Dioxin Behavior in Fluidized-Bed Swirl Incinerators for MSW Disposal

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Abstract

A demonstration plant incorporating a fluidized-bed swirl incinerator for the disposal of municipal waste was constructed in order to study the formation of dioxins and their precursors as well as their homologue distribution. Sampling was performed along the gas flow. It was found that more polychlorinated dibenzofurans (PCDFs) than dioxins are formed in the combustion chamber, but as more polychlorinated dibenzo-p-dioxins (PCDDs) are formed downstream, the ratio of PCDF/PCDD is reversed. While lower chlorine homologues become more prominent for dioxins further downstream, their precursors are more prominent in the combustion chamber. Good prospects of achieving 0.5 TEQ ng/m^{3}N or less for the equivalent dioxin concentration toxicity in the induced draft fan (IDF) outlet were realized through optimizing combustion conditions and maintaining a low flue gas temperature in the bag filter.

Key words: PCDDs, PCDFs, Municipal Solid Waste, Fluidized-Bed Swirl Incinerator, Dioxin Precursors, Polychlorophenols, Polychlorobenzenes

1. Introduction

Notable progress has been made in the emission control of dioxins from municipal waste incinerators, mainly through improved combustion and dust removal. Yet the emission level that the Ministry of Health and Welfare set forth several years ago as a guideline remains difficult to meet.

Various combustion methods were tested on several experimental incinerator designs, at which time we found that a configuration we call the "fluidized-bed swirl incinerator" is highly promising for dioxin control.[1] We built a demonstration plant and recorded the changes in dioxin concentration as well as precursors, polychlorophenols (CPs) and polychlorobenzenes (CBs) along the gas flow, starting from the swirling secondary combustion chamber (SC) to the IDF.

In this paper, we report and discuss the observations made on the behavior of dioxins, CPs, CBs and other parameters while testing the overall performance of the demonstration plant.

2. Testing Facility and Measuring Methods

2-1. Facility and Test Method

Fig.1 shows the flow chart of the demonstration plant incorporating the 20t/day fluidized-bed swirl incinerator. It features a swirling secondary combustion chamber into which unburnt matter, typically charcoal, is returned for additional combustion. The matter is removed from the fluidized bed together with the bed material overflow. This process achieves near perfect combustion and ensures effective separation of flyash.

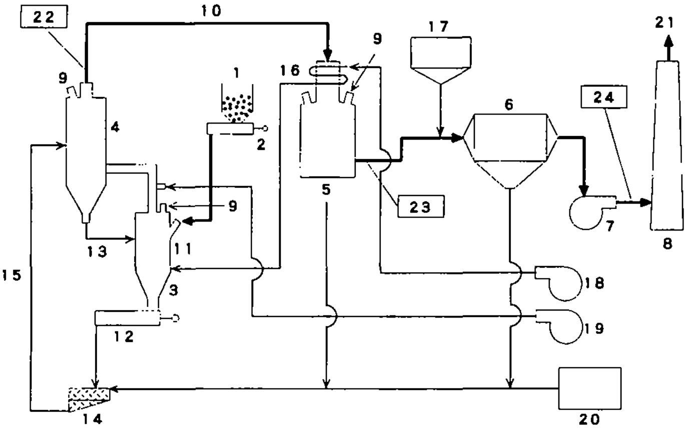

Fig.1 Plant flow chart.

1 : Municipal Solid Waste
2: Feeder
3: Fluidized Bed
4: Swirling Secondary Combustion Chamber
5: Gas Cooler
6: Bag Filter
7: Induced Draft Fan
8: Stack
9: Cooling Water
10: Flue Gas
11: Air Disperser
12: Unburnt Matter Discharger
13: Flyash、Sand
14: Bed Sand Sieve
15: Return Sand
16: Air Preheater
17: Lime Bin
18: Forced Draft Fan
19: Secondary Air Blower
20: Dust Storage Bin
21: Atmosphere
22: SC Exit
23: Gas Cooler Exit
24: IDF Exit

The combustion gas from the secondary combustion chamber is cooled in the gas cooler (GC), injected with pulverized slaked lime to control hydrochloric acid(HCl) (not discussed in this paper), the dust and flyash removed utilizing a bag filter (BF), and purified gas exhausted out of the stack.

Table 1 lists the operating conditions. Note that the flue gas temperature at the SC exit was maintained at over 850 ℃ , and the temperature at the GC exit at 200 ℃ for Runs 1 ~ 4 and 170 ℃ for Runs 5 ~ 8. The carbon monoxide(CO) content was held below 10ppm at the SC exit. The gas temperature of the BF outlet was left to fluctuate naturally.

As the feed , we utilized a laminated paper made from discarded vinyl chloride known for its uniform properties and well-tested likeness to real municipal waste.

2-2. Analytical Procedure and Method

Gas analyses were conducted on samples taken at the SC exit, the GC exit and the IDF exit, respectively. The sampling sites are designated in Fig.1 by rectangular enclosures.

A gas chromatography/mass spectrometer(GC-MS) was utilized to analyze the dioxins for tetra to octa-chlorinated homologues of 4 ~ 8 Cl, in accordance with the official manual. 2) The CPs and CBs, on the other hand, were first captured in an alkaline-hexane solution, extracted and concentrated in hexane, and subjected to analysis by GC-MS. The CPs were analyzed for isomers of mono- through penta-chlorinated homologues, while CBs were checked for mono- through hexa-chlorinated isomers. The amounts of CO and O_2 were also determined at the same time.

3. Results

3-1. Dioxin Behavior

The dioxin concentrations are presented in Fig. 2 as the sum of two major species of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) at the sampling site. It was noted that, for Runs 1 ~ 4, the dioxin total was greater at the IDF exit than at the GC and SC exits, while for Runs 5 ~ 8, the sequence was reversed to a greater dioxin total at the SC exit than the GC and IDF exits. Furthermore, in the case of the IDF exit, the dioxin concentration was markedly lower for Runs 5 ~ 8 than for Runs 1 ~ 4.

Table.1 Operation conditions.

	SC exit			GC exit	BF exit
RUN No.	Temp (℃)	O_2 (%)	CO (ppm)	Temp (℃)	Temp (℃)
1	903	7.8	11	196	180
2	989	6.5	15	203	184
3	892	8.9	<1	203	173
4	893	9.0	<1	200	179
5	907	7.6	9	170	158
6	894	8.4	9	170	160
7	887	8.5	<1	167	157
8	905	8.3	<1	176	158

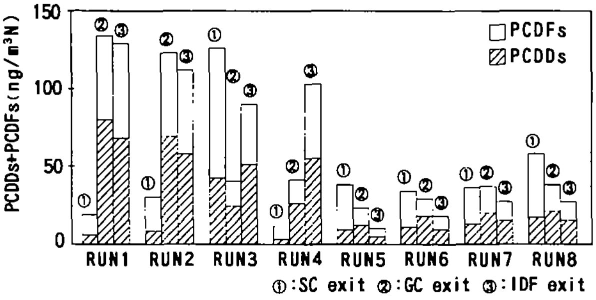

Fig.2 Occurrence of dioxins along plant flowline.

Since the only operational difference between these two sets is a lower GC exit gas temperature, we ascribe the improved dioxin capture efficiency to this practice (Fig. 3).

The relative occurrence of PCDDs and PCDFs is shown in Fig. 4. More PCDFs were generated in the combustion chamber, creating an average PCDF/PCDD ratio of 2.4 at the SC exit. This relative abundance was reversed downstream, to a ratio of 0.7 at the GC exit, and 0.89 at the IDF exit.

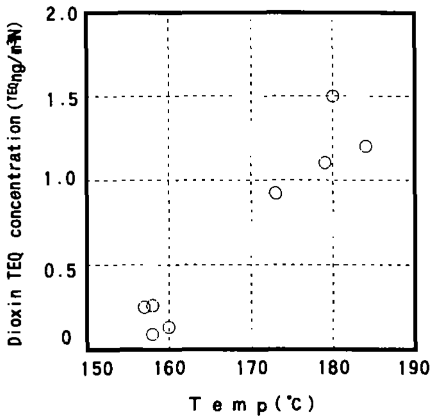

Fig.3 Effects of gas temperature on dioxins at the bag filter.

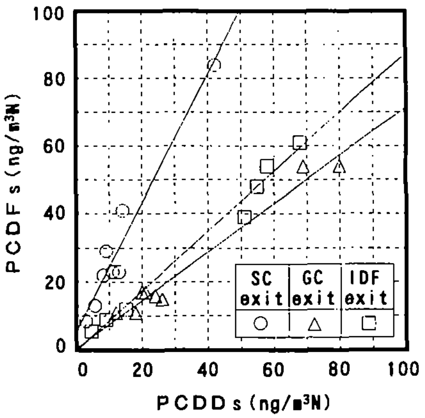

Fig.4 Relation of occurrence between PCDFs and PCDDs.

Fig. 5 shows the formation habits of the two components in terms of their respective homologues. At the SC exit, the PCDD concentration is higher, the higher the Cl number. At the GC and IDF exits, however, PCDD concentration peaks with hexachloride, while the PCDF homologues decrease as the Cl number increases.

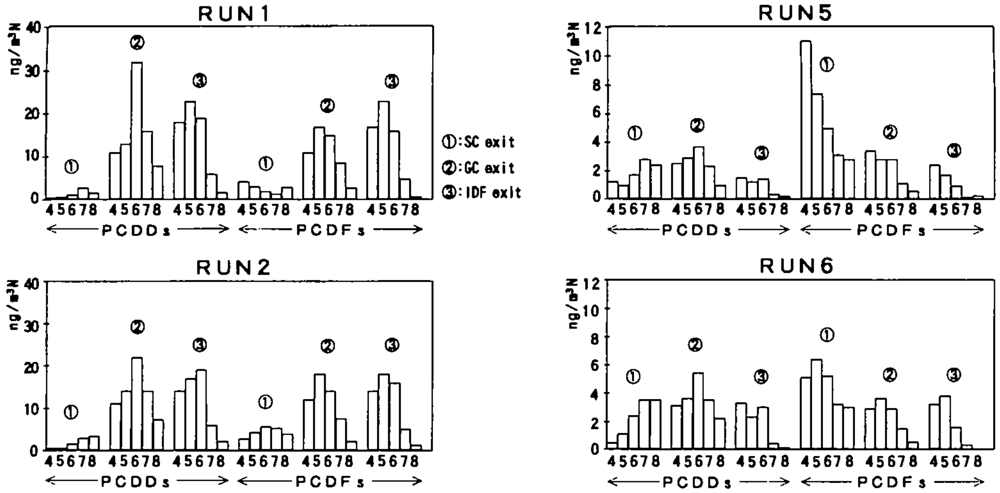

Fig.5 Dioxin homologues.

3-2. CPs and CBs

The occurrence of CPs and CBs is depicted in Fig. 6. Both CPs and CBs showed a general trend to increase downstream, although concentrations were higher for Runs 1 ~ 4 (i.e., higher GC exit temperature) than for Runs 5 ~ 8.

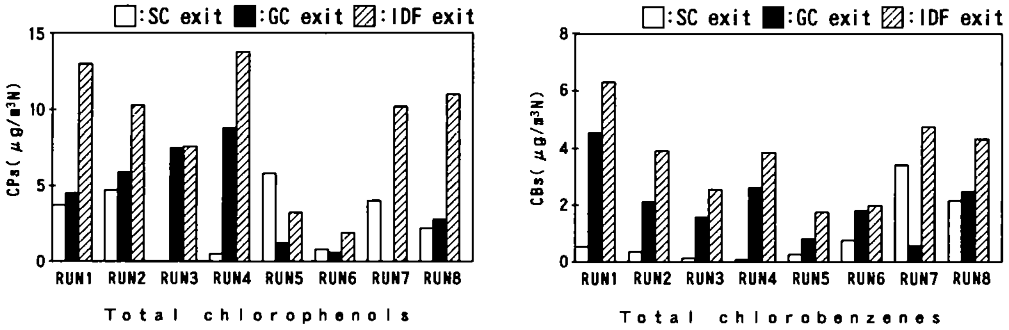

Fig.6 Occurrence of chlorophenols and chlorobenzenes.

The homologue distribution is shown in Fig. 7. In the case of CPs, where the major component is dichlor at the SC exit, an increase in other isomers, particularly mono– and tri–chlorinated isomers, was observed at the GC exit. Even more notable was the distribution at the IDF exit, where a marked increase in pentachloride was seen .

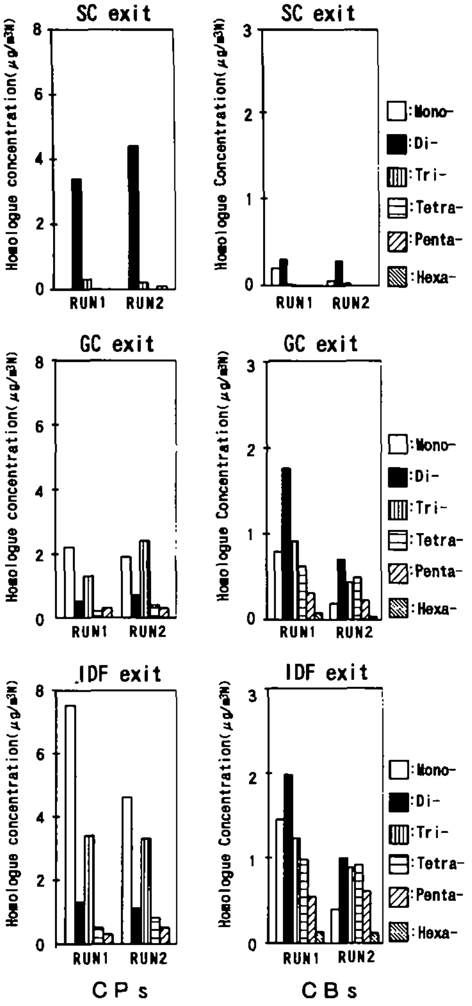

Fig.7 Homologue distribution of CPs and CBs.

In the case of CBs, on the other hand, mono- and di-chlorinated isomers were most present at the SC exit. However, at the GC exit, mono- through pentachlorinated isomers increased; particularly the higher chlorinated members, tri- through penta-chlorine.

Fig. 8 shows the relation between CPs, CBs and dioxins in terms of their concentrations. The correlation factor is clearly low in the combustion chamber and at the GC exit.

4. Discussion

4-1. Mechanism of CP and CB Formation

As reported in the preceeding section, CP and CB concentrations increase downstream. From this observation, we derived that the basic formation mechanism is the chlorination of phenol and benzene in the combustion gas by Cl_2, whict is liberated from HCl through the Deacon reaction. 3)

The chlorination reaction of phenol is of the endoelectron substitution type with ortho-para directionality. The general trend of chlorination is 2-MCP → 2,4-DCP → 2,4,6-T_3CP → 2,3,4,6-T_4CP.

The chlorination reaction of benzene also has ortho-para directionality. Unlike difference to the CPs, here the relative proportion of the subordinate reaction is higher, constituting a second route for the reaction to proceed in parallel. The main route is 1,4-DCB → 1,2,4-T_3CB — 1,2,3,4-T_4CB.

4-2. Mechanism of PCDD and PCDF Formation

Even though some of the details have been left for future research, we derived the in-line chain of reactions as follows: 1) the generation of benzene and phenol as the polymers decompose, or polymerization of smaller C2 units to aromatic backbone; 2) the formation of CBs and CPs, particularly of the lower chlorinated homologues; and 3) the synthesis of PCDDs and PCDFs, particularly of the higher chlorinated homologues, all taking place in the combustion chamber concurrently.

As the outgas flows downstream, however, Cl is liberated from HCl which chlorinates benzene and phenol into CBs and CPs. PCDFs, and subsequently PCDDs, are formed from these reactions due to exposure to polychlorophenyl phenol and polychlorodiphenyl ether. 4)

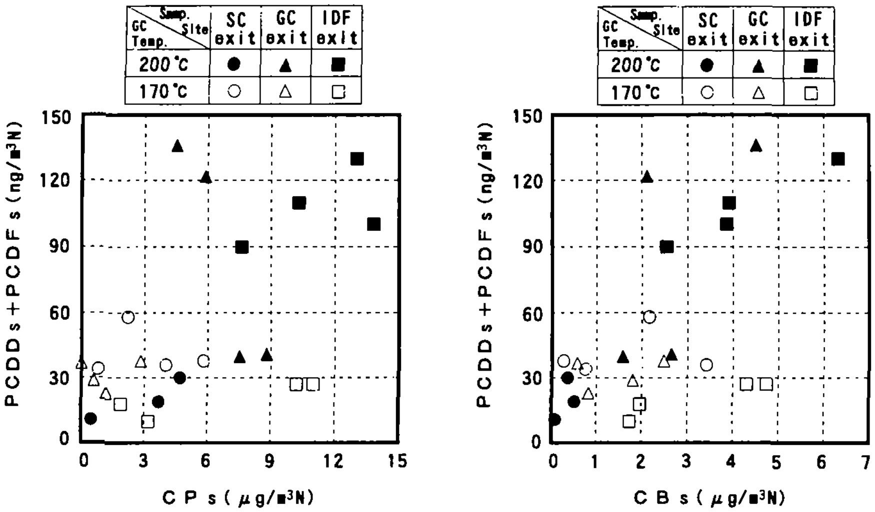

Fig.8 Relative concentrations of dioxins、CPs and CBs.

5. Conclusions

By studying the behaviors of dioxins, PCs and CBs in the flue gas of a fluidized bed swirl incinerator sampled at the SC exit, GC exit and IDF exit, the following observations have been made:

1) Of the two major dioxin components, the combustion chamber produces more PCDFs than PCDDs. However, as more PCDDs are generated as the gas flows downstream, PCDD concentration becomes higher at the GC exit.

2) Regarding the homologue distribution of dioxins, distribution is heavier for higher chlorinated isomers at the SC exit , but lower chlorinated isomers increase downstream.

3) Both CPs and CBs tend to increase downstream, with homologue distribution being greater for lower chlorinated isomers at the SC exit , but reverting to a greater volume of higher chlorinated isomers downstream.

4) The formation routes of CPs and CBs have been clarified fairly well.

5) It is highly probable that 0.5 TEQ ng/m^{3}N or less for equivalent dioxin concentration toxicity can be achieved at the IDF exit through optimizing combustion conditions and maintaining a low flue gas temperature .

6.References

1) Asai M., et al. Ishikawajima–Harima Engineering Review, Vol.27 (2), pp.50–54 (1994) April.

2)Japan Waste Research Foundation, Manual for Analyzing and Determining Dioxins in Disposable Wastes

3) Griffin R. 78th Annual Meeting of the Air Pollution Control Association, 85–75A. 10. 1–12 (1985) June.

4) Ballschmiter K., et al. Kurze Mitteilungen, pp.125–127 (1987).