorine, as shown in Eq. (4). According to the data shown in Table 6, as the freeboard temperature was increased from 800 to 900°C, the concentration of SO2 in the flue gas from the combustion of C1, C3, S1, and S3 decreased from 47 to 24 ppm, 146 to 131 ppm, 286 to 229 ppm, and 695 to 618 ppm, respectively. This decrease in the SO_2 emissions can be attributed to the consumption of SO_2 by the reaction with Cl_2, as shown in Eq. (4). The experimental data obtained in this study agreed with the phenomena indicating that sulfur can

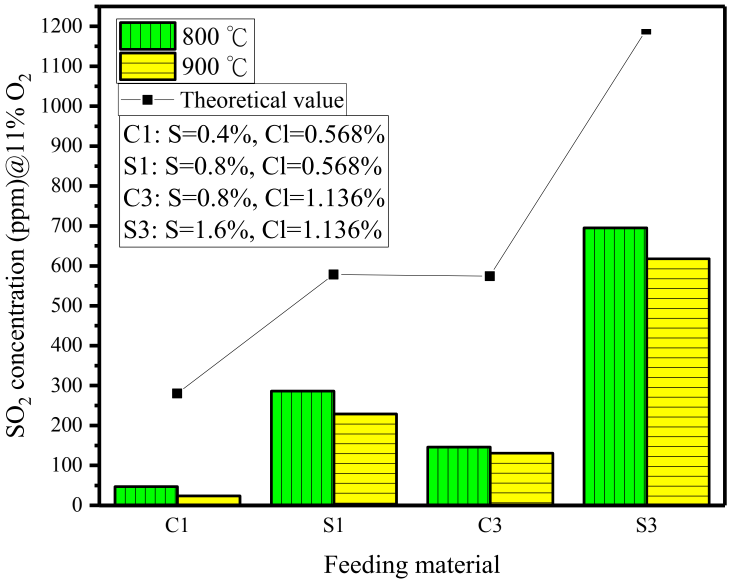

Fig. 3. SO_2 emissions from the combustion of various feeding materials without the addition of calcium at various freeboard temperatures.

Table 6. Flue gas emissions and combustion efficiencies of the various feeding materials.

	B1	B2	C1	C2	C3	C4	S1	S2	S3	S4
800°C										
CO (ppm)	20	19	26	43	45	36	43	40	60	55
CO_2 (vol%)	9.0	9.1	8.9	8.9	8.8	8.9	9.1	9.0	8.9	9.3
SO_2 (ppm)	ND	ND	47	14	146	25	286	17	695	50
Combustion efficiency (%)	99.86	99.78	99.78	99.70	99.70	99.52	99.57	99.65	99.76	99.50
900°C										
CO (ppm)	11	6	7	9	22	9	10	9	18	23
CO_2 (wt%)	8.8	8.9	8.8	8.8	8.6	8.7	8.8	8.8	8.6	9.1
SO_2 (ppm)	ND	ND	24	7	131	20	229	12	618	45
Combustion efficiency (%)	99.96	99.94	99.94	99.89	99.94	99.83	99.90	99.90	99.92	99.87

ND: none detected.

All the pollutants were calibrated to residual oxygen at an 11% dry base.

inhibit the formation of dioxin at higher temperatures.

The lack of chlorine caused by the inhibition of SO_2 is not conducive to the *de novo* reaction, and thus reduces the production of dioxin. It was expected that the formation of dioxin would decrease with increases in the freeboard temperature. When the freeboard temperature was increased from 800 to 900°C, the I-TEQ values of the fly ash from the combustion of C3 and S3 decreased from 3.08 to 2.89 ng I-TEQ g^{-1} and 2.75 to 2.48 ng I-TEQ g^{-1}, respectively. The inhibitory effect of sulfur with a higher S/Cl ratio (S3) on dioxin formation was higher than that with a low S/Cl ratio (C3).

Effect of Calcium Content on PCDD/Fs in the Fly Ash Collected from the Baghouse

The results reported by Matsukata *et al.* (1996) indicated that the chlorination reaction of calcium oxide was inhibited, and the sulfurization reaction was enhanced when desulfurization and de-chlorination occurred simultaneously. Tagashira *et al.* (1999) conducted an experiment on desulfurization and de-chlorination at a ratio of Ca/(S + 0.5Cl) = 2, and their results demonstrated that the added calcium hydroxide can simultaneously adsorb hydrogen chloride and sulfur dioxides, and thus reduce dioxin production. Experimental data regarding the effects of calcium addition in the presence of both sulfur and chlorine on dioxin formation are still required. In this study, the effect of the simultaneous addition of sulfur and calcium on dioxin formation in fly ash was studied with a Ca/(S + 0.5Cl) ratio of 1.98.

Table 2 shows the calcium content of C2, C4, S2, and S4 was 1.62%, 3.25%, 2.61%, and 5.23%, respectively. Fig. 4 shows the emissions of SO_2 with various calcium and chlorine contents added to the feeding material, where it can be seen that they were significantly reduced with the addition of a calcium compound, which was consistent with our expectations. When calcium and sulfur were added, desulfurization and dechlorination reactions occurred simultaneously. Lin and Chyang (2016) found that chlorination is significantly suppressed as chloride begins to vigorously react with SO_2, leading to the indirect enhancement of sulfation and the re-release of HCl into the gas phase, as shown in Eq. (5).

$$CaCl{\cdot}H_2O + SO_2 + O_2 = CaSO_4 + HCl \tag{5}$$

At a freeboard temperature of 800°C and chlorine content below 1%, the I-TEQ value of the fly ash from the combustion of C2 (Ca = 1.62) was higher than that of C1 (Ca = 0), and that of the fly ash from the combustion of S2 (Ca = 2.61) was higher than that of S1 (Ca = 0). For chlorine content higher than 1%, the I-TEQ value of the fly ash from the combustion of C4 (Ca = 3.25%) was lower (22%) than that of C3 (Ca = 0), and that of the fly ash from the combustion of S4 (Ca = 5.23%) was lower (5%) than that of S3 (Ca = 0). The results obtained in this study indicate that a calcium content of 3.25% or more inhibits the formation of dioxins, which agrees with the results of a study conducted by Xie *et al.* (2000). Qin *et al.* (2017) indicate that the increase of CaO/S was beneficial for suppressing PAHs formation and capturing SO_2. With the injection of more limestone into the combustor, it was expected that more hydrogen chloride would be captured by the limestone. It was then expected that the formation of PCDD/Fs would reduce remarkably. If the amount of calcium added is insufficient, dechlorination will be decreased, resulting in an increase in dioxin formation.

Fig. 5 shows the I-TEQ values of the fly ash collected from the baghouse from the combustion of various feeding materials at different freeboard temperatures. As the freeboard temperature was increased from 800 to 900°C, the I-TEQ values of the fly ash for the combustion of C2 increased from 2.72 to 3.42, and those of C4, S2, and S4 increased from 2.41, 3.11, and 2.61 to 2.80, 3.38, and 2.79, respectively. High temperatures reduced the ability of calcium to adsorb HCL, resulting in an increase in dioxin formation. The results of Piao *et al.* (1998) indicate that the best temperature for hydrogen chloride removal is 600°C, and a removal rate of 70% can even be obtained at temperatures higher than 900°C. The results reported by Corella *et al.* (2008) showed that the reaction temperature for the CaO adsorbent should not exceed 772°C. If the temperature exceeds 800°C, which is above the melting point of the product, the activity of CaO-based solids is very low.

When both calcium and sulfur were added to the feeding materials, desulfurization and dechlorination reactions

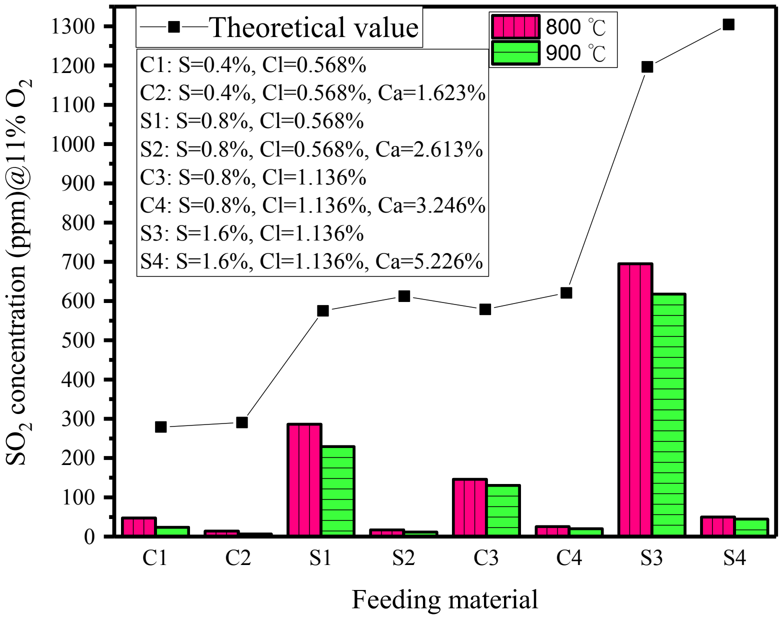

Fig. 4. SO_2 emissions from the combustion of various feeding materials with/without the addition of calcium at various freeboard temperatures.

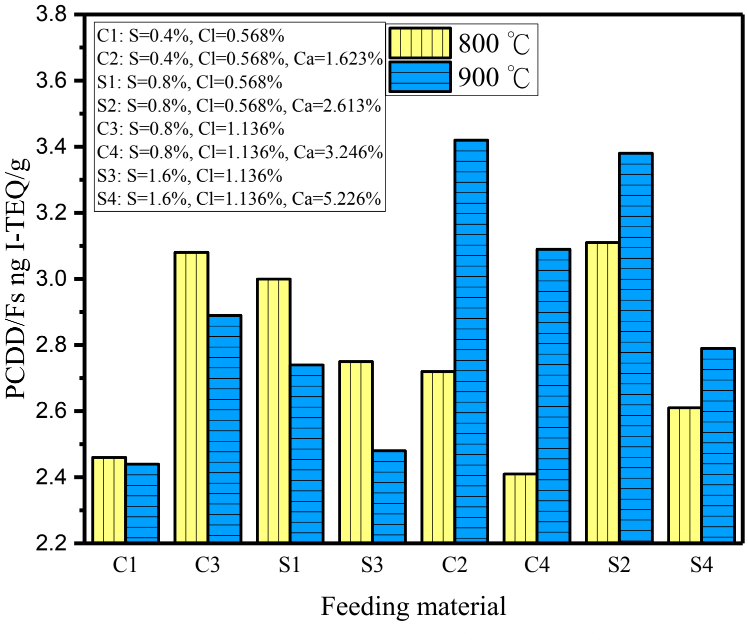

Fig. 5. I-TEQ values in the fly ash from the combustion of various feeding materials at different freeboard temperatures.

occurred simultaneously. Owing to the competition between desulfurization and dechlorination, it was expected that SO_2 would be consumed by reacting with CaO to form $CaSO_4$, thus reducing their ability to inhibit dioxin formation. The experimental data indicated that the dioxin content of fly ash from the combustion of a feeding material with a sufficient calcium content could still be reduced. As the freeboard temperature was increased from 800 to 900°C, the ability of calcium to adsorb HCl decreased, resulting in an increase in the dioxin content of the fly ash collected from the baghouse. Owing to the inhibitory effects of sulfur, the I-TEQ values for C4 and S4 were lower than those of B2, which did not receive calcium and sulfur.

Profiles of the Homologs and Congeners of PCDD/Fs in the Fly Ash Collected from the Baghouse

Fig. 6 shows the congener profiles of the seventeen PCDD/Fs. Each congener was normalized by the sum of the seventeen PCDD/Fs, and the profiles obtained in each experiment were similar. Fig. 6(a) shows that the most prevalent congeners in the ash were 1,2,3,4,6,7,8-HpCDF (19.7–23.4%), OCDD (12.9–17.3%), and OCDF (9.1–

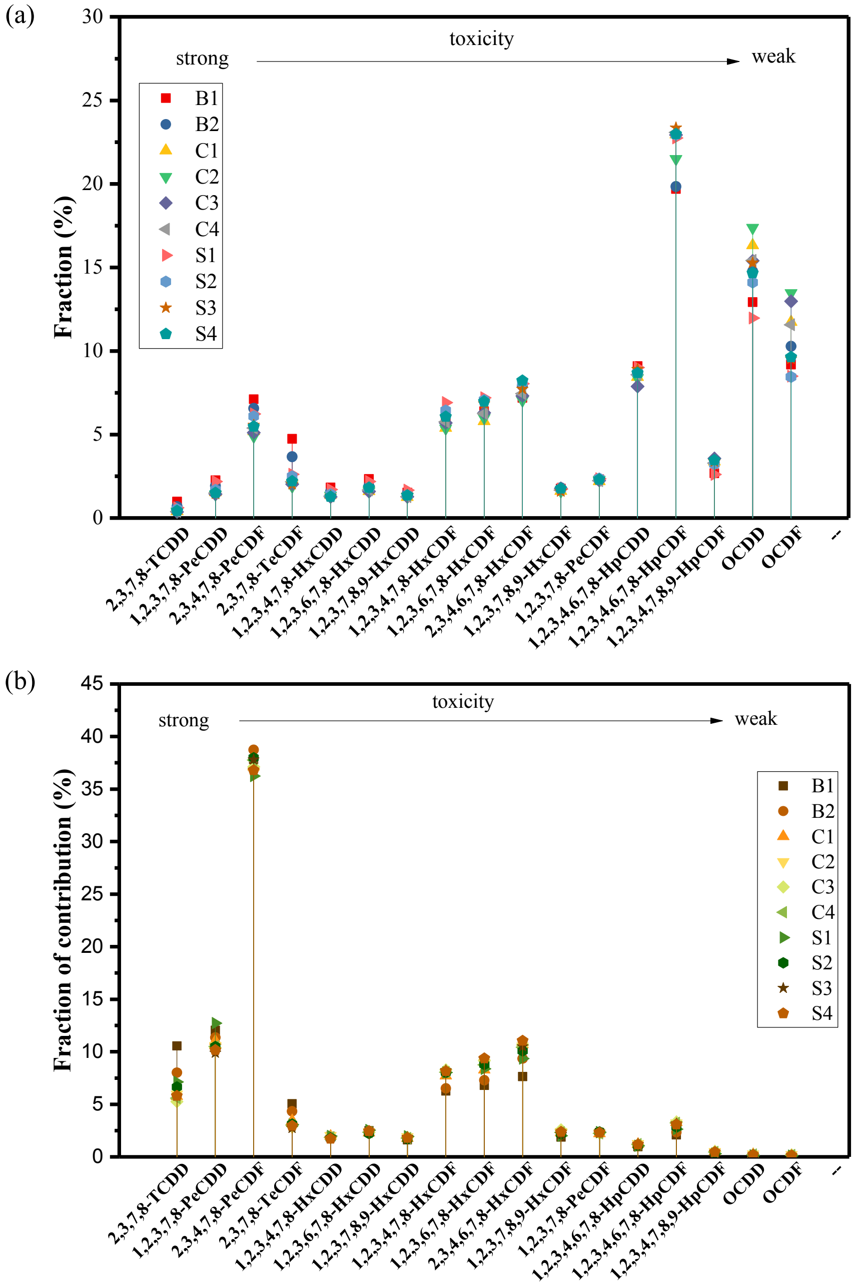

Fig. 6. Congeners of the 2,3,7,8-substituted PCDD/Fs of the fly ash obtained from the combustion of various feeding materials at a freeboard temperature of 800°C. (a) Fraction of PCDD/Fs and (b) Fraction of contribution to I-TEQ values.

13.5%). HxCDF and HpCDF were the two dominant homologs, results which were similar to those of Liu *et al.* (2017). From the viewpoint of the contribution to the total I-TEQ values (as shown in Fig. 6(b)), the greatest contributor was 2,3,4,7,8-PeCDF (36.72–38.66%), which was a similar finding to that of other researchers (Han *et al.*, 2017; Hsieh *et al.*, 2018; Lin *et al.*, 2018; Zhan *et al.*, 2018).

The results of this study were compared in Fig. 7 with those obtained from previous studies (Cains *et al.*, 1997; Shin and Chang, 1999; Moon *et al.*, 2002; Hsi *et al.*, 2007; Lundin and Marklund, 2008; Chang *et al.*, 2011). The figure shows the distribution of the PCDD/Fs homologs from the combustion of various feeding materials. According to the data shown in Fig. 7, the distribution of the PCDD homologs was dominated by OCDD, while the dominant contributors to the PCDF distribution varied. Other than the combustion of fuels, this may have been caused by the injection of activated carbon into the flue gas for the purpose of incineration. In the absence of activated carbon, low-chlorinated PCDD and PCDF were not easily adsorbed by the fly ash in the baghouse, resulting in a high chloride bond distribution in PCDD and PCDF. After the injection of activated carbon, the concentration of low-chlorine bonds adsorbed on the activated carbon increased. The distribution of the PCDF homologs changed significantly due to *de novo* synthesis (PCDF > PCDD) (Vermeulen *et al.*, 2014).

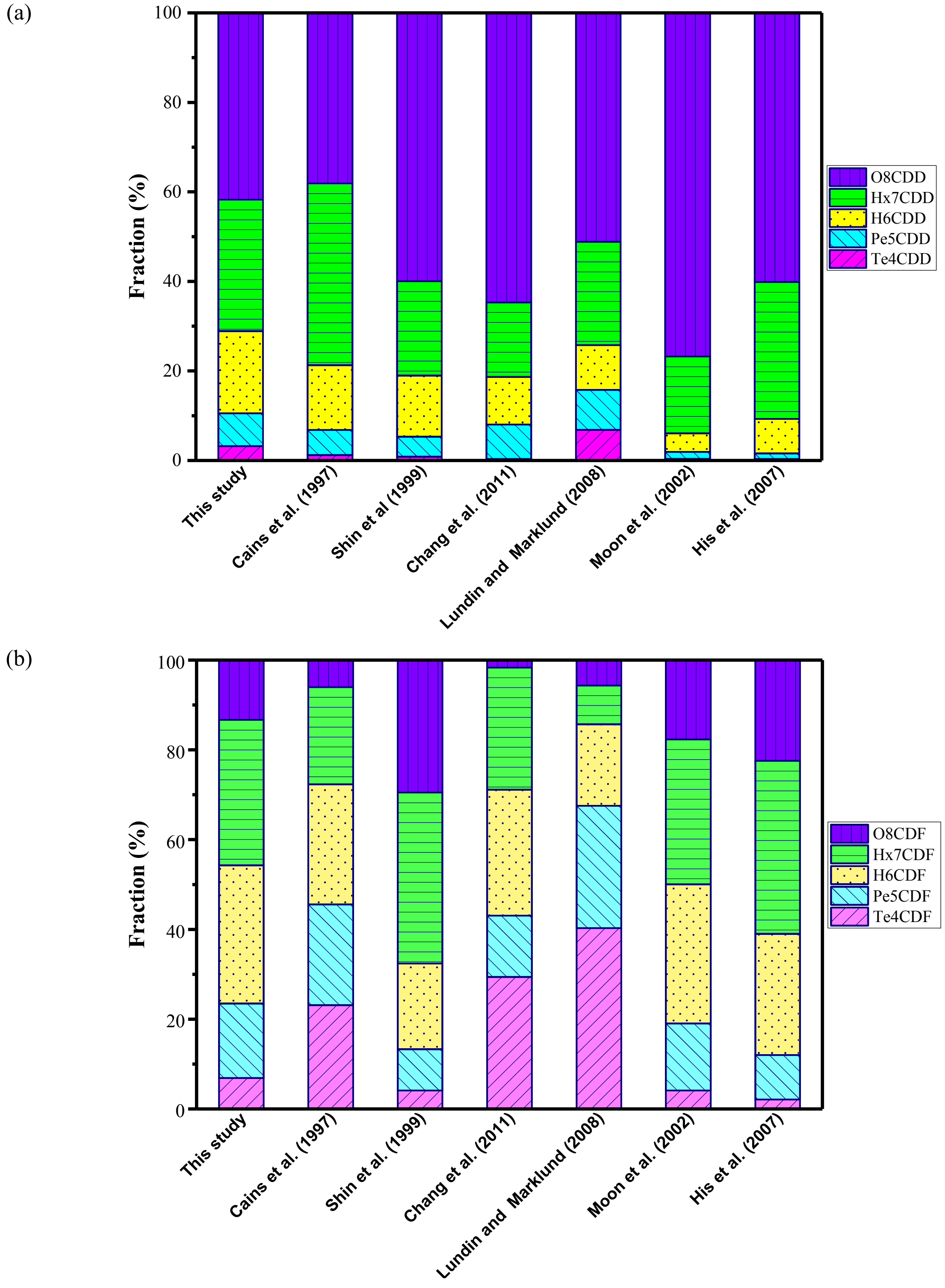

Fig. 7. Comparison of the distribution of PCDD/F homologs in fly ash based on the results of various studies. (a) PCDD and (b) PCDF.

Some researchers have reported a linear correlation between the 2,3,4,7,8-PeCDF concentration and I-TEQ values (Fiedler *et al.*, 2000; Kato and Urano, 2001; Iino *et al.*, 2003). A positive correlation was observed in this study, as shown in Fig. 8, which was similar to the result of Kato and Urano (2001).

Influence of Flue Gas Emissions and Residual Carbon on PCDD/Fs

As the combustion temperature of the freeboard was increased, it was expected that the combustion efficiency would increase, resulting in lower carbon monoxide emissions, as shown in Table 6. The results of a regression

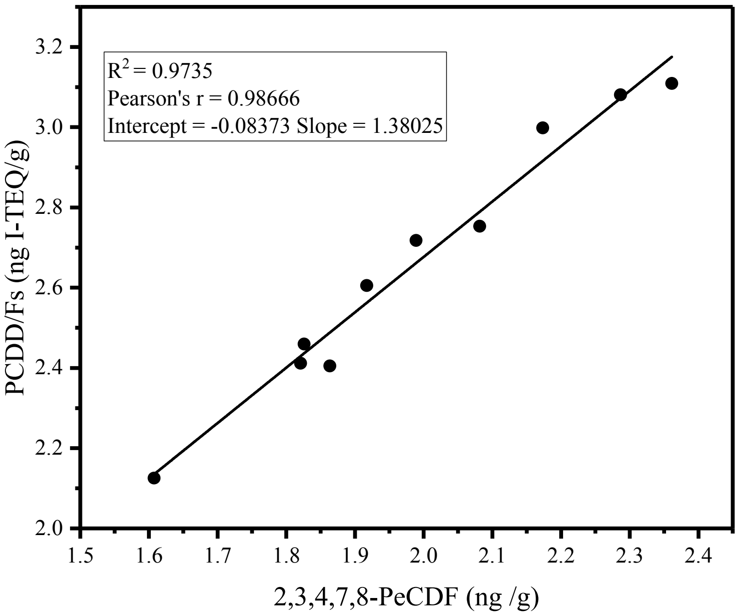

Fig. 8. Relationship between the concentration of 2,3,4,7,8-PeCDF and the I-TEQ values.

analysis (not shown in this report), carbon monoxide and dioxide did not correlate with the concentrations of PCDD/Fs in the fly ash. Lenoir *et al.* (1991) observed no relationship between PCDD/Fs and CO in a pilot-scale fluidized-bed incinerator under normal operating conditions with CO levels ranging from 2–210 mg m^{-3}. Yan *et al.* (2006) also demonstrated that there is no direct correlation between the PCDD/Fs levels and CO.

Brna and Kilgroe (1992) suggested that reliable predictions can be made for CO concentrations above 150–200 ppm, but, below this range, the discrepancy between observed and predicted values is very large. Kaune *et al.* (1994) indicated that the correlation between PCDD/Fs and CO is sustained under poor combustion conditions. As soon as the incinerator operating conditions are optimized, other factors that affect the emission of PCDD/Fs become more important. From the data shown in Table 6, the CO emissions in this study were very low, at < 100 ppm. This may be a reason for the lack of a correlation between dioxin and CO emissions.

CONCLUSIONS

The main purposes of this study were to investigate the effects of sulfur and calcium content on the concentration of dioxin in fly ash from FBC. The conclusions are as follows:

1. The concentration of dioxins in the fly ash collected from the cyclone (0.025–0.284 ng g^{-1}) was much lower than that of the fly ash collected from the baghouse (21.937–48.722 ng g^{-1}), and lower than the standard value of 1 ng/g. *De novo* synthesis did not occur at the bottom of the cyclone, and dioxin was mainly derived from precursors. The PCDD/Fs of the fly ash from the baghouse were mainly formed through *de novo* synthesis.
2. The increase in chlorine content from 0.568 to 1.136 wt% resulted in the increase 27.4% of PCDD/Fs in the fly ash collected from the baghouse. From the data obtained from this study, we can state that the amount of dioxins formed in the baghouse is dependent not only on the chlorine content of the feeding material, but also on the copper content.
3. The inhibitory effect of sulfur on dioxin formation is not clear and can be attributed to the lack of copper (average 387 ppm), as it did not result in a significant decrease in the formation of dioxins.
4. When both calcium and sulfur were added to the feeding materials, desulfurization inhibited de-chlorination, and a specific amount of calcium was required to reduce the formation of dioxins in the fly ash. The adsorption ability of calcium was decreased as the temperature increased from 800 to 900°C, resulting in an increase in the dioxin content (average 10%) of the fly ash collected from the baghouse.
5. From the viewpoint of the contribution of I-TEQ g^{-1}, the dominant contributor was 2,3,4,7,8-PeCDF since a positive relationship (R^2 = 0.9735) between the 2,3,4,7,8-PeCDF concentration and the I-TEQ values was obtained in this study.
6. In this study, no relationship was observed between the CO emissions and PCDD/Fs concentrations in the fly ash from the baghouse. This was attributed to the narrow range and low emissions of CO.

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