

MASS BALANCE OF DIOXINS AROUND DUST COLLECTION SYSTEMS AND FLUE GAS MONITORING WITH SURROGATE ORGANIC HALOGENS

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Introduction

Recent progress on combustion techniques has greatly reduced dioxins (DXNs) in flue gas. However, the possible formation of DXNs during the gas cooling process may cause an increase in the pollutants in ash around dust collection systems, which may require additional treatment of the ash. Therefore, it is necessary to develop an appropriate index that indicates any change in the dioxin concentrations of both flue gas and ash. Furthermore, measurements with the index should be easy and quick. In this context, several surrogates have been developed and one type was examined for monitoring flue gas under startup conditions in incinerators^{1,2}. OHC (Organic Halogen Compounds), which determined the amount of organic halogens employed in a previous study¹, is also used in this study with a modified detection method. This work investigates the formation and transfer of dioxins in the flue gas cleaning process and investigates OHC as an easily measured monitoring index.

Material and methods:

Flue gas and ash sampling

Measurements were conducted in two kinds of incineration plants as shown in Figure 1. Plant A has a kiln-stoker type continuous (65t/24h) industrial waste incinerator in which gas sampling was performed at the inlet and outlet of the bag filter (BF) while fly ash was being sampled. Lime and activated carbon mixtures were injected into the duct in front of the BF inlet to remove acidic gases and DXNs. Plant B has a stoker type semi-continuous (60t/16h) municipal waste incinerator equipped with a catalyst packed tower after the electrostatic precipitator (EP) to remove NO_x and DXNs. The material processed in plant B includes solid waste generated by an airport. Fly ash was sampled 4 to 8 times during the flue gas DXN measurement over a period of 4 hours, and then sent for analysis after being combined.

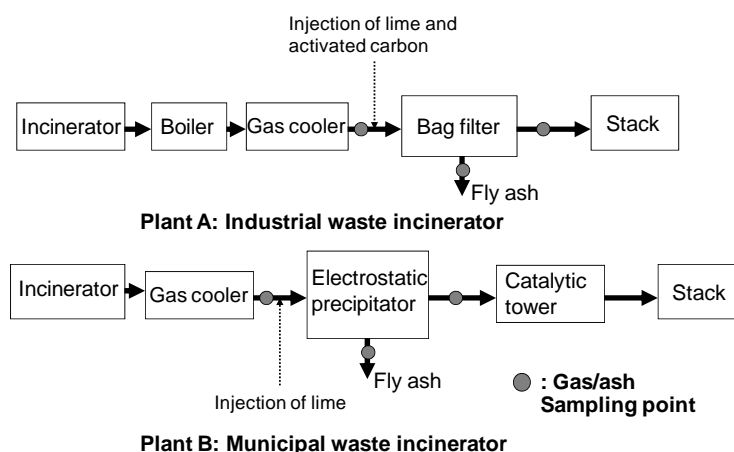


Figure 1 Incineration plant flow and sampling point

Table 1 Experimental conditions in two plants

Plant A			Plant B		
Run No.	Temperature at BF inlet (°C)	Injected activated carbon (mg/m ³ _N)	Run No.	Temperature at EP inlet (°C)	Temperature at furnace outlet (°C)
A-1	165	122	B-1	290	950
A-2	165	43	B-2	290	1050
A-3	200	191	B-3	260	950
A-4	199	141	B-4	290	950
A-5	200	79	B-5	290	950

Plant operation

Flue gas sampling was conducted under various experimental conditions taking account of such factors as the temperature at the BF and EP inlets, the activated carbon dose, and the stability of combustion. Table 1 shows the experimental setups designed for the two plants. The BF temperature and the amount of injected carbon were changed in plant A and the temperatures of the furnace outlet and EP inlet were changed in plant B.

Analysis

The DXNs in flue gas and fly ash samples were analyzed using HRGC-HRMS. The OHC constituents of flue gas were collected with an adsorption tube employing two types of graphite carbon adsorbents at the plant site, and the tubes were analyzed using atomic emission spectrometry employing radio-frequency helium plasma³. Organic chlorines and bromines were determined separately by their atomic absorption at specific wavelengths, and components with low and high volatility were collected by two kinds of adsorbents.

Results and discussion:

DXNs in flue gas and fly ash

The measurement data for DXNs in flue gas and fly ash samples are summarized in Table 2. The results have certain

Table 2 Measurement results of DXNs in two plants (ng/m³_N@12%O₂ for gas and ng/g for fly ash)

Plant A				Plant B			
Run No.	Gas at the inlet of BF	Fly ash	Gas at the outlet of BF	Run No.	Gas at the inlet of EP	Fly ash	Gas at the outlet of EP
A-1	370 (7.5)*	45 (0.93)	0.12 (0.00013)	B-1	18 (0.26)	92 (1.1)	210 (3.3)
A-2	890 (20)	220 (4.1)	0.22 (0.0014)	B-2	18 (0.27)	65 (0.98)	160 (3.0)
A-3	380 (6.2)	80 (1.3)	1.6 (0.023)	B-3	6.5 (0.10)	11 (0.19)	19 (0.33)
A-4	460 (9.0)	74 (1.5)	1.6 (0.023)	B-4	10 (0.19)	53 (0.97)	77 (1.3)
A-5	490 (12)	92 (2.0)	1.6 (0.024)	B-5	12 (0.21)	17 (0.32)	40 (0.83)

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

distinctive features. Plant A, which incinerates industrial waste including paper, plastics and medical waste, produces a relatively high amount of DXNs at the BF inlet. High CO concentrations that reached a maximum of about 250 ppm over a short period were observed in this plant and there was a high correlation between the average CO and DXN concentrations. However, the dust collection process in the BF with lime and activated carbon injection significantly reduces the DXN levels, which results in relatively high concentrations in the fly ash samples. On the other hand, plant B, which incinerates municipal waste, produces a lower concentration of DXNs, whereas the concentrations in the EP outlet are moderately high. This shows that *de novo* synthesis occurs in the dust collection process in an EP operated at 260 ~ 290 °C. There was no relationship between CO and DXNs in Plant B. The average CO concentration of the plant was very low (< 2 ppm). The EP flue gas is further cleaned by passing it through the catalytic tower before exhaustion (< 0.1 ng-TEQ/m³_N).

As for the influence of BF temperature and carbon injection, we found that low temperature operation and a higher injected amount reduce the DXN concentrations at the BF outlet as shown in runs A-1 and A-2. When the temperature is high (~200 °C), it is apparent that the injected amount of activated carbon does not affect the concentration at the BF outlet (A-3 ~ A-5). These facts suggest that temperature is the most important operational factor with respect to BF application.

Mass balance of dioxins

Table 3 shows mass balance data for DXNs obtained under different operating conditions in two plants and the results show the difference between the balance features of the two plants. First, in plant A, where the dust collection

process is performed at a relatively low temperature (165 °C), the DXN amounts are roughly equal in the BF inlet gas and the fly ash. It is difficult to obtain precise data, especially in fly ash, because of the variations in solid sample generation and DXN concentration. However, the runs appear to provide good results except for Run A-3.

Second, in plant B, where *de novo* synthesis tends to occur, the amounts both at the EP

Table 3 Mass balance calculations of DXNs in two plants (mg/h)

Plant A				Plant B			
Run No.	Inlet of BF	Fly ash	Outlet of BF	Run No.	Inlet of EP	Fly ash	Outlet of EP
A-1	8.2	7.3	0.0025	B-1	0.51	8.3	4.9
A-2	29	23	0.0065	B-2	0.55	4.2	3.9
A-3	8.5	14	0.037	B-3	0.13	0.61	0.36
A-4	9.0	11	0.033	B-4	0.26	4.7	1.7
A-5	12	10	0.043	B-5	0.31	0.90	0.80

outlet and in the fly ash increased about ten times or more compared with the amount at the EP inlet except for Runs B-3 and B-5. The reason for the increase with Run B-3 being relatively small may be attributed to the low operating temperature (260 °C), but the reason for the Run B-5 result was unclear.

Figures 2 and 3 show the results for the congener distribution patterns of PCDD/Fs with the mass balance data for DXNs obtained in two runs. These figures also indicate the qualitative difference between the two flue gas treatment processes. The distribution patterns of the PCDD/Fs in flue gas at the BF inlet (plant A) and those of the fly ash are

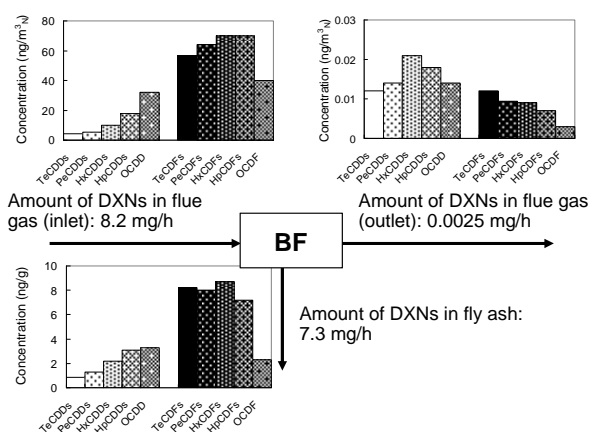


Figure 2 Congener distribution patterns of PCDD/Fs with mass balance data of DXNs (Run A-1)

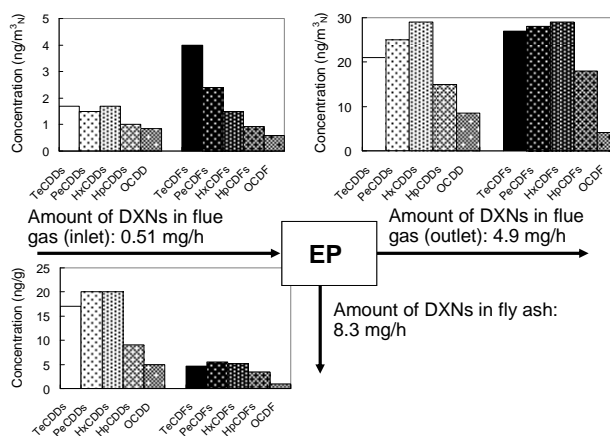


Figure 3 Congener distribution patterns of PCDD/Fs with mass balance data of DXNs (Run B-1)

very similar, which suggests that almost all the DXNs in the flue gas are collected and deposited in the BF. By contrast, three of the PCDD/F distribution patterns in plant B were clearly different from each other, which suggests that those 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 low chlorinated congeners of PCDFs in addition to PCDDs. This difference may reflect the physical and chemical properties of the compounds such as vapor pressure.

Relationship between OHC and DXNs

Figures 4 and 5 show semi-continuous measurement data for OHC in flue gas at the outlet of the dust collector in plants A and B collected over five days. The DXN data are also plotted in this figure. Of the OHC constituents, volatile organic chlorines show a higher concentration over the entire measurement and chlorobenzenes would be included in this group². The total concentrations of organic and volatile chlorines and bromines vary significantly. If any correlation between OHC and DXNs could be found, it would be very useful for rapid decision-making when managing dioxins¹. From this point of view, a good relationship was observed between semi-volatile chlorine concentrations at the outlet of BF and DXN concentrations at the inlet of BF in plant A as shown in Figure 6. The

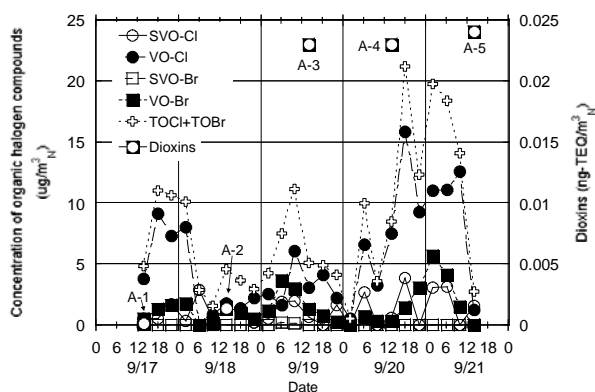


Figure 4 Change in OHC by semi-continuous sampling and measurement in plant A with the manual measurement data of DXNs (SVO: semi-volatile organic, VO: volatile organic, TO: sum of SVO and VO)

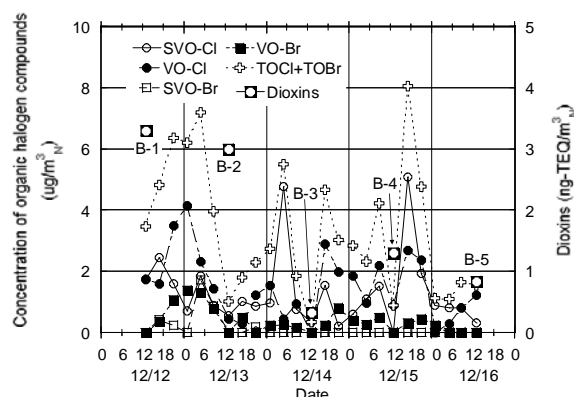


Figure 5 Change in OHC by semi-continuous sampling and measurement in plant B with the manual measurement data of DXNs (SVO: semi-volatile organic, VO: volatile organic, TO: sum of SVO and VO)

concentration of DXNs at the inlet of BF directly affected the amount of DXNs in fly ash as seen in Figure 2.

Therefore, it would be very useful to monitor the concentration of OHC in exhaust gas by using more rapid and easy method than the measurement of DXNs that takes longer time.

These facts and estimation suggest that rapid daily monitoring of flue gas by using a simple surrogate such as OHC is expected to be used to detect any change of DXN concentration/content of gas and solid residue. The monitoring may also enable to promptly take measures to deal with the change, especially the increase of DXN concentrations.

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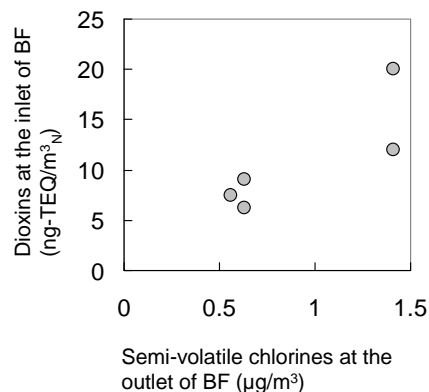


Figure 6 Relationship between semi-volatile organic chlorines at BF outlet and DXNs at BF inlet