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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.

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, de-NO_x catalytic

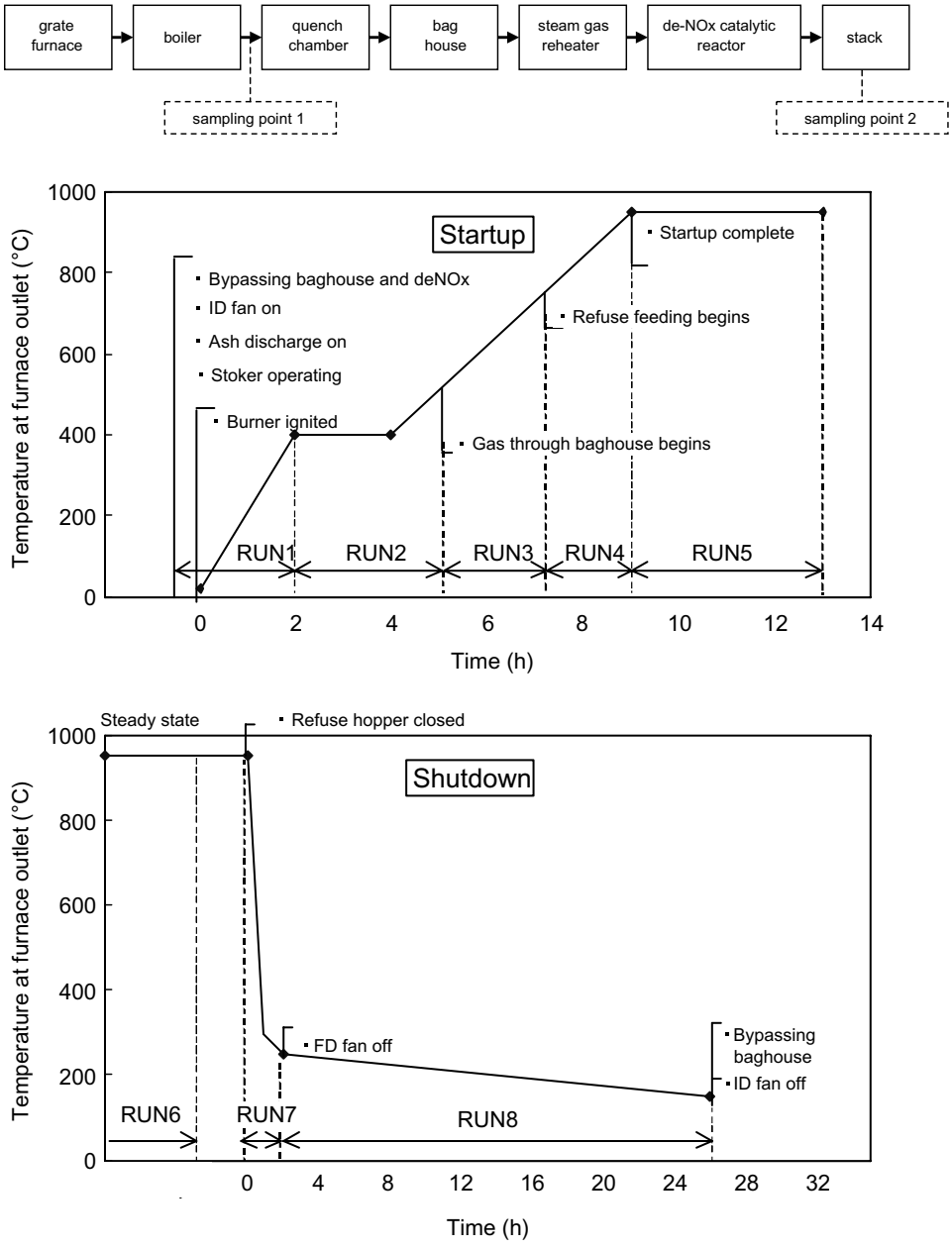

Fig. 1. Schematic flow diagram of the plant and startup, shutdown procedures.

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

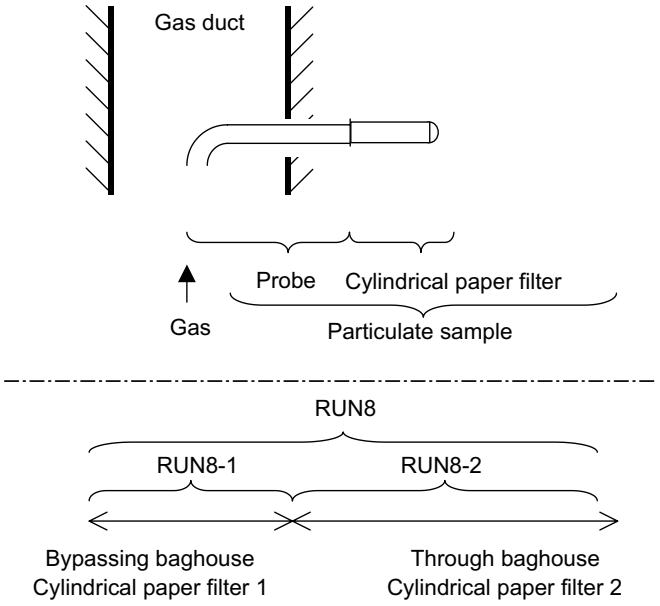

Fig. 2. Conceptual drawing of RUN8 sampling.

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

Sample	Time	Concentration (ng WHO-TEQ/m^3_N)		
		Particulate		Gaseous
		Probe	Cylindrical paper filter	
RUN8-1	19:05–23:50	3.4	14	0.76
RUN8-2	23:50–19:00		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-RUN4), but another hour was needed for steam generation to stabilize. During burner-only combustion, the CO concentration was nearly 300 mg/m^3_N while refuse-only combustion produced roughly 20 mg/m^3_N. NO_x concentrations were 10 mg/m^3_N or so with burner alone and 50 mg/m^3_N with refuse-only combustion.

In the steady state condition, CO remained at 10–100 mg/m^3_N whereas NO_x varied between 70 and 110 mg/m^3_N.

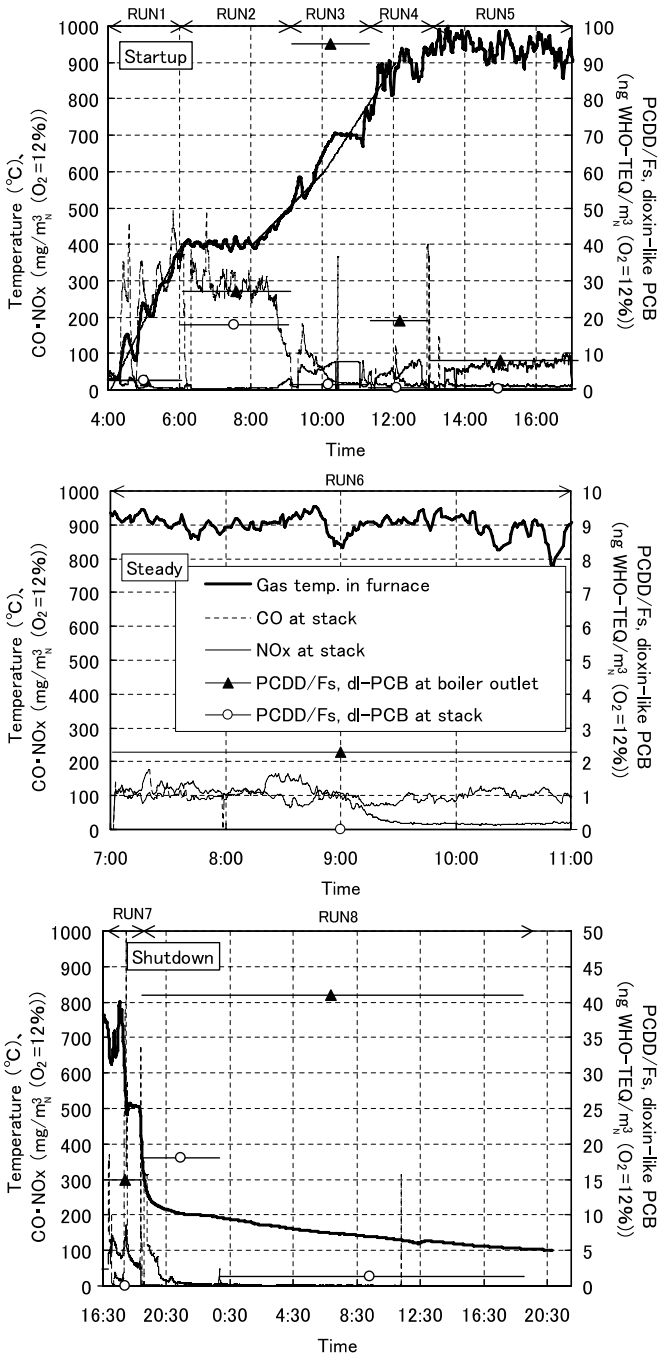

Fig. 3. Gas temperature inside the combustion chamber. CO and NO_x concentrations at stack. PCDD/Fs, dioxin-like PCB concentrations at boiler outlet and stack.

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 material 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 m^3_N/h of flue gas flowed until the sampling was finished.

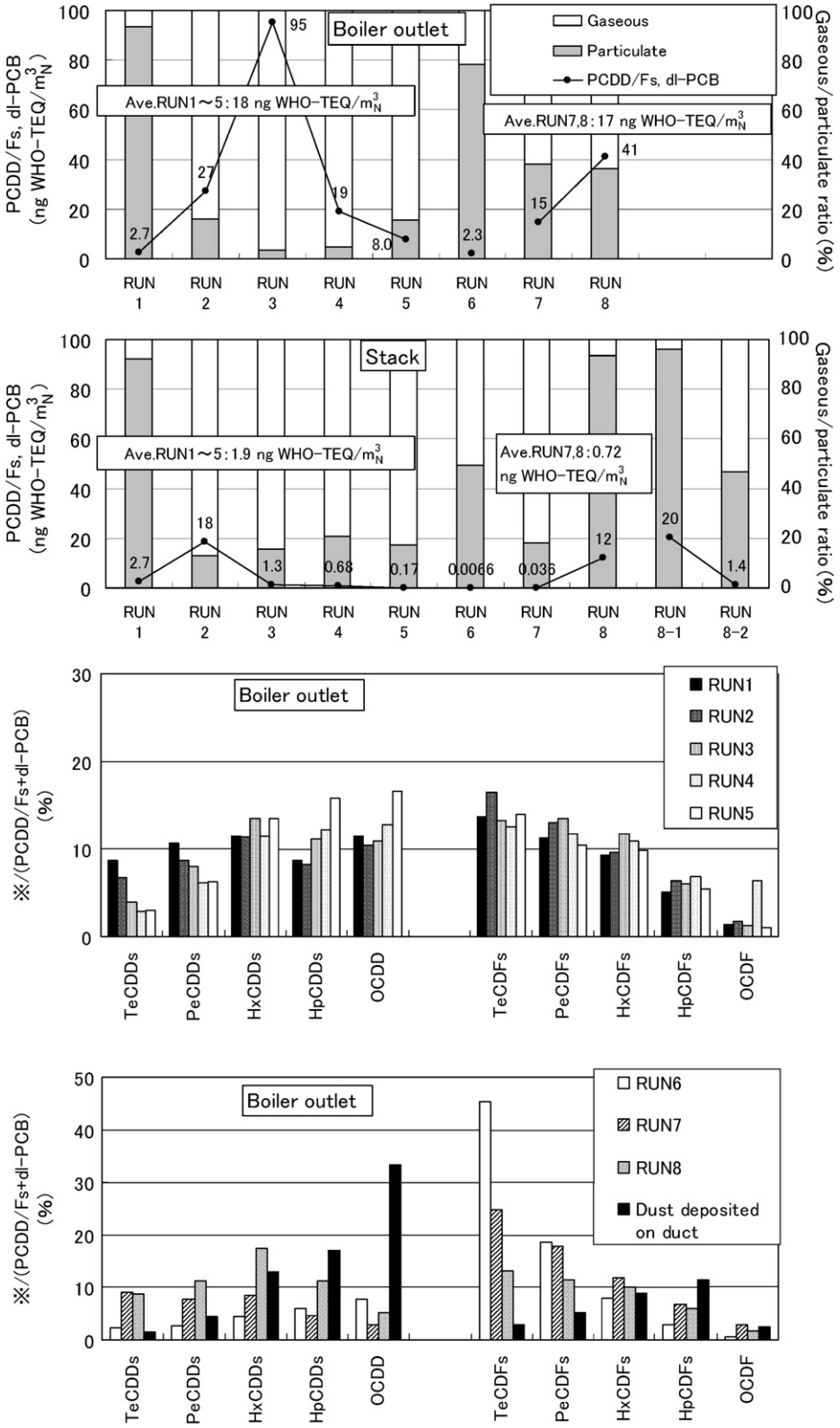

Fig. 4. PCDD/Fs, dl-PCB concentrations, gaseous/particulate ratio. Congener distribution of boiler outlet PCDD/Fs (no TEQ conversion).

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/m^3_N at the boiler outlet, and 1.9 ng WHO-TEQ/m^3_N at the stack. The regulatory limit for this facility is 0.1 ng WHO-TEQ/m^3_N, 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/m^3_N on RUN3 at its peak. It began to fall after the refuse feeding began, to 19 ng WHO-TEQ/m^3_N, and down to 8 ng WHO-TEQ/m^3_N 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/m^3_N. 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 m^2), and the specific gravity of the dust (0.3 t/m^3), 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 10^6–10^7 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 ($m^3_N/h(O_2 = 12\%)$)	PCDD/Fs, dl-PCB at stack (ng WHO-TEQ/m^3_N)	Emission (μg 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^3_N 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^3_N, one-fifteenth of the legal limit for this facility, 0.1 ng WHO-TEQ/m^3_N.

During shutdown (RUN7, 8), the average was 17 ng WHO-TEQ/m^3_N at the boiler outlet and 0.72 ng WHO-TEQ/m^3_N at the stack. At RUN7, 15 ng WHO-TEQ/m^3_N, 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^3_N, 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^3_N, but RUN8-2 with the baghouse filtration operating, it was reduced to 1.4 ng WHO-TEQ/m^3_N, 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 μg WHO-TEQ (total of RUN1–RUN5) * 3 times/year = 2700 μg WHO-TEQ/year/unit.

Emissions under steady state: 2.3 μg WHO-TEQ/4 h * 24 h/d * 280 d/year = 3900 μg WHO-TEQ/year/unit.

Emissions at shutdown: 8.7 μg WHO-TEQ[1] (total of RUNs7 and 8) * 3 times/year = 26 μg WHO-TEQ/year/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/m^3_N.
In a steady state: 0.0066 ng WHO-TEQ/m^3_N.
Average of total shutdown process: 0.72 ng WHO-TEQ/m^3_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/m^3_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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