



Memory Effects of Polychlorinated Dibenzo-*p*-dioxin and Furan Emissions in a Laboratory Waste Incinerator

Jhong-Lin Wu^{1,2,3†}, Ta-Chang Lin^{1,2*}, Lin-Chi Wang⁴, Guo-Ping Chang-Chien^{5,6}

¹ Department of Environmental Engineering, National Cheng Kung University, 1, University Road, Tainan 70101, Taiwan

² Sustainable Environment Research Laboratories, National Cheng Kung University, 1, University Road, Tainan 70101, Taiwan

³ Environmental Resource and Management Research Center, National Cheng Kung University, 1, University Road, Tainan 70101, Taiwan

⁴ Department of Civil Engineering and Geomatics, Cheng Shiu University, 840, Chengching Road, Kaohsiung 83347, Taiwan

⁵ Super Micro Mass Research and Technology Center, Cheng Shiu University, 840, Chengching Road, Kaohsiung 83347, Taiwan

⁶ Department of Cosmetic and Fashion Styling, Cheng Shiu University, 840, Chengching Road, Kaohsiung 83347, Taiwan

ABSTRACT

Laboratory wastes are discharged from experimental, testing, or analysis processes, and contain various toxic chemical compounds with a high heating-value and a high chlorine content (> 9%). Elevated PCDD/F (polychlorinated dibenzo-*p*-dioxin and furan) emissions during start-up stages are caused by combustion of waste with high chlorine contents, incomplete combustion, and so called "memory effects". Even though the duration of cold start-up is short compared with the hours of continuous steady operation in a waste incinerator, its negative effects with regard to PCDD/F emissions on both human health and the environment cannot be neglected. A full-scale laboratory-waste incinerator which is operated for 10 days in each run and has 15 to 20 runs annually was investigated in this study. Eleven PCDD/F samples of stack flue gas were collected during the cold start-up periods (for 60.5 hrs). The gas temperature of the primary combustion chamber was above 850°C, and was maintained at between 850 and 900°C by injecting diesel fuel without waste feed. For first 1.5–7.5 hours, the PCDD/F concentration in the stack flue gas was as high as 0.656–1.15 ng I-TEQ/Nm³. Afterward, during hours 10.5–35.5 and 54.5–60.5, this reduced to 0.159–0.459 and 0.218–0.254 ng I-TEQ/Nm³, respectively. Based on principal component analysis (PCA) and the L/H ratio, the results revealed a higher L/H ratio (1.23) before hour 32, indicating that less chlorinated PCDD/F homologues (tetra and penta) dominated, while after hour 32 more chlorinated PCDD/F homologues (hexa, hepta and Octa) had a higher mass concentration and the L/H ratio fell to 0.42. These results indicate that the PCDD/F emissions during cold start-up were caused by memory effects and thermal desorption. Therefore, in order to reduce the PCDD/F emissions from the stack flue gas of waste incinerators, is highly recommended that a higher amount of activated carbon injection is used in front of the bag filters.

Keywords: PCDD/Fs; Stack flue gas; Laboratory waste; Incineration; Memory effect.

INTRODUCTION

Laboratory wastes containing various hazardous chemical reagents and reactants are often discharged from experimental, testing, or analysis processes. Typical contents

of laboratory liquid wastes include solvents, metal ions, anions, organics, oxidants, reductants, complexes ions, other impurities and water.

The PCDD/Fs are often found to from the emissions of thermal treatment processes and have been drawing extensive concern because of their significant toxicity and adverse effects on human health. Those PCDD/Fs with chlorines on the 2, 3, 7, and 8 positions are especially toxic (Rappe *et al.*, 1987; McKay, 2002). Due to their highly hydrophobic nature and long biological half-lives, PCDD/Fs tend to adsorb onto sludge solids, soil and accumulate mainly in the human fat tissue. PCDD/Fs have a potential toxicity that affects the reproductive, hormonal, and immunological systems, causing developmental defects, neurological deficits,

* Corresponding author.

Tel.: +886-6-209-3155; Fax: +886-6-275-2790

E-mail address: tachang@mail.ncku.edu.tw

† Corresponding author.

Tel.: +886-6-384-0136 ext. 230; Fax: +886-6-384-0143

E-mail address: p58001079@mail.ncku.edu.tw

and cancer in the general population (Chao *et al.*, 2007).

Several researchers studied the emission of waste incinerators during start-up stage and reported that higher concentration of PCDD/F emissions were observed during the cold start-up stage (Löthgren and van Bavel, 2005; Neuer-Etscheidt *et al.*, 2006; Wang *et al.*, 2007b). After an incinerator has been shut and cooled down to room temperature for several days for maintenance, a cold start-up is needed, which include the following procedures: (1) burning with the fuel oil at the maximum feed rate until the gas temperature of combustion chamber exceeds 850°C. (2) start and increase the waste feed rate until the design load is reached (Wang *et al.*, 2007b).

Several previous studies suggested that high-concentration PCDD/Fs formed during start-up stage are originated from the intermediate products of incomplete combustion (PICs). PICs formed at the high temperature zone, such as combustion chamber, was carried away by the flue gas or the fly ash and deposited on the walls in the cooling section (McKay, 2002; Neuer-Etscheidt *et al.*, 2006; Wang *et al.*, 2007b; Cunliffe and Williams, 2009). This is so called as "memory effects" of PCDD/Fs.

Other studies reported that the elevated PCDD/F concentrations during start-up stage can be attributed to the "memory effects", which are divided into "high temperature" and "low temperature" memory effects (Neuer-Etscheidt *et al.*, 2006; Li *et al.*, 2011). This phenomenon, so called "memory effect" (Zimmermann *et al.*, 2001; Weber *et al.*, 2002; Hunsinger *et al.*, 2003; Li *et al.*, 2011), occurred at a significant time lag, can occur in all kinds of incinerators with different cleaning devices such as semi-dry scrubbers, bag filters and wet scrubbers. Most studies reported that PCDD/Fs are slowly and continuously released later from the packing materials, which results in an elevated PCDD/F concentration that last for a few days or months (Weber *et al.*, 2002; Wilken *et al.*, 2003; Löthgren and van Bavel, 2005; Wang *et al.*, 2007b; Löthgren and Andersson, 2008; Cunliffe and Williams, 2009; Li *et al.*, 2011).

The formation of PCDD/Fs correlates positively with the contents of chlorine in the waste feed, particularly, when the chlorine contents in wastes are higher than the threshold value of 0.8%–1.1% (Wikström and Marklund, 2001; Wang *et al.*, 2003). However, when the chlorine contents was below the threshold value of 1%, there was almost no correlation between the chlorine contents and quantities of PCDD/Fs formed during the combustion process (Wikström *et al.*, 1996).

Elevated emissions of PCDD/Fs during start-up stage can be attributed to incomplete combustion, memory effects, and combustion of waste with high chlorine contents. In general, the period from heating up the burner to a stabilized operation condition is called the "start-up stage", which can be further divided to two types — cold and warm start-ups. For the batch-type incinerators, there is no distinct difference between the two types of start-ups.

By determining and identifying the profiles of PCDD/F during cold start-up stages, this study is the first time to look more insight on the memory effects, by running with diesel fuel only (Cl contents < 0.1%), without any waste

feed throughout the experiment. The objectives of this study were to describe the characteristics of PCDD/F concentrations, PCDD/F congener profiles in the matrixes (include stack flue gas, ash, wastewater of wet scrubber) of laboratory waste incinerator during the cold start-up stages and then the relating formation mechanism of PCDD/Fs were discussed.

EXPERIMENTAL

Laboratory Waste Incinerator

The Environment Resource and Management Research Center (ERMRC), was funded by the Minister of Education, Taiwan in 2000. In ERMRC, the annual treatment capacity of laboratory wastes was 615 tons in 2011, which included organic wastes (67%), inorganic wastes (33%). Three treatment processes, incineration, physicochemical, and plasma melting processes, are used to treat laboratory wastes and intermediates (such as ashes and sludge), respectively.

Table 1 showed that in the liquid laboratory wastes (1) the average chlorine contents was closed to 10%, which was more than 10 times higher than those in the municipal solid waste (MSW) (chlorine contents between 0.2 and 0.8%) (Wang *et al.*, 2003); (2) the moisture and heat value were above 30% and 3,300 kcal/kg, respectively; (3) the catalyzing metal (such as Cu, Fe, and Mn) contents were high (Tuan *et al.*, 2012).

Flow chart of incinerator configuration in this study is shown in Fig. 1. The incinerator is composed of two combustion chambers, two cooling towers, a bag filter unit, and a wet scrubber. The operation temperatures of primary and secondary combustion chamber are 850°C and 1050°C, respectively. The flue gas was cooled from 1050°C to 180°C by two cooling towers. Activated carbon was injected prior to the bag filters to remove both particulate matter (PM) and PCDD/Fs. A wet scrubber was installed to remove acids and decrease the temperature of the flue gas from 180°C to 80°C.

Stack, Ash and Wastewater Sampling for PCDD/Fs

The PCDD/F samples in stack flue gas during cold start-up stage were collected for analyses. At the first, the

Table 1. Typical composition of the laboratory liquid wastes.

	2010 (n = 100)	2011 (n = 150)
Heat value (kcal/kg)	3,617	3,331
Moisture (%)	31.1	41.0
Special gravity	0.93	0.99
Sulfur (mg/L)	582.6	1,740
Chlorine (%)	9.83	10.98
As (mg/L)	1.85	0.97
Hg (mg/L)	3.72	38.2
Cu (mg/L)	64.1	181
Cd (mg/L)	21.26	14.4
Cr (mg/L)	39.0	13.1
Ni (mg/L)	4.90	2.21
Pb (mg/L)	1.20	3.81
Zn (mg/L)	5.23	231

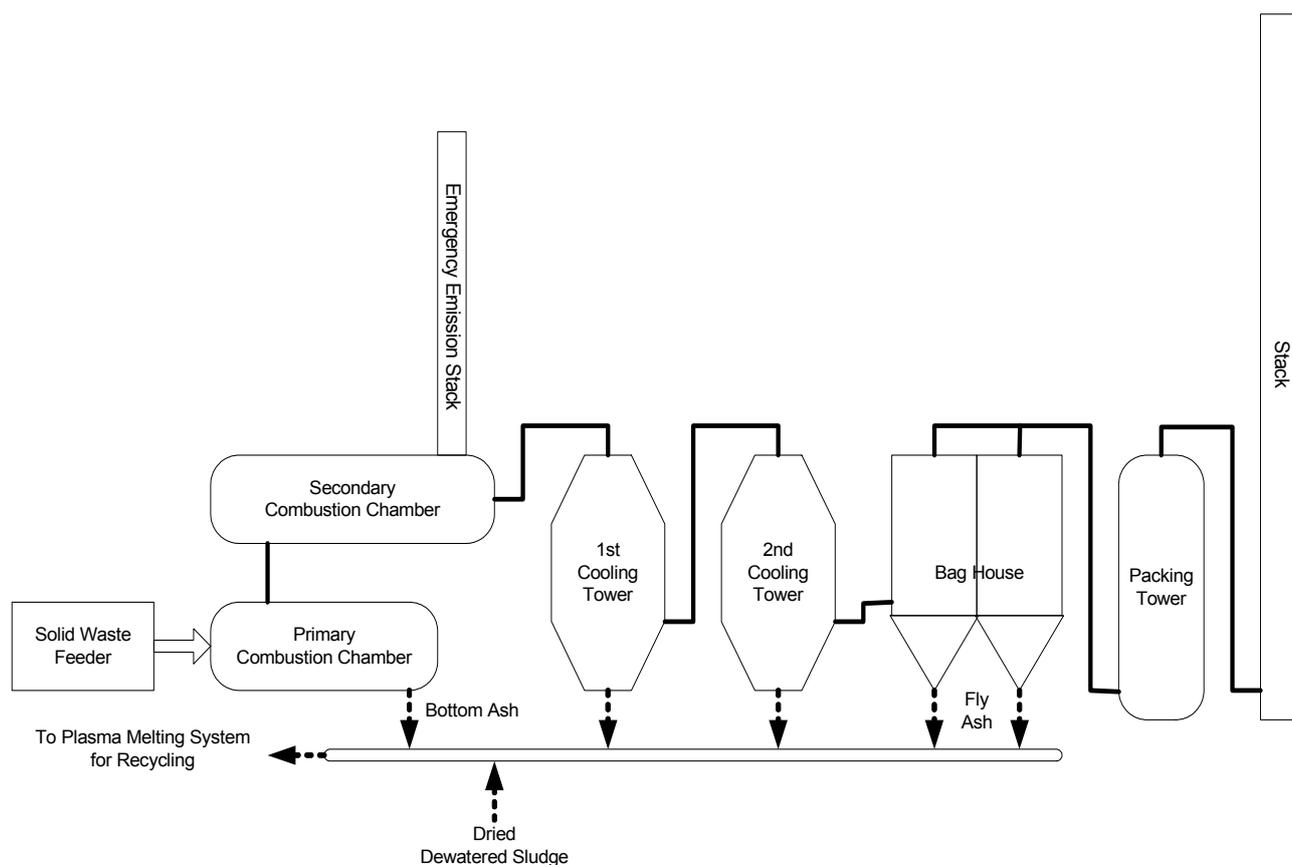


Fig. 1. Incineration process of a laboratory waste treat plant.

incinerator was preheated with diesel (19 L/h) only, and the activated carbon was injected (1.83 kg/hr) after the outlet temperature of the combustion chamber was above 400°C. For approximately 8 hours, the outlet gas temperature of primary combustion chamber had been reached and over 850°C and then the operation temperature was controlled between 850 and 900°C by injecting diesel fuel without waste feed. From now, the time was defined as "hour zero". After that, eleven start-up samples were collected and analyzed at hour 1.5, 4.5, 6.5, 7.5, 10.5, 14, 32, 35.5, 54.5, 57.5 and 60.5.

This study investigated the PCDD/F concentrations in the liquid-waste, the ashes from the first, and second cooling towers and from the bag filter, the wastewater of the wet scrubber, and stack flue gases between the start-up and operation periods (only stack flue gases).

To comply with the Taiwan EPA requirement, after the start-up stage, the operator must wait until the gas temperature in the combustion chamber exceeds 850°C and the hourly mean CO mean level is lower than 100 ppm before feeding the waste. Once the gas temperature of primary combustion chamber reached 850°C, the gas was then kept between 850 to 900°C with diesel fuel only, while no waste was fed into the chamber. This condition helped eliminate the effect due to incomplete combustion.

Analyses of PCDD/Fs

Analyses of stack flue gases followed the US EPA

modified method 23, while analyses of filters and fly ash samples conformed to the U.S. EPA Modified Method 1613. All chemical analyses were carried out by the Super Micro Mass Research and Technology Center at Cheng Shiu University – the accredited laboratory in Taiwan for PCDD/F analyses.

Prior to analysis, each collected sample was spiked with a known amount of the $^{13}\text{C}_{12}$ -labeled internal standard to the extraction thimble. Next, toluene was added to fill the reservoir to approximately 2/3 full. The Soxhlet Extractor was controlled to recycle three times per hours. After 24 h of extraction each extract was concentrated and treated with concentrated H_2SO_4 , followed successively by a series of cleanup and fractionation procedures using a multilayer silica gel column, alumina column and activated carbon column. Each eluant was concentrated to approximately 1 mL and transferred to a vial. The concentrate was further blown to near dryness using a stream of ultra pure nitrogen. Immediately prior to the analysis, a standard solution for recovery check was added to the sample. The recoveries of PCDD/F internal standards for the tetra- through hexachlorinated homologues were between 65% and 98%, meeting the criteria range of 40–130%, while that for the hepta and octachlorinated homologues were between 52% and 101%, which met the criteria range of 25–130%.

PCDD/Fs were measured by a high-resolution gas chromatograph (HRGC), coupled with a high-resolution mass spectrometer (HRMS). This HRGC (Hewlett Packard

6970 Series gas, CA, USA) was equipped with a DB-5MS (J&W Scientific, CA, USA) fused silica capillary column (L = 60 m, ID = 0.25 mm, film thickness = 0.25 μm) and with a splitless injection. Helium was used as the carrier gas. However, if a valley between peaks is more than 25% of the lower of the two peaks for 2,3,7,8-TCDD and 2,3,7,8-TCDF, the column had to be changed to DB-225 to recheck isomer. The oven temperature program was set according to follows: begin at 150°C (held for 1 min), then increased at 30 °C/min to 220°C (held for 12 min), then increased at 1.5 °C/min to 240°C (held for 5 min), and finally increased at 1.5 °C/min to 310°C (held for 20 min). The HRMS is a Micromass Autospec Ultima (UK) mass spectrometer with a positive electron impact (EI+) source. The analyzer mode was selected ion monitoring (SIM) at a resolving power of 10000. The electron energy and source temperature were set to 35 eV and 250°C, respectively (Wang *et al.*, 2007b).

Principal Component Analysis (PCA)

PCA is a useful statistical technique that has found application in reducing number of variables in regression analysis and clustering analysis. The principal component can explain the most of the variation in the data (Wang *et al.*, 2003). In this study, PCA was applied to group PCDD/Fs according to the degree of chlorination. To avoid differences in scale between the species, all observations included various congeners divided by the total PCDD/F concentrations. Prior to the principal component analysis each datum for each congener was normalized by dividing with the total amount of all dioxins and furans in that sample, thus eliminating the influence of different scales in concentration.

RESULTS AND DISCUSSION

PCDD/F Congeners Profiles in Stack Flue Gas

According to the operation guide (gas temperature of primary combustion chamber > 850°C and the hourly mean CO level < 100 ppm), most waste incinerators start feeding and increasing feed rate of waste. At this moment the raw gas must be treated, for example, with injection of activated carbon before the bag filters to remove PCDD/Fs. Since there are several formation pathways of PCDD/Fs which are difficult to be identified, no waste was fed, gas temperature of primary combustion chamber was kept at operation temperature (850–900°C) throughout this experiment. Therefore, the PCDD/F profiles of concentrations versus time during cold start-up stage (cold start-up and non-feeding stage) could be described in more detail.

Table 2 shows that the PCDD/F concentration in the stack flue gas was high up to 1.15 ng I-TEQ/Nm³ even at hour 1.5, which was higher than the emission limit of Taiwan regulated standard (0.5 ng I-TEQ/Nm³). During the following hour 4.5–7.5, the PCDD/F concentrations were remaining a high level (0.656–1.04 ng I-TEQ/Nm³). Afterward, the PCDD/F concentrations of the stack flue gas were reduced to 0.453 I-TEQ ng/Nm³ at hour 10.5. The PCDD/F concentrations in the stack flue gas during the hour 14–35.5 were 0.159–0.459 ng I-TEQ/Nm³. At the last stage (hour

Table 2. The PCDD/Fs characteristics of the flue gas during the cold start-up stage.

Sample denotations	Test 1					Test 2					
	a	b	c	d	e	f	g	h	i	j	k
Passed time after temp > 850°C (h)	1.5	4.5	7.5	6.5	10.5	14.0	32.0	35.5	54.5	57.5	60.5
Passed time after burner started (h)	9.5	12.5	15.5	14.5	18.5	22	40	43.5	62.5	65.5	68.5
Temperature of the primary combustion chamber (°C)	858	866	873	863	866	872	890	893	887	886	885
Total PCDD/Fs (ng/Nm ³)	7.73	5.92	3.89	6.66	2.83	2.86	2.19	3.70	2.29	1.96	2.25
I-TEQ (ng/Nm ³)	1.15	1.04	0.656	0.895	0.453	0.459	0.159	0.437	0.241	0.218	0.254
Degree of chlorination	5.73	5.47	5.59	5.79	5.32	5.39	6.84	6.03	6.24	6.25	6.20
PCDFs/PCDDs ratio	4.83	8.99	7.31	4.55	4.93	4.34	0.96	5.01	4.01	3.65	3.60

54.5–60.5), the PCDD/F concentrations reduced to 0.218–0.254 ng I-TEQ/Nm³.

In the cold start-up stage, the profiles of PCDD/F homologues at various time after the operation temperature reached were shown in Fig. 2. The total PCDD/F concentrations and homologues pattern in stack flue gas had a unique minimum at hour 32 during start-up stage. At this time, the minimum PCDD/F concentration (0.159 ng I-TEQ/Nm³) was observed. The congener profiles of PCDD/Fs changed clearly before and after this time (hour 32). Unstable and stable stage are classified by pre- or post- hour 32, respectively. The PCDD/F concentrations increased at hour 35.5, subsequently decreased slowly and remained stable around 0.2 ng I-TEQ/Nm³ after hour 54.5.

TeCDF and PeCDF were the major homologues at hour 1.5 to 14 (Figs. 2(a)–2(f)). They show that lower degree chlorinated PCDF homologues was dominating during the unstable stage. The major PCDD/F homologues at hour 32 were OCDD (Fig. 2(g)). Figs. 2(h)–2(k) shows that the HxCDF and HpCDF were dominating congeners at hour 35.5 to 60.5.

The total mass of the PCDD/F produced during the cold start-up stage contributed at least half of the annual mass of the whole operations (Gass *et al.*, 2002; Tejima *et al.*, 2007; Wang *et al.*, 2007b). This phenomena showed that memory effect increases the emission of the PCDD/F even with the injection of activated carbon. Wang *et al.* (2007b) reported that even at 18 hours after the injection of activated carbon in MSWIs (municipal solid waste incinerators), the PCDD/F concentrations were still 40 times higher than the emission limit of Taiwan EPA (0.1 ng I-TEQ/Nm³). This implies the existence of a long and lasting

"memory effect" and thermal desorption in incineration.

PICs, such as soot and unburned carbon, deposited on the inner surfaces in the cooling section downstream and reacted with chlorine, hydrogen chloride or chlorinated compounds to form PCDD/Fs by de novo or precursor synthesis (Zimmermann *et al.*, 2001; McKay, 2002; Wang *et al.*, 2007a; Li *et al.*, 2011). The incomplete combustion conditions, resulted from start-up, waste feeding and increasing feed rate, can significantly elevate the emission concentration of PCDD/Fs in the stack flue gas (Gass *et al.*, 2004; Wang *et al.*, 2007b).

Moreover, incomplete combustion can also be caused by a temperature variation in the combustion chamber. However, it is important to point out here, that, at this feeding moment the walls of combustion chamber and the cooling section have not yet reached a thermal equilibrium, so PICs result from abnormal operating conditions, such as start of feeding waste, changing feeding rate and heat-up stage. Also, a thermal equilibrium was not reached even though the combustion chamber was heated up to the operation temperature.

Since the PCDD/F levels decreased with the time during the start-up stage when the burner temperature was kept between 850 and 900°C with diesel fuel only without feeding the waste, it can be inferred that the emission of PCDD/Fs during the cold startup was primarily caused by memory effects of start-up and thermal desorption.

PCDD/F Congeners in the Stack Flue Gas

The homologues of the PCDD/F emission were calculated by using the PCA and divided to two factors from the congener profiles of PCDD/Fs in the stack flue gas. Factor 1

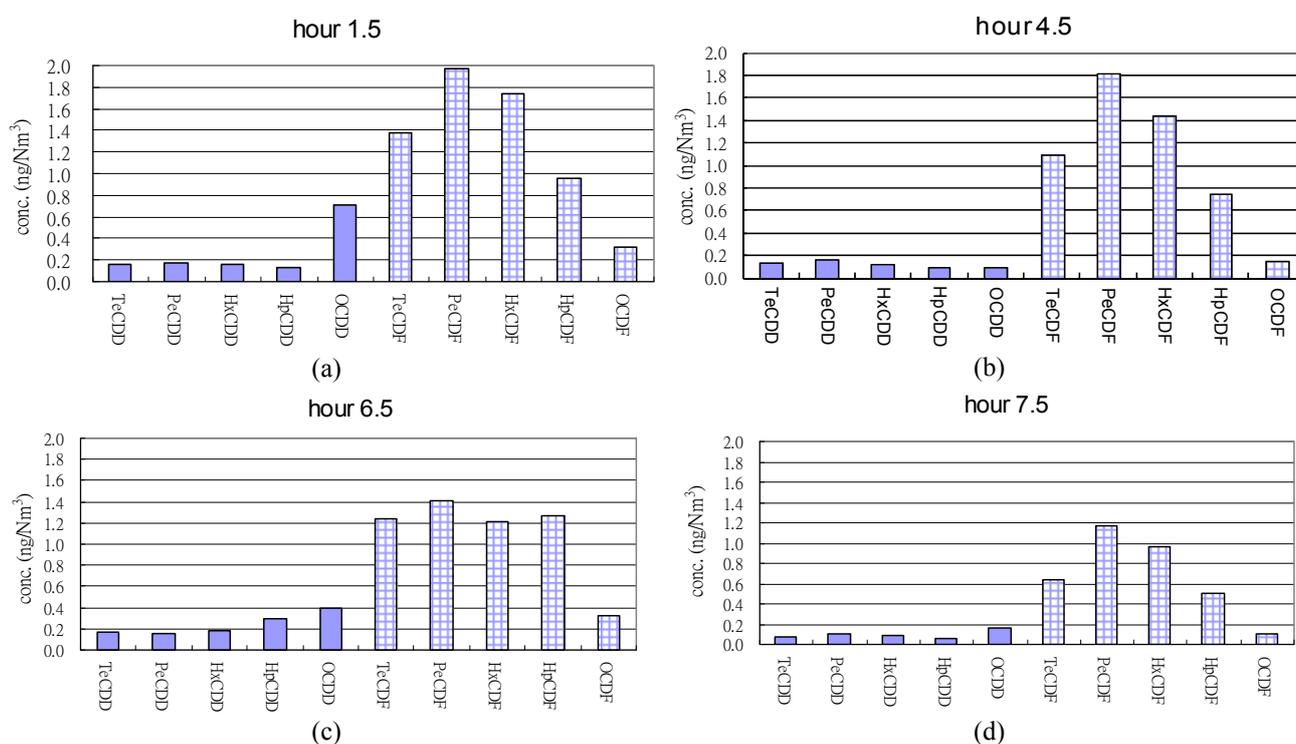


Fig. 2. PCDD/F homologue profiles of the stack flue gas during the cold start-up stage.

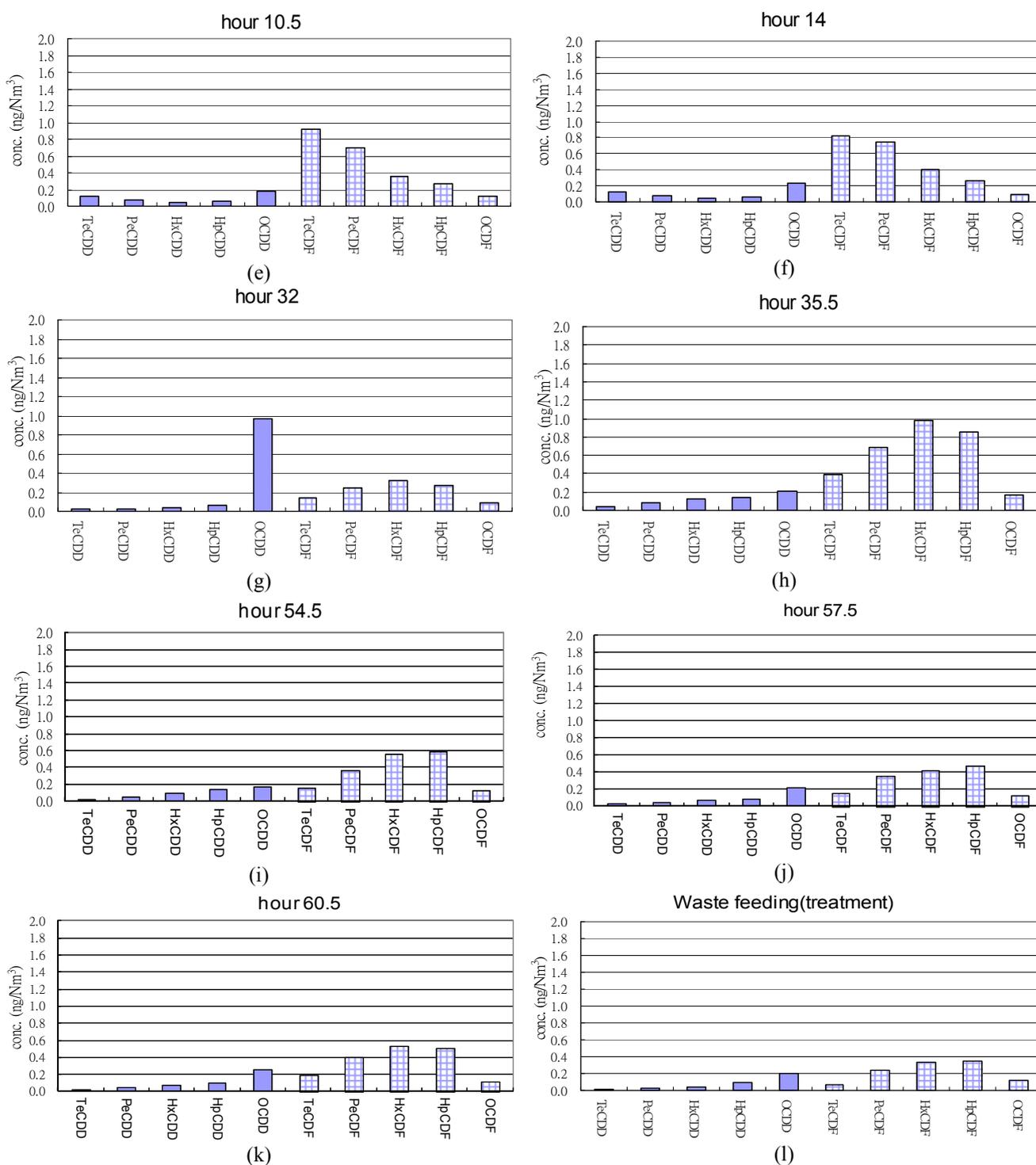


Fig. 2. (continued).

accounts for 53.7% of the total variance, while factor 2 accounts for 29.9% of the total variance. Together, they explained 83.6% of the total variances.

Fig. 3 offers information relating to the PCDD/F congeners. It clearly shows that the lower chlorinated (tetra- + penta-) congeners are located in the upper zone of factor 2, while the hexa- and hepta-chlorinated congeners are clustered to the right of factor 1, and the octa-chlorinated

congeners are situated toward lower values in loading factor 1. Two clusters splitting on the opposite sides of factor 2 indicate a different correlation between octa-, and tetra- + penta-chlorinated homologues. The score plot from PCA shows that the data are clustered into two separated groups — the tetra- + penta- chlorinated homologues and the hexa- + hepta- + octa- chlorinated homologues. It is therefore proposed that both tetra- and penta-chlorinated

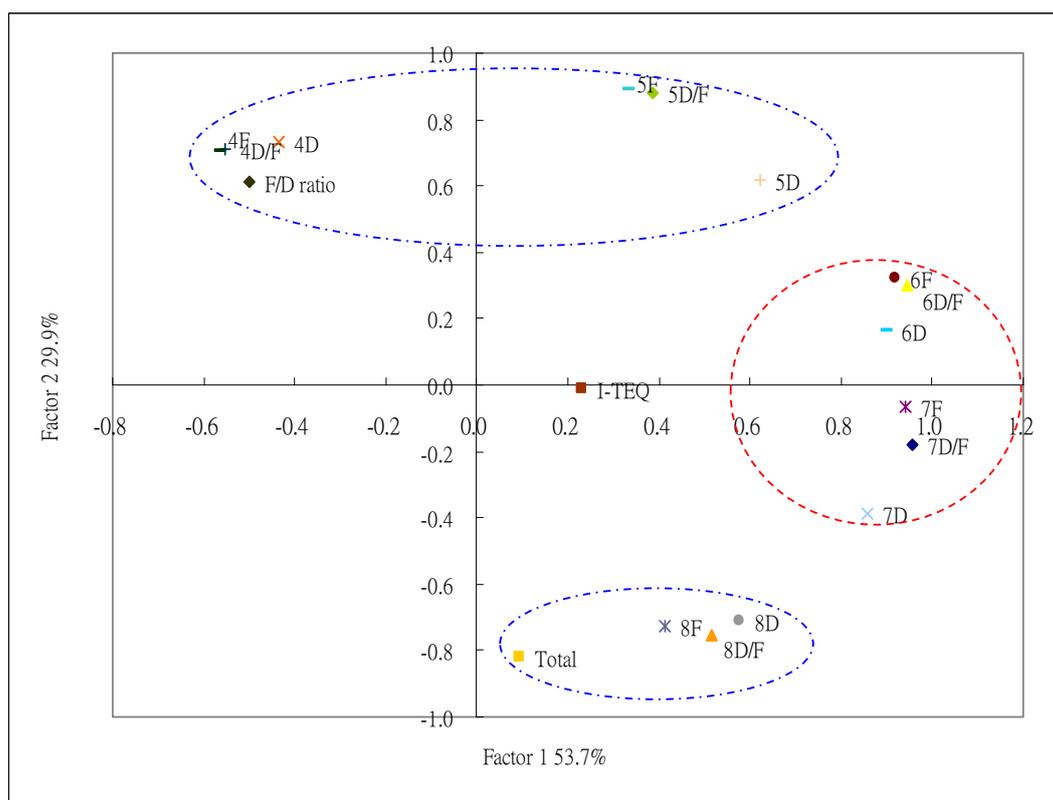


Fig. 3. Result of PCA evaluation with two principal components.

Abbreviations:

4D – Tetra-CDD;	4F – Tetra-CDF;	4D/F – Tetra-CDD/Fs;
5D – Penta-CDD;	5F – Penta-CDF;	5D/F – Penta-CDD/Fs
6D – Hexa-CDD;	6F – Hexa-CDF;	6D/F – Hexa-CDD/Fs
7D – Hepta-CDD;	7F – Hepta-CDF;	7D/F – Hepta-CDD/Fs
8D – Octa-CDD;	8F – Octa-CDF;	8D/F – Octa-CDD/Fs

PCDD/Fs be grouped together and defined as the low-chlorinated homologues (L), while hexa-, hepta- and octa-chlorinated PCDD/Fs be grouped together and defined as the high-chlorinated homologues (H).

A new index, the L/H ratio, is also proposed in this study. It is defined as the ratio of total mass of all low-chlorinated congeners and that of all high-chlorinated congeners. A value of L/H ratio was 1.23 at unstable stage (hour 1.5–32.0) indicates that the dominance of lower chlorinated homologues, while L/H was 0.42 displayed that at stable stage (hour 32.0–60.5), the stack flue gas were primarily associated with higher chlorinated homologues. The results of PCA also revealed that the tetra- and penta-chlorinated congeners decreased with the increase of the octa-chlorinated congeners (Fig. 3).

Table 2 shows that PCDF/PCDD ratio ranged from 4.34 to 8.99 (averaged 5.83) during the unstable stage and the ratio dropped to the range of 3.6–5.01 (averaged 4.07) during the stable stage, the PCDF levels are greater than PCDD levels in both stages.

Table 3 shows that the low-chlorinated PCDFs dominated in the unstable stage, the degree of chlorination (the average number of chlorine substituent) was 5.55 and the

PCDD/F mean concentrations was 0.775 ng I-TEQ /Nm³. On the contrast, under stable conditions, the high-chlorinated PCDFs dominated the corresponding numbers changed to 6.18, and 0.288, respectively. Moreover, compares the concentrations of PCDDs and PCDFs during stable and unstable stage. The concentrations of high-chlorinated PCDFs reduced by 34.7% (1.90 to 1.24 ng/Nm³) and low-chlorinated reduced by 73.3% (2.32 to 0.619 ng/Nm³) between unstable and stable stage. The concentrations of high-chlorinated PCDDs increased by 5.6% and low-chlorinated reduced by 70.1% between unstable and stable process during cold start-up stage. The variation patterns between low-chlorinated homologues of PCDD and PCDF are similar, but the high-chlorinated congeners were different, only the OCDD increased during the whole cold start-up stage while other high-chlorinated PCDD/Fs decreased.

The degree of chlorination at unstable stage (5.32–5.79, averaged 5.55) are less than those of stable stage (6.03–6.25, averaged 6.18). Although, the decrease in degree of chlorination and increase in the I-TEQ value (lower chlorinated PCDD/F congeners have more toxicity) can be used to point the homologue pattern towards the lower chlorinated PCDD/F congeners (Hajizadeh *et al.*, 2011).

Table 3. Mean level of PCDD/Fs distribution parameters in unstable and stable stages.

Parameters	Unstable stage ⁽¹⁾	Stable stage ⁽²⁾
Total PCDD/Fs ng/Nm ³	4.98	2.55
High-Chlorinated DDs (ng/Nm ³)	0.516	0.545
Low-Chlorinated DDs (ng/Nm ³)	0.25	0.075
High-Chlorinated DFs (ng/Nm ³)	1.9	2.32
Low-Chlorinated DFs (ng/Nm ³)	1.24	0.619
PCDD/Fs (ng I-TEQ/Nm ³)	0.775	0.288
Degree of chlorination	5.55	6.18
L/H ratio	1.23	0.42
PCDDs L/H ratio	1.43	0.49
PCDFs L/H ratio	0.57	0.19
PCDFs/PCDDs ratio	5.83	4.07

⁽¹⁾ 1.5–32 hours after operation temperature reached; ⁽²⁾ at hour 32–60.5.

A PCDFs/PCDDs ratio greater than 1 means domination of de novo synthesis, while a ration less than 1 indicates domination of precursor mechanism. (Huang and Buekens, 1995). The result shows that lower chlorinated homologues were dominating at the unstable stage. Also, the degree of chlorination increased with time during the unstable stage.

The change of PCDD/F congeners profiles was caused by thermal desorption or release. Kreiszi *et al.* (1996) experimented that the thermal PCDD/Fs desorption of various packing materials in the wet scrubbers was a function of temperature and a function of time. The thermal adsorption/desorption of PCDD/DFs on the packing materials caused of the elevated PCDD/DF levels in the wet scrubbers (Löthgren and van Bavel, 2005). The thermal desorption rates of PCDD/Fs depend on the temperature and their boiling points, which are 438–507°C for PCDFs and 447–510°C for PCDDs (Rordorf, 1989).

This study use L/H ratio from the results of PCA to discuss the distribution of PCDD/F homologues. The fact that L/H ratio of PCDF congeners exceeds 1 at unstable stage implies that the low-chlorinated congeners, due to their lower boiling points, are desorbed and released from the walls faster than high-chlorinated congeners. Since throughout this experiment no waste was fed, it is inferred that at this point the gas temperature was finally high enough to vaporize the previously PCDD/Fs condensed on the walls.

During the heat-up stage, the walls temperatures of combustion chamber and cooling section was lower than the flue gas temperature. As the temperature of the walls and surfaces slowly increased and sequentially passed the boiling points of the lower chlorinated congeners of PCDFs, PCDDs, and eventually PCDD/Fs. Finally, the vapor pressure of PCDD/Fs in this area would be adequately high and thermal desorption of PCDD/Fs occurred. When the wall temperature was above the boiling points of lower chlorinated PCDD congeners, higher emissions of PCDD/Fs (as I-TEQ) were observed. Afterwards, the concentrations of lower chlorinated PCDD congeners further decreased as the temperature of walls became higher. The lower emissions of PCDD/Fs occur at the temperature of walls above the boiling points or under thermal equilibrium. Therefore the emission continuously decreased and approached a stable

value after hour 54.5, when a thermal equilibrium was established.

Effects of Air Pollution Control Devices (APCDs) on the Formation of PCDD/Fs

Table 4 indicated that the higher PCDD/F concentrations of ash were observed in the cooling section and the bag filters. The L/H ratios of stack flue gas (0.316–1.08) were higher than those of other samples, which ranged from 0.055 to 0.225. It is thus inferred that the high-chlorinated homologues of PCDD/Fs tend to deposit on particulates and thus are easily removed. In contrast, the removal of low-chlorinated PCDD/F homologues are more difficult and insufficient at APCDs. The higher PCDD/F concentrations were observed in the fly ash from the first cooling tower and the bag filter. The fact that PCDFs/PCDDs ratio of all samples were greater than 1 indicate that PCDFs were dominated. The L/H ratios of stack flue gases were higher than that in the ash of the bag filter, it means that the activated carbon was heavily loaded. These results together imply that more activated carbon should be injected in order to remove PCDD/Fs, especially the low-chlorinated PCDD/F homologues, more efficiently.

In the cooling section, the gas temperature decreased rapidly from 1050°C down to 180°C by using water. The low-chlorinated congeners can pass through first cooling section as the gas phase and are deposited downstream. That is why the L/H ratio at the ash of second cooling section and bag filter were higher than the other samples at APCDs. It is suggested that the PCDD/F congeners tend to deposit on the surfaces of either the solid phase or in the cooler section or be caught by the bag filter. On the other hand, the low-chlorinated PCDD/Fs tend to exist either in the vapour or gas phase, or they are adsorbed and carried by the particulate material into the gas stream. In the second cooling section the temperature is lower than boiling points of PCDD/Fs. Consequently. The PCDD/Fs will deposit on the walls or they are absorbed by the powdered activated carbon.

Many studies have discussed the low temperature memory effect of the wet scrubber. Due to chlorinated PCDD/Fs have low volatility and are highly hydrophobic, they tend to adsorb to packing materials or fly ash. They are unexpectedly

Table 4. The PCDD/F concentrations of input wastes, APCDs residues and the flue gas.

Samples	Waste		Ash		Waste water		Stack flue	
	Input	2	First cooling tower	Second cooling tower	Bag filter	Wet scrubber	Operation stage	Start-up stage
Outlet temp (°C)	-	216–236	103–137	93–101	59–68	130–133	4	6
Additions	-	Water	NaOH + water	Activate carbon	NaOH + water	-	-	-
I-TEQ	38.8 pg/L	11.8 ng/g	0.147 ng/g	11.3 ng/g	40.2 pg/L	0.365 ng/Nm ³	0.775 ng/Nm ³	
Total PCDD/Fs	1259 pg/L	198 ng/g	1.69 ng/g	163 ng/g	1299 pg/L	3.46 ng/Nm ³	4.98 ng/Nm ³	
L/H ratio	0.055	0.099	0.225	0.133	0.061	0.316	1.076	
PCDF/PCDD ratio	1.60	1.09	1.17	2.37	1.54	1.57	5.50	

APCD: Air Pollution Control Device.

released into emission gases, consequently increasing the PCDD/F concentrations in the stack flue gas (Gass and Neugebauer, 1999; Choi *et al.*, 2007). The de novo synthesis is the main reaction pathway at lower temperatures between 250 and 400°C with the presence of carbon, oxygen, hydrogen and chlorine (McKay, 2002; Xhrouet and Pauw, 2003; Ryu *et al.*, 2005; Tuan *et al.*, 2012). Since the vapor pressures of the low-chlorinated PCDD/Fs are higher than those of the high-chlorinated PCDD/Fs, the low-chlorinated congeners are more easily released from the wastewater or the packings of wet scrubber.

Although some incinerator are not equipped with wet scrubbers, they require either a lot of water to lower the temperature rapidly in the cooling sections or higher moisture contents of waste. In the presence of water increase the I-TEQ concentration, especially being after the wet scrubber, the profiles of the PCDD/F homologous significant shift towards the lower chlorinated PCDD/F congeners (Gass and Neugebauer, 1999; Löthgren and van Bavel, 2005; Li *et al.*, 2006; Briois *et al.*, 2007; Wang *et al.*, 2007a). However, the presence of water or vapour will change the profiles of generated PCDD/Fs and the homologue distribution.

In terms of boiling points, PCDF congeners are lower than PCDD congeners, while the low-chlorinated PCDD/F homologues are lower than high-chlorinated ones. Therefore, the low-chlorinated PCDFs are desorbed or vaporized more easily than PCDDs or high-chlorinated PCDD/Fs during the start-up stage. The low-chlorinated PCDD/F congeners are easily carried by the gas stream through the cooling section as vapor molecules or by the in-stream fine particulates onto which they adsorb. These contaminations are subsequently captured and removed by the activated carbon in the bag filter. That may explain why the ashes in the bag filter and in the second cooling tower have higher L/H ratios.

In this study, using diesel fuel without waste feeding during the cold start-up stage can cut off the supply of chlorine and keep the outlet temperature in the combustion chamber in the range of 850–900°C. It also minimized the variation in the start-up testing stage and prevented the incomplete combustion. Since the emissions of PCDD/Fs declined monotonically from a high level down to the low normal value, it is inferred that, during start-up stage in this investigated interval, the high emission of PCDD/Fs is attributed solely by the re-desorption of PCDD/Fs which were deposited in previous runs.

The fact that the L/H ratios in stack flue gases were higher than those in other samples deserve further attention, because the lower chlorinated PCDD/Fs have higher toxicity equivalence factors and will result in a higher PCDD/F I-TEQ concentration in the stack flue gases. Therefore, injection of more amount activated carbon in front of the bag filter is highly recommended. The emissions of PCDD/Fs are 0.365, 0.288 and 0.155 I-TEQ ng/Nm³ by adding activated carbon in 1.34, 1.83 and 2.68 kg/h, respectively. In this case, we suggest that injecting activated carbon more than 3 kg/h (by regress) or 0.0315 kg activated carbon/kg liquid waste in order to removal more PCDD/Fs and decrease to less than 0.1 ng I-TEQ/Nm³ as high chlorine content liquid waste treating.

CONCLUSIONS

During the cold start-up stage, a 32 hours of preheating was required as a clean-up measure to remove the condense or deposited PCDD/Fs from previous operation. It needed more than 54 hours after reaching the operation temperature reached, when the system reached a thermal equilibrium (or), waste feeding could be started without significantly disturbing or upsetting the stable combustion.

Since no waste was fed in this study, it is concluded that the emission of PCDD/Fs solely came from the desorption or release of the older deposited products rather than newly synthesized PCDD/Fs. The observed high concentrations of PCDD/Fs in the stack flue gas during cold start-up stage without waste feeding provides a proof and an additional example of the memory effect.

These low-chlorinated PCDD/Fs are dominating at unstable period (within hour 32) during the start-up stage. It is important to remove them during the initial cold start-up stage for incineration operation when they are redesorbed into the gas stream.

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Received for review, May 30, 2013

Accepted, August 18, 2013