



Influence of start-up on PCDD/F emission of incinerators

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Abstract

This study aims to evaluate the influence of start-up on polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) concentration in the stack flue gas of incinerators and its contributing PCDD/F emission. The PCDD/F emission of the first sample among three consecutive stack flue gas samples of five intermittent incinerators, which sampled at a stable combustion condition after start-up, is 2–3 times higher than the mean of the others. For verifying the PCDD/F characteristics of incinerators during start-up, one continuous MSWI was investigated for two years. The elevated PCDD/F emissions of the MSWI during start-up could reach 96.9 ng I-TEQ N m⁻³ and still maintained a high PCDD/F emission (40 times higher than the Taiwan emission limit) even 18 h after the injection of activated carbon, indicating the memory effect. Taking the MSWI for example, which consists of four incinerators, the estimated annual PCDD/F emission from normal operational conditions was 0.112 g I-TEQ. However, one start-up procedure can generate ~60% of the PCDD/F emissions for one whole year of normal operations. And the PCDD/F emission, which is the result of the start-ups of four incinerators, was at least two times larger than that of a whole year's normal operations, without consideration for the PCDD/F emission contributed by the long lasting memory effect.

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1. Introduction

After polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were discovered in the flue gases and fly ash of municipal solid waste incinerators (MSWIs) in 1977 (Olie et al., 1977), PCDD/Fs have become a serious issue in many countries because of their toxicological effects and associated adverse health implications.

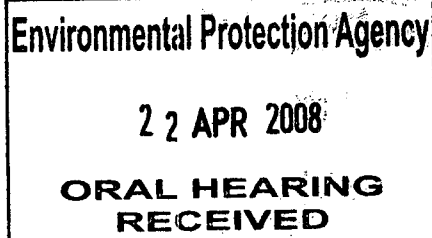
Most research investigated the PCDD/F characteristics and the induced hazardous effect of incinerators during

normal operations. Till recently, several studies (Gass et al., 2002; Löthgren and van Bavel, 2005; Neuer-Etscheidt et al., 2006) have focused on the high PCDD/F emission during the start-up of incinerators. The start-up of continuous MSWIs is usually a cold start-up, which occurs after a plant revision and consists of the following procedures: (1) Oil burning with a maximum fuel feed rate until the suitable temperature for incineration (850 °C) is reached. (2) Start of waste feeding and increasing feed rate until design load is reached (Gass et al., 2002). However, for intermittent incinerators, the start-up procedure is a warm start-up, which can be characterized by the furnace's remaining temperature when it is started up again the next day.

Löthgren and van Bavel (2005) measured the PCDD/F levels after a polishing wet scrubber continuously for

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18 months using long-time sampling equipment at a hazardous waste incineration facility in Sweden. Each sampling period lasted two weeks. Two dramatic risings of TEQ levels were observed, both in the period just after a maintenance stop of the plant, from 0.02 to 0.25 ng TEQ m⁻³ and from 0.03 to 0.15 ng TEQ m⁻³. Gass et al. (2002) reported raw flue gas PCDD/F concentrations during the start-up of a MSWI of up to 250 ng I-TEQ m⁻³ in the heat-up phase. In contrast, Neuer-Etscheidt et al. (2006) reported that PCDD/F I-TEQ crude gas concentrations during the heat-up period were a little lower than those during normal operations with waste as the fuel. One reason for this difference may be the state of cleaning of the boiler section. Immediately after waste was fed, PCDD/F concentrations (46 ng I-TEQ m⁻³) in the crude gas increased by one order of magnitude compared to normal operating conditions (3–4 ng I-TEQ m⁻³). Even for a ship's main engine, the highest PCDD/F emissions have been measured for the start-up samples (0.1–0.4 ng WHO-TEQ kW h⁻¹ vs. 0.03–0.1 ng WHO-TEQ kW h⁻¹ during normal operations), which are characterized by relatively poor combustion conditions (also high CO emissions) (Cooper, 2005). However, still little research estimated the generated PCDD/Fs during start-up to what extent. Consequently, it is not yet possible to evaluate the exposures and potential health risks during these conditions (Mckone and Hammond, 2000).

In this study, five intermittently operating incinerators, including one industrial waste incinerator (IWI), one waste liquid incinerator (WLI) and three medical waste incinerators (MWIs) were measured for PCDD/Fs in the stack flue gases when combustion condition reached stabilization after start-up to evaluate the influence of memory effect caused by start-up on PCDD/F emission. For verifying the PCDD/F characteristics of incinerators during start-up, one large scale continuously operating MSWI was chosen to be investigated for two years. In the first year, a total of five start-up stack flue gas samples were collected. For more detailed characterization, the next year, a total of 10 stack flue gas samples were sampled and the sampling time was changed so it's more accordant with the start of waste feeding. Only the 2,3,7,8-PCDD/F congeners in the stack flue gases of the incinerator were measured because

of their toxicities. The obtained results were not only compared to the typical concentrations during normal operations of the MSWI but also evaluated for the PCDD/F emission during start-up.

2. Experimental section

2.1. Basic information concerning the incinerators

The basic operation information concerning the intermittent incinerators, including one IWI, one WLI and three MWIs is described in Table 1. The feeding waste and air pollution control devices (APCDs) between these three categories of incinerators are not similar, but each kind of incinerator possesses its representation.

The continuously operating MSWI investigated for two years in this study consists of four 450 ton day⁻¹, two-stage, starved-air modular incinerators, each of which includes its own heat recovery system, dry scrubber, activated carbon injection, bag filter and stack. During start-up, the incinerators were preheated by burners operated with diesel.

2.2. PCDD/Fs sampling

On a usual day, the intermittent incinerators were started up in the morning and operated during the day. At night, the combustion chamber cooled down. However, in this study, the feeding waste was accumulated to enough for three consecutive 3 h stack flue gas samples during normal operations after start-up, which is characterized by the stable reading of combustion temperature and traditional pollutant, like CO concentration.

The sampling time of each stack flue gas sample of the MSWI during start-up was about 2–3 h and a total of five samples were collected in the first year. For more detailed characterization, the next year, the sampling time was changed to once an hour and a total of 10 stack flue gas samples were sampled.

The PCDD/F samples were collected isokinetically from the stack flue gas of the selected incinerators according to US EPA modified Method 23. The sampling train adopted in this study is comparable with that specified by US EPA

Table 1
Basic information concerning these five intermittent incinerators

Emission sources	IWI	WLI	MWI	MWI	MWI
Denotation	A	B	C	D	E
Feeding waste (kg h ⁻¹)	Industrial waste (420)	Waste liquid (200)	Infectious and pathological waste (400)	Infectious and pathological waste (300)	Infectious and pathological waste (300)
Auxiliary fuel (l h ⁻¹)	–	Diesel (0.1)	Diesel (22)	Diesel (21)	Diesel (19)
APCDs in sequence (operation temperature) (°C)	Cyclone (200) BF (160)	VS (90)	DS (250) ACI BF (150)	QC VS (90)	DS (250) ACI BF (160)
Mean stack flue gas flow (N m ³ h ⁻¹)	8500	2900	4500	4000	6000

Activated carbon injection: ACI; Bag filter: BF; Dry scrubber: DS; Quench chamber: QC; Venturi scrubber: VS.

Modified Method 5. Prior to sampling, XAD-2 resin was spiked with PCDD/F surrogate standards pre-labeled with isotopes, including $^{37}\text{Cl}_4$ -2,3,7,8-TCDD, $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDD, $^{13}\text{C}_{12}$ -2,3,4,7,8-PeCDF, $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF and $^{13}\text{C}_{12}$ -1,2,3,4,7,8,9-HpCDF. The recoveries of PCDD/F surrogate standards were 101–123%, and met the criteria within 70–130%. To ensure the free contamination of the collected samples, one trip blank and one field blank were also taken during the field sampling was conducted. Details are similar to that given in our previous work (Wang et al., 2003).

2.3. Analyses of PCDD/Fs

Analyses of stack flue gas followed the US EPA modified method 23. 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. Add toluene to fill the reservoir approximately 2/3 full. Adjust the heat source to cause the extractor to cycle three times per hour. After being extracted for 24 h, the extract was concentrated, treated with concentrated sulfuric acid, and then followed by a series of sample cleanup and fractionation procedures, including multilayer silica gel column, alumina column and activated carbon chromatography. The eluate was concentrated to approximately 1 ml and transferred to a vial. The concentrate was further concentrated to near dryness, using a stream of nitrogen. Immediately prior to analysis, the standard solution for recovery checking was added to the sample. The recoveries of PCDD/F internal standards for the tetra- through hexachlorinated homologues were between 65% and 98%, and met the criteria within 40–130%, while that for the hepta- and octachlorinated homologues were between 52% and 101%, and met the criteria within 25–130%.

A high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS) was used for PCDD/Fs analyses. The HRGC (Hewlett Packard 6970 Series gas, CA, USA) was equipped with a DB-5MS fused silica capillary column ($L = 60\text{ m}$, $\text{ID} = 0.25\text{ mm}$, film thickness = $0.25\text{ }\mu\text{m}$) (J&W Scientific, CA, USA), 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 $150\text{ }^\circ\text{C}$ (held for 1 min), then increased at $30\text{ }^\circ\text{C min}^{-1}$ to $220\text{ }^\circ\text{C}$ (held for 12 min), then increased at $1.5\text{ }^\circ\text{C min}^{-1}$ to $240\text{ }^\circ\text{C}$ (held for 5 min), and finally increased at $1.5\text{ }^\circ\text{C min}^{-1}$ to $310\text{ }^\circ\text{C}$ (held for 20 min). The HRMS (Micromass Autospec Ultima, Manchester, UK) was equipped with a positive electron impact (EI+) source. The analyzer mode of the selected ion monitoring (SIM) was used with resolving power at 10000. The

electron energy and source temperature were specified at 35 eV and $250\text{ }^\circ\text{C}$, respectively. Details of analytical procedures are given in our previous work (Wang et al., 2003).

3. Results and discussion

3.1. Influence of memory effect resulted from start-up on PCDD/F emissions of the intermittent incinerators

The PCDD/F profiles of three consecutive stack flue gas samples of these five intermittent incinerators were illustrated in Fig. 1 and revealed that the PCDD/F emission of the first stack flue gas sample, which was sampled at a stable combustion condition after start-up, was considerably higher than that of the follow-up samples. For toxicity basis, the first stack flue gas sample was 2–3 times higher than the mean PCDD/F emission of the second and third one. Fig. 1 also revealed that the PCDD/F profiles of the three consecutive stack flue gas samples for each incinerator declined with time. The reason for this is that the memory effect that resulted from the high PCDD/F emission of the start-up contributed and changed the subsequent concentration and profiles significantly. But as time went by, the influence of the memory effect on the PCDD/F emission faded away.

The memory effect caused by the wet scrubber resulted from that PCDD/Fs are adsorbed on scrubber fillings (typically polypropylene (PP) plastics) and thus leading to unexpected PCDD/F releases when the plant is running under more stable conditions (Hunsinger et al., 1998; Adams et al., 2000; Takaoka et al., 2003). Compared to that caused by start-up procedure, the memory effect caused by the start-up can occur in all kinds of incinerators with different APCDs, not only for those with wet scrubbers, for examples, the incinerators in this study are no exception to this.

3.2. PCDD/F emission in the stack flue gases of the MSWI under normal conditions

For more understanding of the memory effect that resulted from the start-up, one continuous MSWI was chosen to characterize the PCDD/F emission during start-up. In the first instance, we need to establish the PCDD/F characteristics of the MSWI during normal operation.

The stack flue gases of the MSWI were sampled five times in different months under normal operation conditions and a total of 25 samples were collected for PCDD/F measurement. The mean PCDD/F concentration (normalized to the dry flue gas conditions of 273 K and $11\%\text{ O}_2$) in the stack flue gas was $0.0358\text{ ng I-TEQ N m}^{-3}$ (range: $0.00273\text{--}0.0946\text{ ng I-TEQ N m}^{-3}$, relative standard deviations (RSD): 66.4%), while their corresponding mean PCDD/F emission factor was $0.249\text{ }\mu\text{g I-TEQ ton waste}^{-1}$ (RSD: 69.0%), which is close to that (mean: $0.251\text{ }\mu\text{g I-TEQ ton waste}^{-1}$, range: $0.0512\text{--}0.561\text{ }\mu\text{g I-TEQ ton waste}^{-1}$) of the other 13 MSWIs in Taiwan (Lee et al.,

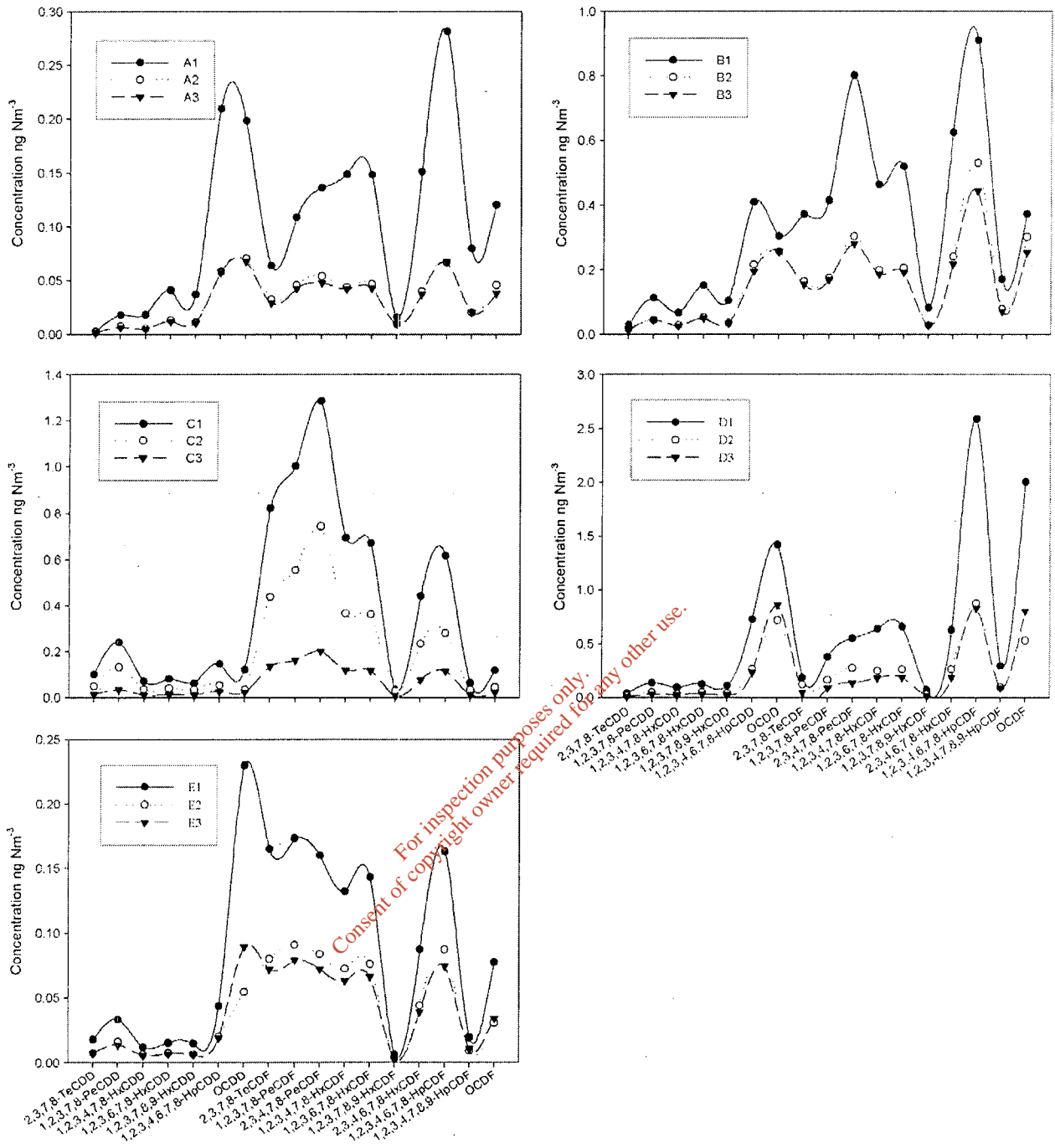


Fig. 1. The PCDD/F profiles of three consecutive stack flue gas samples of the five intermittent incinerators.

2005) and is comparable to that ($0.17 \mu\text{g I-TEQ ton waste}^{-1}$) of the MSWI (400 ton day^{-1}) in accordance with the best control technologies (Giugliano et al., 2002). Furthermore, five raw flue gas samples sampled in front of the activated carbon injection and bag filter were also measured for PCDD/Fs and the mean PCDD/F concentration was $0.610 \text{ ng I-TEQ N m}^{-3}$ (range: $0.231\text{--}1.52 \text{ ng I-TEQ N m}^{-3}$, RSD: 86.1%).

According to statistical data, there were $\sim 448,000$ tonnes of waste incinerated by the MSWI investigated in

this study in 2005. By directly adopting the mean emission factors that were obtained from this study ($0.249 \mu\text{g I-TEQ ton waste}^{-1}$), the total emission amount of PCDD/Fs from the MSWI is $\sim 0.112 \text{ g I-TEQ yr}^{-1}$.

3.3. PCDD/F emission in the stack flue gases of the MSWI during start-up

Table 2 listed the operation conditions and their corresponding PCDD/F emission in the stack flue gases during

Table 2
PCDD/F emission in the stack flue gases of the MSWI during start-up in the first year's investigation

Sample denotations	Sampling day				
	Day one		Day two		
	a	b	c	d	e
Sampling time	15:30–17:40	19:25–20:55	23:40–3:15	10:10–12:35	13:42–16:10
Passed time after burner started (h)	5.5–7.7	9.4–11	13.7–17.3	24.2–26.6	28–30.2
Passed time after waste fed (h)	–	–	–	5.2–7.6	9–11.2
Auxiliary fuel ($l\ h^{-1}$)	660	830	650	4	7
Temperature of combustion chamber ($^{\circ}C$)	310	490	850	900	920
Primary air flow rate ($N\ m^3\ h^{-1}$)	37500	34300	30900	50400	51000
Temperature in the inlet of superheater ($^{\circ}C$)	190	240	360	490	500
Temperature in the inlet of economizer ($^{\circ}C$)	150	210	300	330	340
O ₂ Concentration after economizer (%)	22	22	22	11	7.3
Temperature of dry scrubber ($^{\circ}C$)	130	160	210	240	230
Lime feeding rate ($m^3\ h^{-1}$)	0	0	0.6	2.2	4.0
Temperature of bag filter ($^{\circ}C$)	120	150	180	160	150
Activated carbon feeding rate ($kg\ h^{-1}$)	0	0	6	10	10
CO concentration in the stack flue gas (ppm)	–	–	–	42	32
O ₂ concentration in the stack flue gas (%)	18	17	14	8.3	8.7
PCDFs/PCDDs ratio	0.66	0.62	0.72	0.92	0.75
Total PCDD/Fs ($ng\ N\ m^{-3}$)	83.8	328	68.2	42.9	10.7
PCDFs/PCDDs TEQ ratio	3.0	2.1	2.4	2.6	2.4
Total I-TEQ ($ng\ I-TEQ\ N\ m^{-3}$)	2.09	12.2	3.34	2.28	0.507

–: No data.

the cold start-up of the MSWI in the first year's investigation. The PCDD/F concentrations (normalized to the dry flue gas conditions of 273 K) in the stack flue gases during the heat-up phase (samples a–c) were ranged at 2.09–12.2 ng I-TEQ $N\ m^{-3}$ while those that were ranged at 0.507–2.28 ng I-TEQ $N\ m^{-3}$ were observed 5 h after the waste feeding process had started.

For more detailed characterization, during the following year, the sampling time was changed to once an hour so it's more accordant with the start of waste feeding (see Table 3). The PCDD/F concentration in the stack flue gases during the heat-up phase (samples a–d) was between 5.16 and 41.5 ng I-TEQ $N\ m^{-3}$, which was higher than the first year's results (2.09–12.2 ng I-TEQ $N\ m^{-3}$). However, the drastic PCDD/F emissions in the stack flue gases during the heat-up phase of the two years' investigation both occurred at the combustion chamber's temperature reaching 490 $^{\circ}C$. When the combustion chamber's temperature reaching 490 $^{\circ}C$, the temperatures in the inlet of the superheater and economizer were between 210 $^{\circ}C$ and 290 $^{\circ}C$, which were a little below the temperature region (250–450 $^{\circ}C$) of the PCDD/F optimal formation. Otherwise, Clarke (2000), Gass et al. (2003) and Neuer-Etscheidt et al. (2006) reported that PCDD/F precursors (e.g., benzenes, phenols and chlorinated forms) are created in the furnace at the highest rate in these temperature regions. In fact, Benestad et al. (1990) reported that PAHs concentration during the start-up period was 2–16 times higher than that during normal operation for three small MSWIs. Yasuda and Takahashi (1998) also determined the PAHs emission of four MSWIs during start-up, burning, and burn-out and reported that during start-up conditions, PAH concen-

trations (77–248 $\mu g\ N\ m^{-3}$) have been shown to be 12–77 times higher during burning (0.1–63.2 $\mu g\ N\ m^{-3}$). Consequently, the drastic PCDD/F emissions occurred during the heat-up phase is more related to the operational temperature of the combustion chamber than to that of superheater and economizer.

But when the temperature of the combustion chamber raised from 490 $^{\circ}C$ to 850 $^{\circ}C$, the PCDD/F emissions decreased from 12.2 ng I-TEQ $N\ m^{-3}$ (no activated carbon injection) to 3.34 ng I-TEQ $N\ m^{-3}$ (activated carbon feeding rate: 6 $kg\ h^{-1}$) during the heat-up phase in the first year's investigation. The injection of activated carbon and the elevated temperature of the combustion chamber, i.e. the more completely combustion condition, may be the reasons of drastic reduction of the PCDD/F emissions, however, due to the intervals of up to several hours where no samples were taken, which one is the most influence factor is needed to be clarified further.

In the first year, the temperature of the combustion chamber reached 490 $^{\circ}C$ after burning for 10 h with the average auxiliary fuel feeding rate of 710 $l\ h^{-1}$ and the average primary air of 35900 $N\ m^3\ h^{-1}$ while in the second year's investigation, reaching the same combustion condition with a higher average auxiliary fuel feeding rate of 1150 $L\ h^{-1}$ and a less primary air of 27700 $N\ m^3\ h^{-1}$. The results revealed that the worse combustion efficiency occurred in the second year and might result in the PCDD/F concentration in the stack flue gases during the heat-up phase (5.16–41.5 ng I-TEQ $N\ m^{-3}$) which has a recording that is higher in the second year than that of the first year (2.09–12.2 ng I-TEQ $N\ m^{-3}$). Otherwise, Neuer-Etscheidt et al. (2006) proposed that the state of

Table 3
PCDD/F emission in the stack flue gases of the incinerator during start-up in the second year's investigation

Sample denotations	Sampling day											
	Day one						Day two					
	a	b	c	d	e	f	g	h	i	j		
Sampling time	18:00–19:00	20:30–21:25	23:10–00:07	01:50–02:57	05:00–06:08	09:50–11:09	12:45–13:58	15:20–16:30	18:04–19:09	20:30–21:41		
Passed time after burner started (h)	2–3	4.5–5.4	7.2–8.1	9.8–11	13–14.1	17.8–19.2	20.8–22	23.3–24.5	26.1–27.2	28.5–29.7		
Passed time after waste fed (h)	–	–	–	–	1–2.1	5.8–7.2	8.8–10	11.3–12.5	14.1–15.2	16.5–17.7		
Auxiliary fuel ($l\ h^{-1}$)	1100	1150	1300	1060	525	2	0	0	0	0		
Temperature of combustion chamber ($^{\circ}C$)	155	230	400	490	900	900	910	880	900	900		
Primary air flow rate ($N\ m^3\ h^{-1}$)	32000	28700	26700	23200	53800	39100	39800	44100	48600	43900		
Temperature in the inlet of superheater ($^{\circ}C$)	140	190	220	250	360	460	490	490	500	500		
Temperature in the Inlet of economizer ($^{\circ}C$)	110	160	190	250	310	330	340	340	350	350		
O ₂ concentration after economizer (%)	19	19	17	17	7.0	9.2	9.1	10	8.6	8.8		
Temperature of dry scrubber ($^{\circ}C$)	90	140	180	210	210	220	230	230	230	230		
Lime feeding rate ($m^3\ h^{-1}$)	0	0	0	0	0	0	0	0	0	0		
Temperature of bag filter ($^{\circ}C$)	80	130	170	170	160	160	150	150	150	150		
Activated carbon feeding rate ($kg\ h^{-1}$)	0	0	0	0	6	6	6	6	6	6		
CO concentration in the stack flue gas (ppm)	–	–	–	–	–	49	43	53	37	21		
O ₂ concentration in the stack flue gas (%)	19	19	13	9.2	8.9	9.1	8.3	8.9	10	8.8		
PCDFs/PCDDs ratio	0.64	0.59	0.95	1.0	1.0	0.69	0.74	0.67	0.69	0.68		
Total PCDD/Fs ($ng\ N\ m^{-3}$)	180	259	111	384	909	339	86.3	99.7	66.5	64.3		
PCDFs/PCDDs TEQ ratio	4.1	3.4	4.0	1.7	2.0	1.9	2.0	2.0	2.1	2.0		
Total I-TEQ ($ng\ I-TEQ\ N\ m^{-3}$)	6.19	8.64	5.16	41.5	96.9	23.1	6.18	6.41	4.30	4.19		

–: No data.

cleaning of the boiler section could also result in the PCDD/F crude gas concentrations during the heat-up period ranging from a little lower than those during normal operations to $250 \text{ ng I-TEQ N m}^{-3}$, which was reported by Gass et al. (2002).

Another drastic elevated PCDD/F concentrations (from 41.5 to $96.9 \text{ ng I-TEQ N m}^{-3}$) in the stack flue gas occurred one hour after waste feeding (Table 3) and it declined to $23.1 \text{ ng I-TEQ N m}^{-3}$ five hours after waste feeding, but still maintained high PCDD/F concentration, $4.19 \text{ ng I-TEQ N m}^{-3}$, 40 times higher than the Taiwan emission limit of $0.1 \text{ ng I-TEQ N m}^{-3}$ even 18 h after the injection of activated carbon, indicating the long lasting memory effect. Neuer-Etscheidt et al. (2006) also observed that immediately after waste was fed, PCDD/F concentrations ($46 \text{ ng I-TEQ m}^{-3}$) in the crude gas increased by one order of magnitude compared to normal operating conditions ($3\text{--}4 \text{ ng I-TEQ m}^{-3}$). In this study, the raw gas in front of the APCD had not been sampled so that it is unclear that if the raw gas PCDD/F levels were still elevated at 18 h after the injection of activated carbon. However, the CO concentration (21 ppm, see Table 3) at that time was already in the range of normal operation condition, representing the well combustion condition and little PCDD/F precursors, like benzenes, phenols and PAHs formed, so we extrapolated that the high PCDD/F concentration, $4.19 \text{ ng I-TEQ N m}^{-3}$ at 18 h after the injection of activated carbon, resulting from rather the memory effect than the incomplete combustion at that time.

During the heat-up phase, no activated carbon is injected prior to the bag filter in order to avoid ignitions of the activated carbon due to the high oxygen concentration in the flue gas (see Tables 2 and 3). Although it may be one of the reasons that the PCDD/F concentration in the stack flue gases was between 5.16 and $41.5 \text{ ng I-TEQ N m}^{-3}$, however, by comparing to the PCDD/F concentration in the raw flue gases in front of the activated carbon injection and bag filter of the MSWI during normal operation (mean: $0.610 \text{ ng I-TEQ N m}^{-3}$, range: $0.231\text{--}1.52 \text{ ng I-TEQ N m}^{-3}$), it revealed that a high PCDD/F emission during the heat-up phase occurred due to the low furnace temperature and the poor combustion condition. The surfaces of the boiler and pipe were thus contaminated by the soot particles as well as hydrocarbons, which improved de novo synthesis of PCDD/F formation during the subsequent increase of the temperatures at these locations. Otherwise, the high PCDD/F emission occurred during the start-up procedure also increased the PCDD/F adsorption on the APCDs, like wet scrubber and bag filter and then released over a longer period of time.

3.4. PCDD/F emission quantity of the MSWI during start-up

The profile of the PCDD/F emission rate of stack flue gas with time during start-up of a two year investigation is illustrated in Fig. 2 and the shadowed areas represent

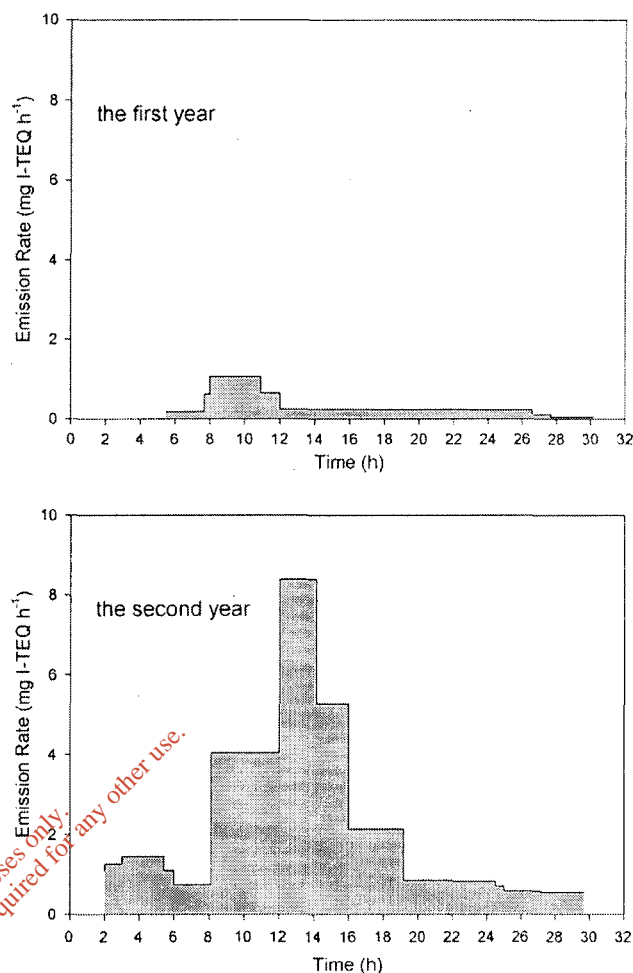


Fig. 2. PCDD/F emission rate from the stack flue gases of the MSWI during startup.

the PCDD/F emission quantity of MSWI during start-up. It revealed that one PCDD/F emission peak exists when the combustion chamber's temperature reaches $490 \text{ }^{\circ}\text{C}$ in both the first and second year. However, owing to the inexperience regarding the sampling strategy, another high PCDD/F emission peak resulted from the poor combustion when waste being fed was not observed in the first year's investigation. After changing the sampling time to be more accordant with the start of waste feeding, the PCDD/F profile clearly showed the phenomenon of PCDD/F generation and two high PCDD/F emission peaks with subsequently slow declination on emission in the second year's investigation. After calculating the shadowed areas, the estimated PCDD/F emission quantity during start-up was 0.0658 g I-TEQ in the second year's investigation.

Incinerators are usually at least shut-down and started-up once a year for maintenance. Taking the MSWI investigated in this study for example, which consists of four incinerators, the estimated annual PCDD/F emission from normal operational conditions was 0.112 g I-TEQ . However, one start-up procedure can generate $\sim 60\%$ of that and the PCDD/F emission quantity resulted from

the start-ups of four incinerators were at least two ($=0.0658 \times 4/0.112$) times larger than that of a whole year's normal operations, without consideration for the PCDD/F emission contributed by the long lasting memory effect because in this study the sampling period ended two days after start-up.

According to the legislation of most countries, PCDD/F measurements of incinerators only have to be conducted once or twice annually and are usually under normal and good operational conditions. Well over a 1000-fold increase in PCDD/F concentration and a two-fold increase in annual PCDD/F emission during the start-up procedures. The days when a cold start-up occurs will thus be much more significant than on the other days of normal operations. After properly evaluating the real total PCDD/F emission, an effective risk management strategy can be developed by assessing the relationship between exposure and health.

4. Conclusions

The memory effect that resulted from the start-up caused the PCDD/F concentration of the first stack flue gas sample of the intermittent incinerators, which was sampled at a stable combustion condition after start-up, elevated as much as 2–3 times higher than the mean of the follow-ups. During the start-up procedure of the MSWI, two high PCDD/F emission peaks in the stack flue gas were observed. One occurred when the combustion chamber's temperature reached 490 °C and the other occurred at the moment when waste was first fed. The elevated PCDD/F concentrations could reach 96.9 ng I-TEQ N m⁻³ and still maintained a high PCDD/F concentration (40 times higher than the Taiwan emission limit) even 18 h after the injection of activated carbon, indicating the long lasting memory effect. The PCDD/F emission over several days resulted from the start-ups of the MSWI were at least two times larger than that from a whole year's normal operations, without consideration for the PCDD/F emission contributed by the subsequent memory effect.

The obtained results revealed that the intermittent incinerators, due to their design or operational characteristics, are prone to start-up procedure and should be replaced by continuous incinerators or the operation schedule from 8 h to 5 days a week should be changed to a continuous two day operation.

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Characteristics of dioxin emissions at startup and shutdown of MSW incinerators

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Abstract

Dioxin concentrations from municipal waste incinerators in Japan and elsewhere often show low concentrations that comply with legal limits (in this paper, the term “dioxin” designates WHO-TEQ: PCDD/Fs + dioxin-like PCB). However, such data is usually generated under normal steady state operational conditions, and there has been little investigation of releases occurring during startup and shutdown. It is important, therefore, to ascertain quantitatively emissions in an unsteady state (startup and shutdown) in order to correctly evaluate the relationship between emissions from a facility and the surrounding environment.

The present study aimed to examine dioxin emissions of a continuously operated incinerator at startup and shutdown, and estimating the time period of greatest emission, and the processes causing dioxin generation.

The startup process was divided into five stages and the shutdown into two; at each stage, dioxins in the flue gas were measured at the boiler outlet and the stack. From the concentration of dioxins and the flue gas volume at each stage, the amount of dioxins at startup and shutdown were calculated, and these were compared with that under steady state conditions.

Dioxin concentration at the stack under steady state conditions was a very low level, while those at startup and shutdown were higher. In the case where dioxin concentration under a steady state is a low level like in this study, it is indicated that the total annual dioxin emission from a facility could be attributed to the startup periods.

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Keywords: MSW incineration; Startup and shutdown; Dioxin; Emissions

1. Introduction

There has been a vigorous drive for the reduction of dioxin emissions from MSW incinerators, and the effects are well known (Tejima et al., 2001). However, these findings were under steady state operational conditions. As emissions under steady state have recently been drastically cut down, it has been assumed that the proportion of the emissions during the unsteady state (startup and shutdown) would have increased compared to the overall amount; this

it is essential that the actual levels be measured in order to evaluate the effects on the surrounding environment. When many batch operation type MSW incinerators existed, studies of the characteristics and reduction of dioxin emissions during unsteady state were undertaken (Tejima et al., 1992). However, these were aimed at very high levels of dioxin emissions, and in older type incinerators than are now in operation.

There have been several reports of measurements of dioxin emissions at startup and shutdown in continuously operated MSW incinerators (Gass et al., 2003; Hunsinger et al., 2003; Michael et al., 2003). In these reports, dioxin concentrations in the flue gas at startup and shutdown phase were clear. However, there are no reports that have

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measured emissions quantitatively, and compared them with those in a steady state. Furthermore, there is insufficient knowledge about the mechanisms involved in dioxin generation under unsteady state conditions.

The present study aimed to measure the amount of dioxin emissions during startup and shutdown at a continuously operated incinerator, and to estimate the time period of the greatest emission. Further, the processes that primarily cause the generation of dioxins were investigated.

Tests were conducted by dividing the startup procedures into five stages, and the shutdown into two; then at each stage, dioxin concentrations were measured at the boiler outlet and the stack. Additionally, dioxin emissions at the

startup and shutdown were calculated from each concentration and the flue gas volume, and these were then compared with those under steady state conditions.

2. Materials and methods

2.1. Process flow, the startup and shutdown procedures of the plant

Fig. 1 shows the schematic flow diagram of the plant, and the passage during startup and shutdown. The facility is a stoker-type MSW incinerator with a throughput class being 10 t/h. The process flow runs as: stoker-type incinerator, boiler, quench chamber, baghouse, steam gas reheater, baghouse, de-NO_x catalytic reactor, boiler, quench chamber, baghouse, de-NO_x catalytic

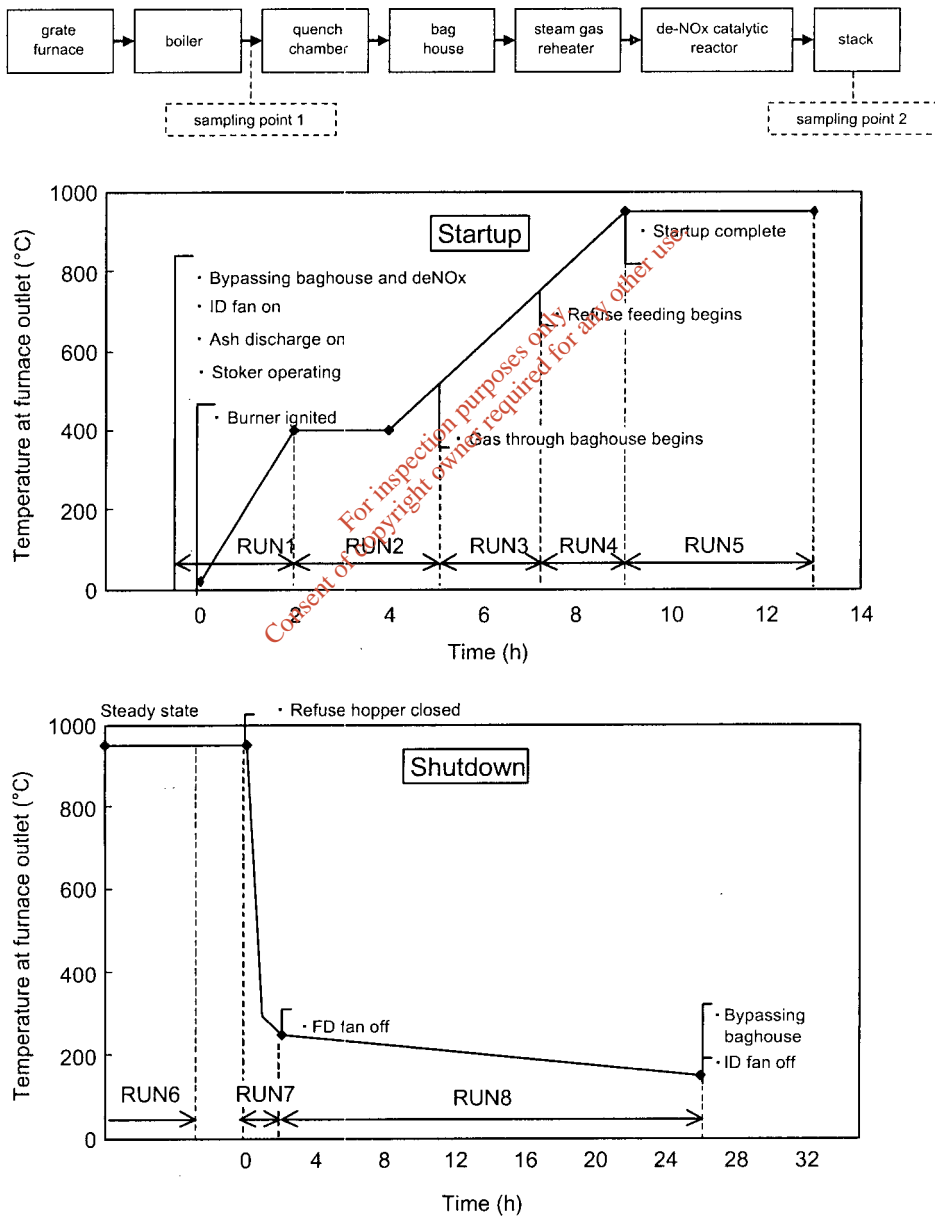


Fig. 1. Schematic flow diagram of the plant and startup, shutdown procedures.

reactor and stack. Samplings were done at the boiler outlet and the stack. The startup and shutdown procedures were as follows.

• Startup

- (1) Temperature is raised using the auxiliary burner (gas temperature inside the combustion chamber: from ambient to 400 °C in 2 h).
- (2) The gas temperature is kept at 400 °C (2 h).
- (3) The gas temperature is further raised by the auxiliary burner from 400 to 600 °C in 2 h, from 600 to 900 °C in 2 h).
- (4) When the gas temperature at the baghouse inlet exceeds 160 °C, the gas flow begins.
- (5) When the gas temperature at the de-NO_x catalytic reactor inlet exceeds 180 °C, the gas begins to flow through the reactor.
- (6) When the combustion gas exceeds 750 °C, the refuse feeding is started. At the baghouse, injections of slaked lime and activated carbon get underway. Operations (4) through (6) are carried out simultaneously with the raising of the temperature under procedure (3).
- (7) When the steam generation rate reaches target, the startup procedures are completed.

• Shutdown

- (1) The refuse hopper is closed. The gas temperature falls from 850 to 400 °C in 2 h). If the temperature drops more than 100 °C below the target temperature, the reheating burner is ignited.
- (2) When the gas temperature inside the combustion chamber falls below 450 °C, the forced draft fan (FD fan) is turned off.
- (3) When the gas temperature at the baghouse inlet falls below 125 °C, the baghouse is by-passed and the induced draft fan (ID fan) is turned off.
- (4) The shutdown procedures are completed.

In actuality, there was a step before shutdown (1), i.e., stopping the refuse supply to the hopper. However, the refuse remaining in the hopper continued to be fed to the furnace even after supply to the hopper was terminated, and for the purposes of this study this period was considered as part of the steady state.

2.2. Experimental methods

During these startup and shutdown procedures, flue gas samplings as shown in Fig. 1 as RUN1–RUN8 were carried out.

- RUN1: ID fan was turned on – temperature was raised by the auxiliary burner (from ambient to 400 °C).
- RUN2: The combustion gas temperature began to be maintained at 400 °C – gas started to flow through the baghouse.

RUN3: Gas started to flow through the baghouse – refuse feed began.

RUN4: Refuse feed began – startup was completed.

RUN5: 4 h after startup was completed.

RUN6: Steady state.

RUN7: Refuse hopper was closed – FD fan was turned off.

RUN8: FD fan was turned off – ID fan was turned off.

The plant had been operated for 50 d from the startup to the steady state sampling. Steady state and shutdown samplings (RUN6, RUN7) was undertaken almost continuously.

The dioxin analyses were fundamentally based on JIS K0311 JIS: Japanese industrial standards). However, this method defines measurement in the steady state, requiring sampling for 4 h under stable combustion conditions. Since this study aims at measurements in an unsteady state, this portion of the method was set aside. Instead, measurements of the flue gas flow were made every 30 min, adjusting suction speed so that isokinetic sampling could be undertaken.

TEQ calculation was based on WHO-TEF (1998). As for the measurement results of the dioxins that were below the quantification limit, TEQ was calculated using one-half of the value for the quantification limit (Hoogerbrugge and Liem, 2000).

The dioxins adhered to sampling probes and cylindrical paper filters were defined as the particulate dioxins, and the rest as gaseous dioxins; these two forms were analyzed separately.

Dust deposited in the duct at the boiler outlet was sampled before starting up the furnace. At startup, bottom ash and fly ash were sampled on RUN5 at other periods, refuse feeding was too small to conduct ash sampling). At shutdown, bottom ash was sampled on RUNs 7 and 8, and the fly ash was sampled on RUN7. In addition, the flue gas temperature was measured at the furnace outlet, and the gas volume, and CO and NO_x concentrations were continuously monitored at the stack.

2.3. Method of measurement during RUN8

Initially, RUN8 was considered to be a single data source. The normal procedure is to shut down the furnace with the gas flowing through the baghouse. On this study, however, the gas temperature at the baghouse inlet accidentally went down below the lower limit of gas flow, activating the bypass in order to protect the filter cloth. The gas returned to flow through the baghouse after approximately 5 h. This was a freak phenomenon that had never happened before. Since this was not a normal shutdown process, attempts were made to evaluate without the baghouse bypass. Particulate dioxins and gaseous dioxins were analyzed separately. The particulate dioxins were further divided into the dust that adhered to the probe and that captured by the cylindrical paper filter as shown in Fig. 2. The filter that served during the baghouse bypass

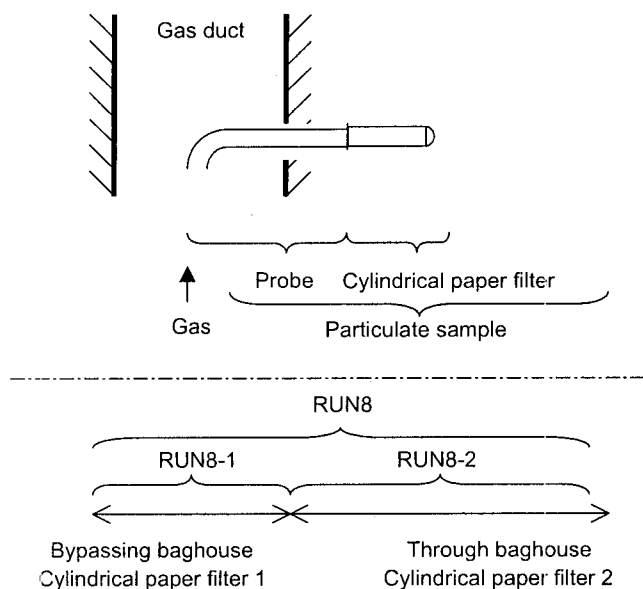


Fig. 2. Conceptual drawing of RUN8 sampling.

Table 1
PCDD/Fs, dioxin-like PCB concentrations during RUN8

Sample	Time	Concentration (ng WHO-TEQ/m ³)		
		Particulate		Gaseous
		Probe	Cylindrical paper filter	
RUN8-1	19:05–23:50	3.4	14	0.76
RUN8-2	23:50–19:00	3.4	0.49	

(since the onset of RUN8) was changed at the gas flow resumption, enabling separation of dioxins for each period, named RUN8-1 and RUN8-2, respectively.

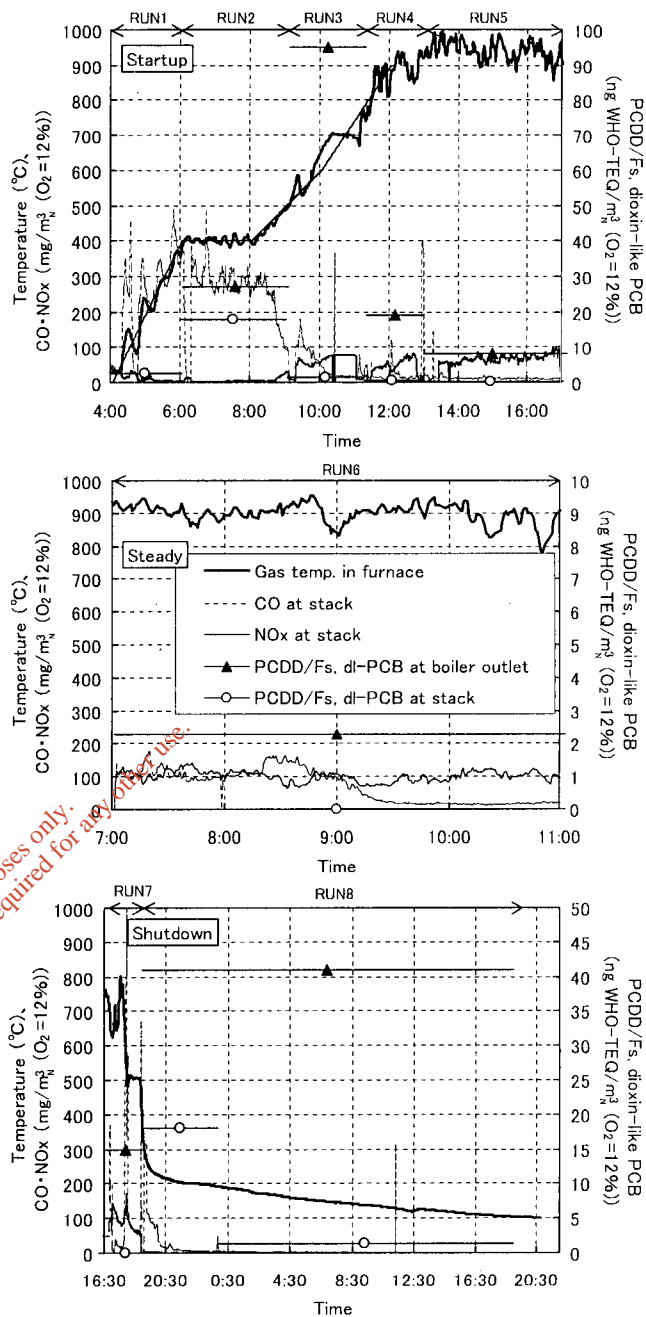
The probe was not replaced, but was used throughout RUN8, and so the ratio of RUN8-1 vs. RUN8-2 could not be determined; thus calculations were made on an assumption that this ratio was the same as that of the particulate dioxins captured by the filter. It was also assumed that the concentrations of gaseous dioxins were the same on RUN8-1 and RUN8-2. As shown in Table 1, particulate dioxins adhered to the cylindrical paper filter were dominant in RUN8, minimizing the importance of the veracity of such suppositions.

3. Results and discussion

3.1. Operation

Fig. 3 shows data of the gas temperature in the combustion chamber, dioxin concentrations at the boiler outlet and the stack, and concentrations of CO and NO_x at the stack. All the measured dioxin, CO and NO_x concentrations in the flue gas are converted to 12% oxygen as required by Japanese law.

The startup operation was performed according to the program. It was completed in 9 h after the start (RUN1-

Fig. 3. Gas temperature inside the combustion chamber. CO and NO_x concentrations at stack. PCDD/Fs, dioxin-like PCB concentrations at boiler outlet and stack.

RUN4), but another hour was needed for steam generation to stabilize. During burner-only combustion, the CO concentration was nearly 300 mg/m³ while refuse-only combustion produced roughly 20 mg/m³. NO_x concentrations were 10 mg/m³ or so with burner alone and 50 mg/m³ with refuse-only combustion.

In the steady state condition, CO remained at 10–100 mg/m³ whereas NO_x varied between 70 and 110 mg/m³.

During shutdown, spikes in CO concentrations were observed at the ignition of reheating burner and at stopping the FD fan (beginning of RUN8). When the FD fan is stopped, the inside of the furnace does not cool down for a while due to the residual heat of the refractory mate-

rial and boiler; it normally requires more than 24 h to reach “below 125 °C at the baghouse inlet,” the condition for the ID fan to turn off. Although the ID fan was turned off, 7000–8000 m³/h of flue gas flowed until the sampling was finished.

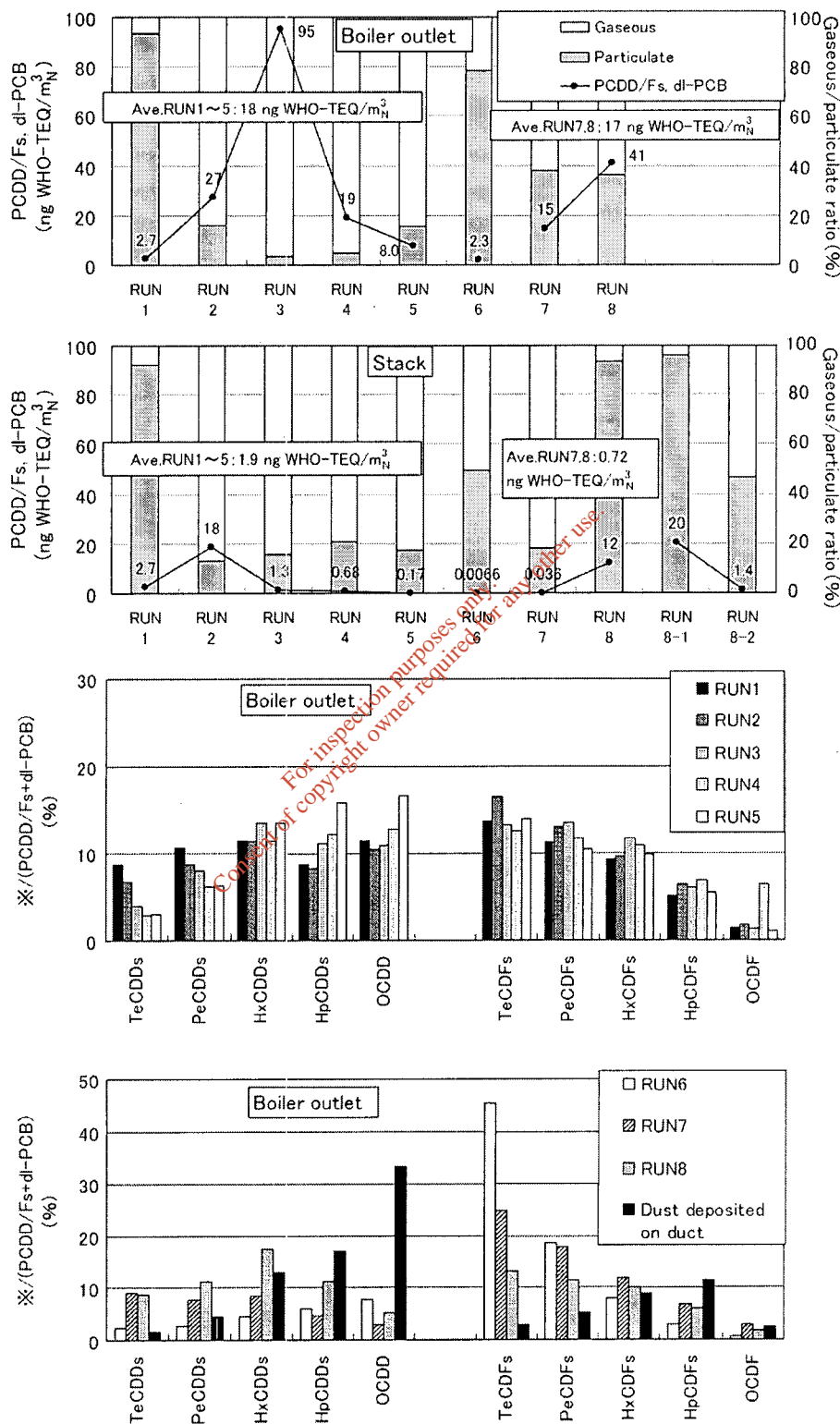


Fig. 4. PCDD/Fs, dl-PCB concentrations, gaseous/particulate ratio. Congener distribution of boiler outlet PCDD/Fs (no TEQ conversion).

The procedures of startup and shutdown we applied in the tests were the same as those normally practiced in this facility, except for the baghouse bypass that occurred on RUN8.

3.2. Dioxins concentration at startup

Fig. 4 shows the results of dioxin concentration measurements in the flue gas, the ratio of gaseous versus particulate dioxins, and PCDD/Fs congener distribution at the boiler outlet. Table 2 lists those of the fly ash, the bottom ash and the dust deposited on the duct.

The average concentration of the dioxins at startup (RUN1–RUN5) was 18 ng WHO-TEQ/m³ at the boiler outlet, and 1.9 ng WHO-TEQ/m³ at the stack. The regulatory limit for this facility is 0.1 ng WHO-TEQ/m³, but it posed no legal problem since the regulation applies only to the steady state.

The dioxin concentrations at the boiler outlet continued to rise during RUN1–RUN3 when burner-only combustion was in effect, and reached 95 ng WHO-TEQ/m³ on RUN3 at its peak. It began to fall after the refuse feeding began, to 19 ng WHO-TEQ/m³, and down to 8 ng WHO-TEQ/m³ on RUN5 with refuse-only combustion. PCDDs have a tendency to shift from low chlorine to higher chlorine congeners as time passes, while PCDFs always resulted in a very high ratio of low-chlorine compounds. As for the distribution of gaseous and particulate dioxins, 80–90% was gaseous, except for during RUN1.

The dioxin concentration in dust deposited on the duct at the boiler outlet was 1.2×10^4 ng WHO-TEQ/kg (Table 2), and the congener distribution indicated that high-chlorine PCDDs were greater in proportion while PCDFs were highest at 7-Cl compounds. As most dioxins in the flue gas at the boiler outlet are gaseous and possess different sets of PCDD/Fs congener distributions, it is unlikely that the main sources of the dioxins are those deposited on the duct and carried away by the flue gas at the startup.

Many studies done in the past have concluded that the reason for the high dioxin concentration at startup is because it is generated from the soot that came from the burner and deposited on the furnace wall and boiler tubes (Gass et al., 2003; Hunsinger et al., 2003). As stated earlier, however, the concentration of dioxins from the dust deposited on the duct at the boiler outlet collected before the

incinerator startup was 12 ng WHO-TEQ/m³. Assuming that the thickness of dust on the furnace and boiler wall was 2–5 mm, and that the dioxin concentration was uniformly distributed over the entire area, with the total heat exchange surface of the boiler (around 3000 m²), and the specific gravity of the dust (0.3 t/m³), it indicates that there were as much as 20–50 mg WHO-TEQ of residual dioxins in the furnace before startup. Meanwhile, the total amount of dioxins in the flue gas during the startup process (RUN1–RUN5) calculated from the flue gas volume and the dioxin concentration at the boiler outlet was 10 mg WHO-TEQ. This approximation indicates that the amount of dioxin in dust deposited on furnace and boiler is equivalent to (or more than) those detected from the flue gas.

Also, Stieglitz et al. (1993) stated that in his test of heating incineration fly ash to 275–350 °C, PCDD/Fs were synthesized to a level of 10⁶–10⁷ ng/kg (no TEQ conversion). This implies that there is a possibility of a new synthesis of ten times as large as the actually measured dust deposited on the duct of 1.2×10^4 ng WHO-TEQ/kg (1.2×10^6 ng/kg; no TEQ conversion).

According to Altwicker et al. (1994), 99% of PCDD/Fs in fly ash existed in solid forms at 250 °C whereas only 6% were in solid forms at 350 °C.

Due to the cooling effect of the water membrane, furnace and boiler wall temperatures are lower than that of the flue gas, and during the startup (particularly in RUN3 and later), many parts would be at around 300 °C for a long period.

There are three possible reasons for the high dioxins concentration at the startup period, particularly with burner-only combustion:

- (1) Dust scattering from the furnace and boiler tube walls.
- (2) Synthesis within the dust deposited on the furnace and boiler tube walls, and evaporation thereof.
- (3) Synthesis from the unburned carbon contained in the exhaust gas from the burner.

From the current study, it appears that reason (2) contributes the most.

When the baghouse was bypassed (RUN1, 2), the results at the stack were the same as those at the boiler outlet. This shows that no synthesis took place at the quench chamber, or duct line, etc. downstream. After RUN3 when the gas flowed through the baghouse, the dioxin concentration at the stack went down. At the boiler outlet on RUN3, the proportion of gaseous dioxins was as high as 97%, and dust removal alone could not remove dioxins. Since no activated carbon injection was done on RUN3 (gas flowing), it was presumed that the activated carbon injected before the last shutdown and remaining on the bag filters showed its effect (activated carbon was injected during RUN4 and afterwards).

Table 2 shows that at the startup, the dioxin concentrations were 4.1×10^2 ng WHO-TEQ/kg for the bottom ash

Table 2
PCDD/Fs, dioxin-like PCB in ash and dust deposited on the duct at the boiler outlet

Sample	Concentration (ng WHO-TEQ/kg)	
	Bottom ash	Fly ash
Startup	4.1×10^2	1.1×10^4
Steady	6.9	6.7×10^2
Shutdown	9.1	1.2×10^3
Dust deposited on duct		1.2×10^4

Table 3
Calculation of total PCDD/Fs, dioxin-like PCB emissions from the stack at startup, steady state, and shutdown

		Measurement period (min)	Gas volume at stack ($\text{m}_N^3/\text{h}(\text{O}_2 = 12\%)$)	PCDD/Fs, dl-PCB at stack ($\text{ng WHO-TEQ}/\text{m}_N^3$)	Emission ($\mu\text{g WHO-TEQ}$)
Startup	RUN1	127	6300	2.7	36
	RUN2	170	13600	18	709
	RUN3	122	21100	1.3	56
	RUN4	77	51600	0.68	45
	RUN5	240	80100	0.17	54
Steady	RUN6	240	87000	0.0066	2.3
Shutdown	RUN7	125	33800	0.036	2.5
	RUN8-1	285	500	20	49 (3.4) ^a
	RUN8-2	1150	100	1.4	2.8

^a RUN8-1, the baghouse bypass was ignored as being an anomaly, the value (3.2) is calculated by using the concentration same as RUN8-2.

and 1.1×10^4 ng WHO-TEQ/kg for the fly ash, higher than the steady state values of 6.9 ng WHO-TEQ/kg and 6.7×10^2 ng WHO-TEQ/kg, respectively. As stated earlier, dioxin concentrations at the boiler outlet on RUN3 was high, and it was lowered by filtration before reaching the stack. Therefore, the dioxins must have moved over toward the fly ash, increasing its concentration. At shutdown, the concentrations were 9.1 ng WHO-TEQ/kg for the bottom ash and 1.2×10^3 ng WHO-TEQ/kg for the fly ash, slightly higher than those during a steady state.

3.3. Dioxin concentrations during steady state and shutdown

In the steady state, the concentration was 2.3 ng WHO-TEQ/ m_N^3 at the boiler outlet, the lowest among all the RUNs. PCDDs with higher chlorine content occupied a larger proportion, while there were more PCDFs with lower chlorination among the congeners. At the stack, the concentration was 0.0066 ng WHO-TEQ/ m_N^3 , one-fifteenth of the legal limit for this facility, 0.1 ng WHO-TEQ/ m_N^3 .

During shutdown (RUN7, 8), the average was 17 ng WHO-TEQ/ m_N^3 at the boiler outlet and 0.72 ng WHO-TEQ/ m_N^3 at the stack. At RUN7, 15 ng WHO-TEQ/ m_N^3 , a value higher than in the steady state, was detected. Since a spike in CO concentration was observed when the FD fan was turned off, it is assumed that there was unburned residue in the furnace causing incomplete combustion. The concentration on RUN8 was even higher at 41 ng WHO-TEQ/ m_N^3 , but the measurement was made at the point where the gas volume was lower by two digits, and since the temperature at the furnace outlet was down to 200 °C within the first 2 h, it is unlikely that any new synthesis contributed to this increase. It was assumed that the memory effect of RUN7 caused an additional emission of dioxins.

As stated, the baghouse was bypassed on RUN8-1 and the concentration at the stack was 20 ng WHO-TEQ/ m_N^3 , but RUN8-2 with the baghouse filtration operating, it was reduced to 1.4 ng WHO-TEQ/ m_N^3 , attesting to the effectiveness of the bag filter. Under ordinary operational conditions, the gas is always directed through the baghouse at shutdown, contributing to a reduction in dioxins emitted.

The congener distributions on RUNs7 and 8 show that PCDDs have a spike on HxCDD, while lower chlorine PCDFs take the majority share. When the furnace was in a startup or shutdown situation, there was an ample supply of chlorine and the proportion of higher-chlorine compounds increased.

3.4. Evaluation of dioxins emission

Table 3 shows the dioxin emission from the stack for each of the RUNs. The dioxin emissions with flue gas of this facility per year were calculated from an assumption of 280 d of operation and four startups per year. The results are as follows.

Emissions at startup: 900 $\mu\text{g WHO-TEQ}$ (total of RUN1–RUN5) * 3 times/year = 2700 $\mu\text{g WHO-TEQ}/\text{year}/\text{unit}$.

Emissions under steady state: 2.3 $\mu\text{g WHO-TEQ}/4 \text{ h} * 24 \text{ h/d} * 280 \text{ d/year} = 3900 \mu\text{g WHO-TEQ}/\text{year}/\text{unit}$.

Emissions at shutdown: 8.7 $\mu\text{g WHO-TEQ}^1$ (total of RUNs7 and 8) * 3 times/year = 26 $\mu\text{g WHO-TEQ}/\text{year}/\text{unit}$.

It is assumed that 41% of the total annual emissions can be attributed to the startup period. The emission at shutdown is roughly only 0.4%, hardly a contributing factor. In the current study, the emission in the steady state is only one-fifteenth of the legal limit, making the emissions at startup and shutdown appear large. When evaluating the influence of the dioxin emissions from MSW incinerators to the surrounding environment, unsteady states must also be considered.

This facility conducts dust removals from the furnace and the boiler at the beginning of each year. The current data represent measurements made at near the end of the year, and thus the time when there would be the highest dust accumulation. It would be meaningful to undertake testing at another time during the year to enable a comparison to be made.

¹ For RUN8-1, the baghouse bypass was ignored as being an anomaly, and a concentration same as RUN8-2 was used.

4. Conclusions

The dioxin concentrations in the flue gas at the stack are:

Average during the total startup process: 1.9 ng WHO-TEQ/m³_N.

In a steady state: 0.0066 ng WHO-TEQ/m³_N.

Average of total shutdown process: 0.72 ng WHO-TEQ/m³_N.

- For both startup and shutdown, the furnace and the boiler are the main sources of dioxins, with no evidence of synthesis along the gas treatment process. The positive effect of gas filtration at the baghouse was clearly demonstrated.
- The dioxin concentration in the flue gas at the boiler outlet at startup reaches its highest level (95 ng WHO-TEQ/m³_N) when burner-only combustion is underway, and tends to decrease when refuse is fed. From analyzing the dioxins in the dust of the boiler outlet duct, it is assumed that the dioxins observed during burner-only combustion come largely from syntheses in the dust deposited on the furnace and the boiler, and from the evaporation thereof. This is a mere assumption at this stage of the study, and it appears that further tests such as heating the dust of the boiler outlet duct would be essential from a standpoint of dioxin emission control.
- The study of the distribution of the congeners of PCDDs has revealed that while refuse feeding is underway, such as in a steady state, compounds with a higher degree of chlorination show definite tendencies to dominate the distribution, compared with the period without refuse feeding, such as early stages of startup and after shutdown.

- From calculations of annual emissions, it is assumed that 41% of the total dioxin emission comes from the startup period. Thus it is necessary to consider emissions during startup when evaluating the effect on the surrounding environment using measured data; as emissions during shutdown amount to a mere 0.4% or so; this time period is hardly a contributing factor.

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