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PCDD/Fs FORMATION IN LABORATORY-SCALE FLUIDIZED-BED INCINERATION: INFLUENCE OF CHLORINE CONTENT IN LOW-TEMPERATURE COMBUSTION

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Introduction

Municipal solid waste incinerators are a major emission source of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in Japan¹. Though the recent developments of dioxin control technologies on the incinerator systems have made it possible to reduce their release significantly, such emission is still a serious problem. The dioxin control technologies in waste incineration systems are roughly divided into two groups. One is measures to decompose or remove PCDD/Fs in flue gas before their release to the environment. Another is to reduce their formation itself. To minimize their emission, it is indispensable to inhibit their formation during incineration through basic research. Many investigations have been conducted to understand the formation mechanisms, which were recently reviewed by Addink and Tuppurainen^{2,3}. However, the formation mechanisms are still unclear, and many problems exist on the prevention of their formation in waste incineration.

Combustion experiments were conducted in a laboratory-scale fluidized-bed reactor with electrical heating to elucidate the influence of forms and levels of chlorine sources in waste on the PCDD/Fs formation during incineration⁴. It reported the experimental data at a higher combustion temperature, 900°C, and concluded that it could not be said that there was a significant difference between the effects of organic and inorganic chlorine sources in waste on the PCDD/Fs formation during incineration in the experimental conditions. It also showed that CO concentration in flue gas became higher and more PCDD/Fs were formed as chlorine content in waste increased. This means that combustion conditions indicated by CO concentration are strongly related to the PCDD/Fs formation during incineration. The aim of this study is to examine the influence of chlorine content in waste on the PCDD/Fs formation during incineration at a lower temperature, 700°C. Comparison of the experimental results at 700°C with those at 900°C gives us some

useful information about the influence of combustion conditions on their formation, which would lead to understanding the formation mechanisms.

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Materials and Methods

Figure 1 shows a schematic diagram of an experimental setup, which was used in the previous paper⁴. A primary combustion zone was the fluidized-bed reactor, which had a diameter of 60 mm and a height of 300 mm. Fluidized material was silica sand of 100-140 μm and the bed height was set to 100 mm. A freeboard as a secondary combustion zone was a straight tube of 30 mm diameter and 1450 mm height. All parts of the main combustion section coming in contact with flue gas were made of quartz. As a post-combustion section, three glass tubes, 30 mm diameter and 300 mm height, were used. Air was supplied to the primary and secondary combustion zones from a compressor. Temperatures of the primary and secondary combustion zones and the post-combustion section were controlled individually using external electric heaters. The input values of the heaters were decided so that the temperature measured by a thermocouple inserted into the reactor was equal to the set temperature of each part of the reactor. The concentrations of CO, CO₂, and O₂ were measured continuously.

Model wastes were produced to define the waste composition strictly. The base ingredients of the model waste were 45% unbleached pulp powder, 40% unbleached flour and 15% wood powder. Properties and elementary composition of the model waste containing only the base ingredients are shown elsewhere⁴. In addition to the base ingredients, polyvinyl chloride (PVC, degree of polymerization $n \cong 1100$, Wako) was mixed as a chlorine source at several concentration levels. Copper chloride (CuCl₂·2H₂O, 0.25%, Wako) was added as the PCDD/Fs formation catalyst. All ingredients were ground separately, mixed mechanically, and then pelletized into particles in the range of 1 to 3 mm in diameter.

The setup was assembled with new sand for the fluidized material. After each experiment, the

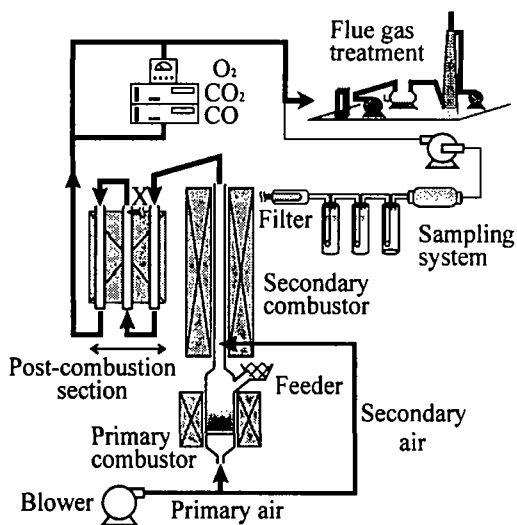


Figure 1. Schematic diagram of experimental setup.

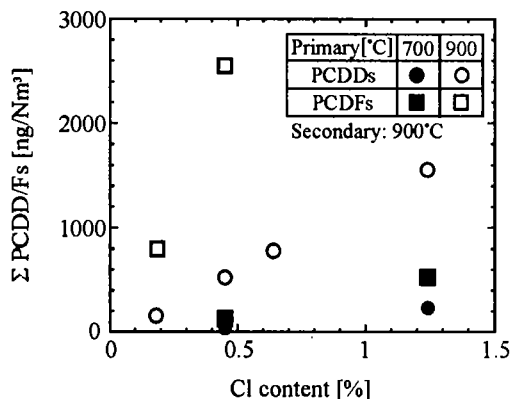


Figure 2. Influence of Cl content in waste on PCDD/Fs concentration at the furnace temperature, 700°C and 900°C, in the primary combustion zone.

Table 1. Experimental Conditions.

temperature	
primary combustion zone	700 °C
secondary combustion zone	900 °C
post-combustion section	350 °C
flow rate	
primary air	0.46 Nm ³ /h ($\lambda = 1.3$)
secondary air	0.26 Nm ³ /h ($\lambda = 0.7$)
fuel feed rate	100 g/h

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quartz surface in contact with flue gas was washed out to avoid the effect of experimental order. In case the inner surface did not become clear enough, the contaminated quartz parts were replaced with new ones. The experimental conditions are listed in Table 1. In the present study, the temperature is set to 700°C in the primary combustion zone and 900°C in the secondary combustion zone. The excess air ratio (λ) is set to 2.0 in total. Sampling was carried out for 4 hours or more after the post-combustion section. Analysis methods are described elsewhere⁴.

Results and Discussion

Figure 2 shows the relation between Cl content in waste and the total concentrations of PCDDs (tetra- to octa-chlorinated dibenzo-*p*-dioxins) and PCDFs (tetra- to octa-chlorinated dibenzofurans). The results of the experiments at 700°C in the primary and 900°C in the secondary combustion zone are indicated as closed keys. The PCDD/Fs concentration rises with Cl content increase. The results of the experiments at 900°C in both the primary and secondary combustion zones are also shown in Figure 2 as open keys. The temperature of the primary combustion zone is different in both series of experiments. PCDFs are formed more than PCDDs and their concentrations depend on Cl content in waste in both series of experiments.

However, the PCDD/Fs concentration at 700°C is significantly lower than at 900°C in the experiment of the waste with the same Cl content.

It is said that PCDD/Fs are mainly formed via two pathways^{2,3}. One is the condensation of precursors such as chlorobenzenes and chlorophenols^{5,6}. Another is the breakdown of carbon/polycyclic aromatic hydrocarbons (PAHs)⁷. As these compounds are products of incomplete combustion (PICs), it is certain that combustion conditions affect the PCDD/Fs formation in waste incineration. Then, CO concentration in flue gas is examined as the representative parameter of combustion conditions. Figure 3 shows the relation between Cl content in waste and the averaged CO concentration in flue gas during the sampling period. The CO concentration increases with Cl content in the experiments at 700°C, but it is apparently lower than at 900°C. Good combustion conditions indicated by the low CO concentration may possibly

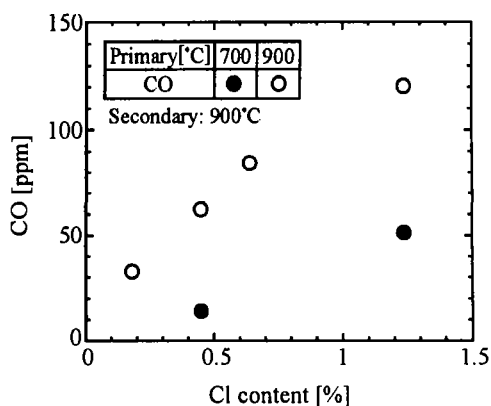


Figure 3. Influence of Cl content in waste on CO concentration at the furnace temperature, 700°C and 900°C, in the primary combustion zone.

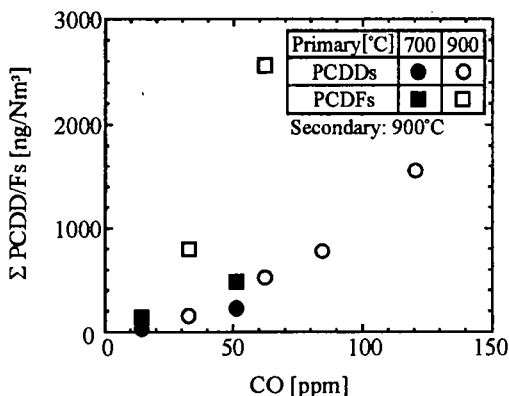


Figure 4. Influence of CO concentration in flue gas on PCDD/Fs concentration at the furnace temperature, 700°C and 900°C, in the primary combustion zone.

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cause the reduction of the PCDD/Fs formation.

The PCDD/Fs concentrations are re-plotted in Figure 4 against the averaged CO concentration. The difference of the PCDD/Fs concentration between the experiments at 700°C and 900°C in the primary combustion zone is smaller than in Figure 2. However, there clearly exists the difference of their concentration in both series of experiments. This means the decrease of the PCDD/Fs concentration with lower temperature of the primary combustion zone cannot be explained only by combustion conditions indicated by the CO concentration. Probably it is directly related to the composition and concentrations of precursors and carbon/PAHs in flue gas formed during incineration. It is necessary to investigate these carbonaceous materials in flue gas in detail.

References

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