

THE FORMATION AND BEHAVIORS OF DIOXINS AND RELATED COMPOUNDS IN DIFFERENT INCINERATION PROCESSES IN JAPAN

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Introduction

Recent progress in combustion and flue gas cleaning techniques has generally reduced dioxin emissions from modern incineration plants. However, the occurrence and changes in dioxins (DXNs) can be observed during gas flow from incinerators to advanced gas cleaning equipment. The authors¹ have demonstrated such formation of DXNs around dust collection processes in different incineration plants and a relationship between DXNs and dioxin surrogate compounds. In this study, further measurements were conducted to show the difference in formation characteristics between a former-type facility including an electrostatic precipitator (EP) and a brand new gasification-melting facility. The results obtained for flue gas and precipitated fly ash may provide help with interpreting the final emission data for DXNs in the latest incineration plants. Hexachlorobenzene and surrogate organic halogens were also measured.

Material and methods

Flue gas and ash sampling in incineration plants

Measurements were conducted in two kinds of incineration plants, as shown in Figure 1, and the measurements

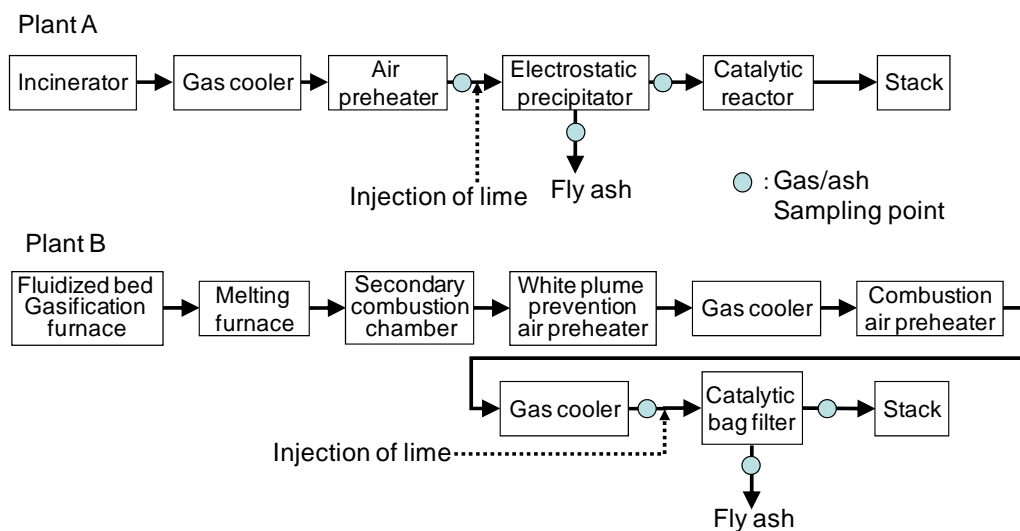


Figure 1 Incineration plant flow and sampling point

at Plant A were also conducted in the same manner as in our previous study¹. Plant A has a stoker-type semi-continuous (60 t/16 h) municipal waste incinerator equipped with a catalyst-packed tower after the electrostatic precipitator to remove NO_x and DXNs. Plant B has a fluidized bed-type gasifier followed by a high-temperature melting furnace. Both these types are becoming increasingly common in Japan. The capacity (70 t/d) of these plants is smaller than average. The bag filter (BF) installed in Plant B contains dioxin decomposition catalysts to break down gaseous dioxins during dust collection. Sampling of gases and fly ash was conducted five times (once a day) per week at the position marked in Figure 1. Fly ash was sampled 4 to 8 times during the flue gas DXN measurement over a period of 4 hours. The dioxin surrogate, comprising organic halogen compounds (OHCs), in the flue gas was sampled at the inlet of the dust collection equipment using an adsorption tube comprising two types of adsorbents in the same way as in our previous paper¹.

Plant operation

At Plant A, flue gas samplings were conducted during daily operation five times per week. However, three experiments (Runs A-1, 2 and 3) were conducted at the EP inlet at 290 °C, and Runs A-4 and 5 were conducted at 260 °C.

At Plant B, flue gas samplings were conducted under various experimental conditions taking account of such factors as the temperature at the bag filter inlet and second air injection rate. Five runs, including Run B-1, were conducted under normal conditions, meaning ordinary operation conditions. The experimental parameters in B-2 to B-5 were different. The temperature at the inlet of the bag filter was raised to 217 °C, higher than for Run B-1. In Run B-3, the second air rate was set higher than for the other runs, meaning that the flue gas recirculation amount increased, to examine its influence on the reduction of dioxin formation. In Run B-5, the amount of MSW was set larger than in normal conditions. The various data, including the temperature and flue gas concentration observed in each run, are shown in Table 1.

Table 1 Experimental conditions at Plant B

Run No.	MSW amount supplied [kg/h]	Second air rate [m ³ _N /h]	Temperature ^a [°C]				Flue gas rate [m ³ _N /h]	Water amount for gas cooler [m ³ /h]	O ₂ in flue gas [vol %]	CO in flue gas [ppm]
			Outlet of gas cooler	Outlet of air heater	Inlet of bag filter	Inlet of SCR ^b				
B-1	1238	1301	449	384	196	198	9015	0.776	9.0	22
B-2	1260	1319	452	384	217	211	8975	0.659	8.4	44
B-3	1238	1383	451	384	199	201	8240	0.806	7.7	120
B-4	1250	1131	450	385	197	197	9637	0.787	7.9	73
B-5	1495	1335	437	372	196	199	10120	0.864	8.7	21

^a Temperature values are the averages of those observed over 4 hours of dioxin measurement.

^b Selective catalytic reactor

Analysis

DXNs in flue gas and fly ash samples were analyzed based on the Japanese Industrial Standard JIS K 0311 using high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS). Hexachlorobenzene was also analyzed for the same samples using a low-resolution GC and quadrupole low-resolution MS system. OHCs were determined separately by their atomic absorption at specific wavelengths

using atomic emission spectrometry employing radio-frequency helium plasma².

Results and discussion

DXNs in flue gas and fly ash

We made five measurements at every plant, as shown in Table 2. However, the measurements in Plant A were once conducted in the previous paper¹. At this time, the critical temperature effect was found in the data for Plant

Table 2 Measurement results of DXNs at the two plants

Run No.	Plant A			Run No.	Plant B		
	Inlet of EP [ng/m ³ _N @12%O ₂]	Fly ash [ng/g]	Outlet of EP [ng/m ³ _N @12%O ₂]		Inlet of BF [ng/m ³ _N @12%O ₂]	Fly ash [ng/g]	Outlet of BF [ng/m ³ _N @12%O ₂]
A-1	36 (0.47) ^a	74 (1.3)	250 (4.7)	B-1	310 (4.0)	38 (0.56)	13 (0.089)
A-2	8.4 (0.11)	36 (0.64)	140 (2.5)	B-2	370 (4.4)	15 (0.22)	13 (0.097)
A-3	15 (0.19)	15 (0.23)	110 (1.8)	B-3	490 (5.3)	74 (0.95)	19 (0.11)
A-4	9.3 (0.12)	35 (0.61)	24 (0.40)	B-4	290 (3.7)	18 (0.25)	13 (0.079)
A-5	13 (0.18)	18 (0.30)	19 (0.32)	B-5	180 (2.4)	27 (0.32)	7.8 (0.049)

a The number in parenthesis shows toxic equivalent ([ng-TEQ/m³_N] or [ng-TEQ/g]).

A, which was the difference between Runs A-1, -2, -3 and Runs -4 and -5. Because the operational temperatures at the inlet of EP were 290 °C for Runs A-1, -2, -3 and 260 °C for Runs A-4 and -5, the flue gas DXN concentrations at the temperature of 290 °C were higher than those at 260 °C, which suggested the *de novo* synthesis in the EP. The inconsistency in fly ash content may be due to difficulties and fluctuations in sampling of solids. However, similar concentrations and content data were observed for the samples at Plant A the former experiment¹ and in this study. At this incineration plant, it was estimated that relatively good combustion is achieved due to the relatively low DXN concentrations at the inlet of the EP. Under these conditions, the average CO concentration of the plant was very low. Lower synthetic potential in the gas cooler and air preheater processes may additionally contribute. The EP flue gas was found to be further cleaned by passing it through the catalytic reactor before exhaustion (< 0.1 ng-TEQ/m³_N).

On the other hand, a major difference can be seen in the results for Plant B. Higher concentrations of over 2.4 ng-TEQ/m³_N were observed at the inlet of Plant B. This fact suggests that *de novo* synthesis took place in the processes between the gas cooler and air preheater because the flue gas was in the temperature range between 200 and 450 °C during the gas cooling process³. Further, the catalytic decomposition effect of the bag filter containing catalysts was seen in the concentration at the outlet of the BF. The reduction ratio of DXNs in flue gas was 96.0 % in total concentration and 97.9 % in toxic equivalent value. However, this included both the filtering effect of the bag filter and the decomposition effect due to the catalyst.

Effect of operational factors on dioxins

Changing the operational factors at Plant B affected the flue gas concentrations at the inlet of BF and also the content of the fly ash samples. This was because the factors were considered to be related to the flue gas nature between gas cooler and bag filter. Three points were examined: 1) the influence of flue gas recirculation (Runs B-3 and B-4), 2) the change in MSW amount supplied to the gasification/melting furnace system (Run B-5) and 3) the temperature of the BF (Run B-2). Of these, a relatively large difference was seen between Runs B-3 and

B-4. Three concentration/content data items for Run B-3 were the highest for all the results in Plant B. This is because reducing the recirculation rate of flue gas caused less air turbulence in the second combustion chamber. Since the gasification of Plant B is performed using a fluidized bed type reactor, the fluctuation in the concentrations of gasified components was considered to be large. Therefore, an effective second combustion may be needed to eliminate various by-products. Indeed, CO concentrations in this plant were relatively high, as shown in Table 1, especially in Run B-3. However, no effects with regard to points 2) and 3) were observed, probably because the effects of these factors were relatively small compared to the influence of completeness of the second combustion and *de novo* synthesis in the gas cooling process.

Another relevant experimental data can be seen in the concentrations of hexachlorobenzene, as shown in Table 3. The flue gas concentrations in Plant B were higher than in Plant A. This was also because there were relatively large amounts of incombustibles in the flue gas. Further, the concentrations were closely similar between the inlet and outlet of

the EP or BF due to the more volatile nature of hexachlorobenzene than DXNs. The result for Plant B also suggests that DXN decomposition catalysts do not effectively eliminate hexachlorobenzene.

Another topic concerns surrogate organic halogens. In this measurement, volatile and semi-volatile chlorines/bromines were measured using a selective sampling method¹. Figure 2 shows the relationship between volatile chlorines, defined as compounds with boiling points between 70 °C and 180 °C, and DXNs at the BF inlet. Considering that the measurement of the surrogate organic halogens is somewhat easier and faster than DXN measurements, the results suggest that DXN concentrations before dust collection can be successfully monitored using the surrogate indicator.

Mass balance of dioxins

Table 4 shows mass balance data for DXNs at the two plants: the results show the difference between the balance features of the two plants. Apparently, at Plant A, at which *de novo* synthesis tends to occur, the amounts both at the EP outlet and in the fly ash increased by tenfold or more compared with the

Table 3 Measurement results of hexachlorobenzene at the two plants

Run No.	Plant A			Run No.	Plant B		
	Inlet of EP [ng/m ³ _N]	Fly ash [ng/g]	Outlet of EP [ng/m ³ _N]		Inlet of BF [ng/m ³ _N]	Fly ash [ng/g]	Outlet of BF [ng/m ³ _N]
A-1	53	(6.2)*	46	B-1	360	21	390
A-2	16	(4.6)	56	B-2	570	41	670
A-3	18	(3.2)	62	B-3	620	41	700
A-4	61	(6.6)	60	B-4	320	28	330
A-5	67	(6.7)	51	B-5	560	29	490

* Parentheses indicate the data to be under the quantification limit.

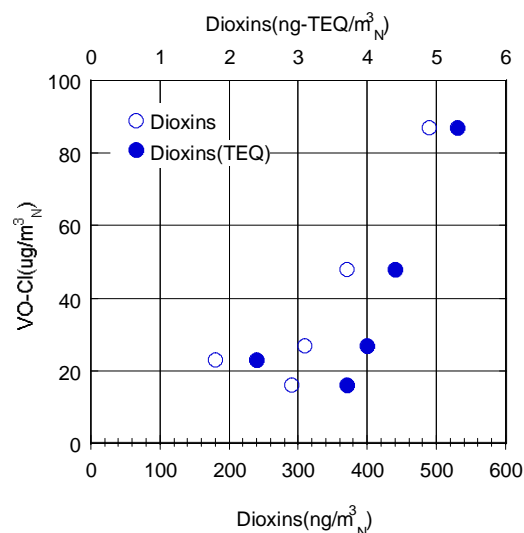


Figure 2 Relationships between dioxins and volatile organic chlorines as surrogate organic halogens at the inlet of the BF in Plant B (Dioxin concentrations are expressed both as total concentration at 12% O₂ condition and in TEQ)

amount at the EP inlet. The data for Runs A-4 and A-5 were relatively small, probably because of the lower operating temperature (260 °C). These were mass increases due to DXN generation in EP; however, the balance at Plant B was regarded as a mass reduction due to decomposition in the catalytic filtering process. Therefore, the DXN amount at the inlet of BF was larger than the sum of the amounts both in fly ash and flue gas at the BF outlet.

Those different aspects can be understood according to the congener distribution patterns of PCDD/F, as shown in Figures 3 and 4, which also indicate the qualitative difference between the two flue gas treatment processes. The three distribution patterns of the PCDD/F at Plant A were clearly different from each other, suggesting that these compounds are generated during the dust collection process. PCDDs and PCDFs were newly formed and the fly ash mainly contained PCDDs, whereas the flue gas at the EP outlet contained equal amounts of PCDDs and PCDFs. However, lower chlorinated Cl4, Cl5 and Cl6 congeners are dominant both in PCDD and PCDF, because these lower chlorinated compounds tend to volatilize more than higher ones. By contrast, the distribution patterns for gases and ash at Plant B are somewhat different (Figure 4). The PCDFs in flue gas at the BF inlet were far higher than PCDDs and low chlorinated congeners were in higher concentrations. After passing BF, the DXNs contained in particles were simply removed by filtration; those contained both PCDDs and PCDFs were roughly equal. On the other hand, gaseous DXNs might be decomposed in the catalytic filter, after which a portion of PCDFs slipped into the effluent gas.

Table 4 Mass balance calculations of DXNs at the two plants (µg/h)

Run No.	Plant A			Run No.	Plant B		
	Inlet of EP	Fly ash	Outlet of EP		Inlet of BF	Fly ash	Outlet of BF
A-1	1,000	6,800	6,800	B-1	1,900	1,200	80
A-2	220	4,900	4,000	B-2	2,200	500	80
A-3	380	3,900	3,200	B-3	2,700	2,300	120
A-4	210	1,700	700	B-4	1,700	900	80
A-5	330	2,300	540	B-5	1,100	1,000	60

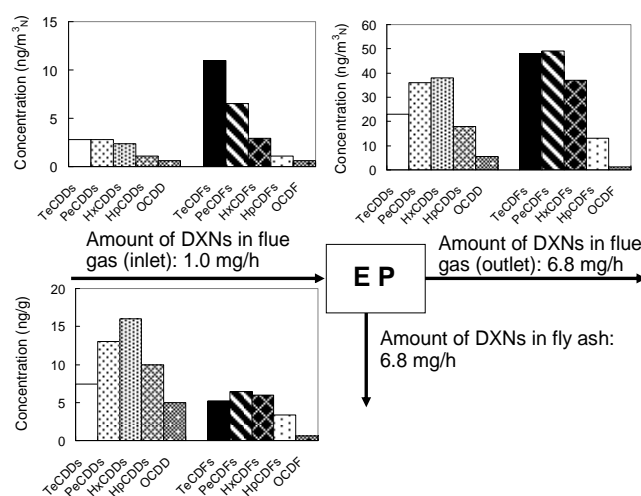


Figure 3 Congener distribution patterns of PCDD/F with mass-balance data for DXNs (Run A-1)

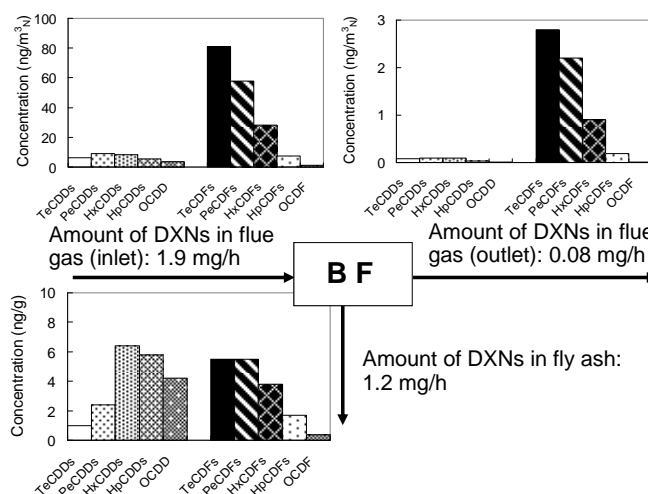


Figure 4 Congener distribution patterns of PCDD/F with mass-balance data of DXNs (Run B-1)

References

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