

ROLE OF CHLORINE IN COMBUSTION FIELD IN PCDD/F FORMATION DURING MODEL WASTE INCINERATION

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Introduction

Municipal waste incinerators are an important source of emissions of PCDDs and PCDFs. These compounds are formed over different temperature ranges in various sections of an incinerator¹. Some studies have shown that PCDD/Fs are formed at relatively low temperatures (650–200 °C) after the combustion chamber². On the other hand, attention has been focused on the formation of PCDDs, PCDFs, and other products of incomplete combustion (PICs) at high temperature (>650 °C)³. To elucidate the mechanisms of PCDD/F formation during incineration, it is important to investigate them in each section of the incinerator. PCDD/Fs are formed through several pathways such as de novo synthesis and condensation reaction of chlorophenol and chlorobenzene¹. Since the formation pathway influences the patterns of PCDD/F congeners, it contributes to the understanding of their formation mechanisms to examine the congener distributions⁴.

The aim of this study is to investigate the role of chlorine in each section of the incinerator in PCDD/F formation by supplying a Cl source at different positions of the incinerator. Chlorine is an essential ingredient in their formation reactions. This study focuses on the changes of the patterns of PCDD/F congeners in the experiments with injection of a Cl source at different positions. The results show that chlorination/dechlorination of PICs is the key reactions in PCDD/F formation after combustion sections.

Materials and Methods

The main combustion section in the experimental setup consisted of primary and secondary combustors (Figure 1). The primary combustor was a laboratory-scale fluidized-bed reactor (60 mm diam., 300 mm tall). The fluidized material was 100–140 μm silica sand, and the static bed height was 100 mm. The secondary combustor was a freeboard section (30 mm diam., 1450 mm tall). All parts of the main combustion section were made of quartz. The postcombustion section connected the main combustion section with the thermal-retention section, which consisted of 3 glass tubes (30 mm diameter, 300 mm tall). These sections were kept at constant temperature with external heaters. Fresh sand was used for the fluidized material in each experiment, because even trace amounts of residues such as chlorine and catalyst in the sand and on the inner surfaces of the reactor

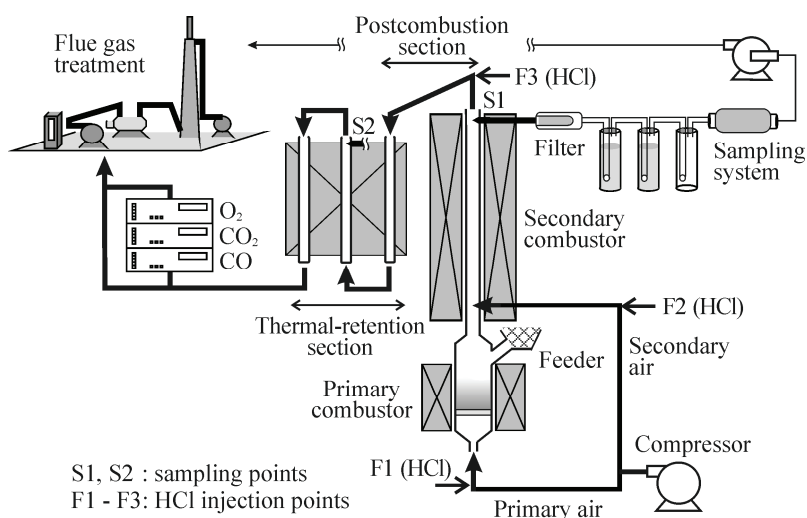


Figure 1: Schematic diagram of experimental setup

strongly affect PCDD/F formation. After each experiment, the inner surfaces of the reactor in contact with flue gas were washed to prevent memory effects. In case washing could not remove the contamination, the quartz parts were replaced with new material. Sampling for PCDD/F analysis was carried out for 4 h at the top of the main combustion section (sampling point S1 in Figure 1) and after the thermal-retention section (sampling point S2). A water-cooled probe was used at the sampling point S1. A model waste was used, so as to have a strictly defined waste composition. The base ingredients of the model waste were 45% unbleached pulp powder, 40% flour, and 15% wood powder. In addition to the base ingredients, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was mixed as a formation catalyst. All ingredients were ground separately, mixed mechanically, and then pelletized into particles (1–3 mm diam.). Cl and Cu contents of the model waste were 0.20 wt% and 0.10 wt%. HCl gas (10% in nitrogen) was injected as a major source of chlorine for PCDD/F formation. The previous paper showed no difference between PVC in model waste and injected HCl in the role as a Cl source in the PCDD/F formation during model waste incineration⁵. The amount of HCl supplied in the combustor was adjusted so that the amount of chlorine supplied was the same as that in the combustion of model waste with 1.24 wt% Cl content. Experimental conditions are listed in Table 1.

Table 1: Experimental conditions

Temperature	
primary combustion zone	700 °C
secondary combustion zone	900 °C
thermal-retention section	350 °C
Flow rate	
primary air	0.46 m ³ _N /h ($\lambda=1.3$)
secondary air	0.26 m ³ _N /h ($\lambda=0.7$)
Fuel feed rate	
	100 g/h

Results and Discussion

Difference of congener distributions in the main combustion and the thermal-retention sections

Congener distributions of T4CDD/Fs and P5CDD/Fs are investigated in the experiment with injection of HCl at F3 to select the congeners that show the distinct difference of the proportions in their homologues at the sampling points S1 and S2 (Figure 2). The total concentrations of tetra- through octa-chlorinated dibenzo-*p*-dioxins and dibenzofurans ($\Sigma\text{PCDD/Fs}$) were 4 ng/m³_N at the top of the main combustion section (S1)

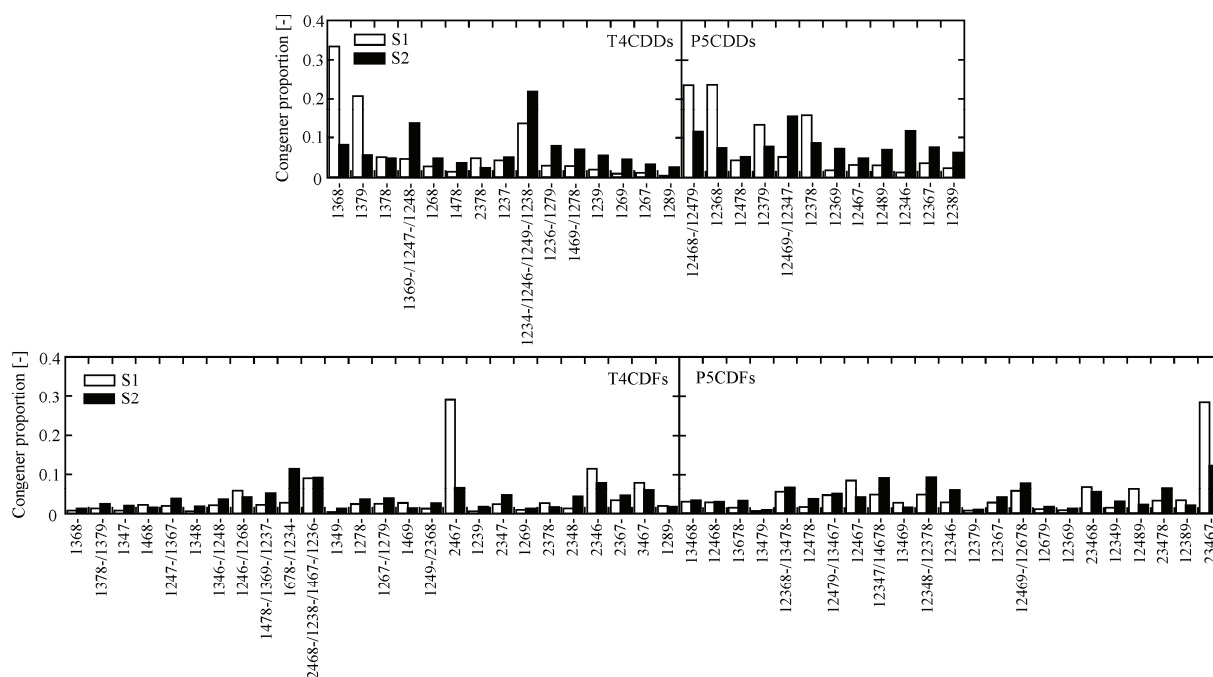


Figure 2: PCDD/F congener proportions at the sampling points S1 and S2 with HCl injection at F3

and 41 ng/m³_N after the thermal-retention section (S2). ΣPCDD/Fs were low in the main combustion section because of low Cl concentration in flue gas. The injection of HCl gas to the post-combustion section (F3) promoted the PCDD/F formation and their concentrations rapidly increased. Figure 2 shows that 1,3,6,8-, 1,3,7,9-T4CDD, 1,2,3,6,8-P5CDD, 2,4,6,7-T4CDF and 2,3,4,6,7-P5CDF were particularly formed in the main combustion section (S1) and no characteristic congeners were observed after the thermal-retention section (S2). The proportions of the five congeners in their homologues are distinctly different between the sampling points S1 and S2. No congeners of H6CDD/Fs to O8CDD/F showed the clear differences of their proportions between the sampling points.

1,3,6,8-, 1,3,7,9-T4CDD and 1,2,3,6,8-P5CDD are representative congeners that are formed via condensation reaction of chlorophenols and chlorobenzenes in flue gas⁶. It seems reasonable to suppose that these congeners were formed via condensation of single-ring compounds in the main combustion section. The formation of these congeners was also observed in the thermal degradation of PCDDs at middle temperature (600-650 °C)⁷. 2,4,6,7-T4CDF and 2,3,4,6,7-P5CDF are predominantly formed via catalytic oxidation/oxychlorination of carbon/polyaromatic hydrocarbons (PAHs) in incineration of model wastes containing copper⁴. It can be said that these are the congeners that directly reflect their formation pathways such as condensation and oxidative breakdown. The characteristic patterns of the congeners at the sampling point S1 mean that these five congeners were little influenced by chlorination/dechlorination in the main combustion section. Conversely, high Cl concentration in the thermal-retention section with injection of HCl at F3 promoted chlorination/dechlorination of single-ring compounds, carbon/PAHs, PCDDs and PCDFs, which resulted in no characteristic congeners at the sampling point S2. These results are also related to the faster degradation of PCDD/Fs formed in the main combustion section and the slower degradation in the thermal-retention section. However, there are assumed to be other causes of the differences of the congener patterns between the main combustion and the thermal-retention sections such as the differences of the formation pathways in the temperature range and PIC concentrations in each section.

Changes of congener proportions with injection of HCl at F1, F2 and F3

The proportions of 1,3,6,8-, 1,3,7,9-T4CDD, 1,2,3,6,8-P5CDD, 2,4,6,7-T4CDF and 2,3,4,6,7-P5CDF in their homologues at the sampling points S1 and S2 are examined in the experiments with injection of HCl at F1, F2 and F3 (Figure 3). ΣPCDD/Fs at S2 were 390 ng/m³_N at F1, 160 ng/m³_N at F2, and 41 ng/m³_N at F3. The proportions of these congeners at S1 increased in the experiments with HCl injection at downstream sections. The changes of the congener proportions and the amounts of PCDD/Fs formed are explained by the decrease of the average Cl concentration in the main combustion section. It is very interesting that the proportions of the congeners largely increased when HCl was supplied at the inlet of the secondary combustor (F2) compared with at the inlet of the primary combustor (F1). The temperature was high enough and unburned hydrocarbon and PICs were burning in the secondary combustor as well as in the primary combustor. However, the congener proportions show that chlorination/dechlorination did not occur in the secondary combustor as often as in the primary combustor. This could not be explained only by the differences of the average Cl concentration and the residence time. These results indicate that unburned hydrocarbon and PICs that were chlorinated in the primary

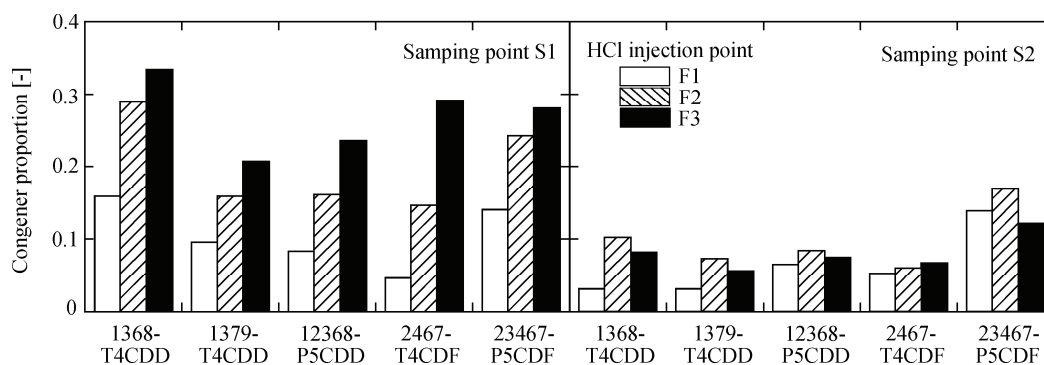


Figure 3: Congener proportions at the sampling points S1 and S2 with HCl injection at F1, F2 and F3

combustor were more important in the PCDD/F formation than those in the secondary combustor.

After the thermal-retention section (S2), the proportions of these congeners did not show the apparent tendency although the congeners were particularly formed in the main combustion section (S1) in the experiments with HCl injection at F2 and F3. This shows rapid chlorination/dechlorination of PICs including PCDD/Fs in the thermal-retention section. These reactions exert a stronger influence on the PCDD/F formation in the thermal-retention section than in the main combustion section because of the slower degradation of PCDD/Fs at the lower temperature. It was shown that compounds that were able to form PCDD/Fs in the thermal-retention section were mainly formed in the main combustion section in the presence of HCl⁵. The results in this study indicate that the mechanisms of the PCDD/F formation in the thermal-retention section are closely connected to chlorination/dechlorination of PICs.

References

1. Tuppurainen K., Halonen I., Ruokojarvi P., Tarhanen J. and Ruuskanen J. *Chemosphere* 1998; 36: 1493.
2. Vogg H. and Stieglitz L. *Chemosphere* 1986; 15: 1373.
3. Ghorishi S. B. and Altwicker E. R. *Hazard. Waste Hazard. Mater.* 1996; 13: 11.
4. Hatanaka T., Kitajima A. and Takeuchi M. *Chemosphere* 2004; 57: 73.
5. Hatanaka T., Kitajima A. and Takeuchi M. *Environ Sci Technol* 2005; 39: 9452.
6. Hell K., Altwicker E. R., Stieglitz L. and Addink R. *Chemosphere* 2000; 40: 995.
7. Hatanaka T., Kitajima A. and Takeuchi M. *Organohalogen Compd.* 2006; 68: 1217.