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EFFECT OF COPPER CHLORIDE ON PCDD/Fs FORMATION IN MODEL WASTE COMBUSTION IN A LABORATORY-SCALE FLUIDIZED BED INCINERATOR

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Introduction

Metals in municipal solid waste can promote the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) during incineration^{1,2}. Stieglitz et al. showed in experiments with model mixtures that copper chloride (CuCl₂) is particularly effective while other divalent metal chlorides such as magnesium, zinc, mercury, cadmium, tin and lead display only limited catalytic activity³. Addink et al. demonstrated that copper chloride catalyzes both ring closure and chlorination of the dibenzofuran and dibenzo-*p*-dioxin rings⁴. These studies indicated possible mechanisms of the PCDD/Fs formation in a combustion chamber during municipal waste incineration. Mattila et al. showed in co-combustion of coal/bark/plastics mixture using a full scale incinerator that the presence of copper in the fuel mixture leads to increased PCDD/Fs formation⁵. They also suggested the addition of copper as a catalyst shifts the congener distribution of PCDF towards the more highly chlorinated species. However, they did not discuss the role of copper in their formation. Since metals in fuel adhere to incinerators and very small amount of metals exerts large effects on the PCDD/Fs formation, it is very difficult to discuss the effects of metals as a catalyst on their formation during incineration in detail.

The aim of this study is to clarify the effects of copper as a catalyst on PCDD/Fs formation in municipal waste incineration. We used a laboratory-scale fluidized bed reactor with electrical heating and an artificial solid waste was prepared. Copper chloride was mixed in the model waste since it was particularly effective as a PCDD/Fs formation catalyst. Polyvinyl chloride (PVC) was mixed to the model waste as a chlorine source.

Materials and Methods

Figure 1 shows a schematic diagram of an experimental setup, which was used in our previous paper⁶. 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 to 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 the 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. Temperature of each part of the reactor was controlled using electric heaters. The concentrations of CO, CO₂, and O₂ were measured continuously.

The artificial solid waste was synthesized to define the waste composition strictly. Two types of wastes were used in this experiment. One had no additive of metals (designated as Fuel 1) and the other contained Cu as a catalyst (Fuel 2). The base ingredients of the artificial waste was 45% unbleached pulp powder, 40% unbleached flour and 15% wood powder. Properties and

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elementary composition of the artificial waste containing only the base ingredients are shown in our previous paper⁶. In addition to the base ingredients, PVC (degree of polymerization $n \cong 1100$, Wako Pure Chemical Industries, Ltd.) was mixed as the Cl source in both wastes. Copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.25%, Wako) was added into Fuel 2 as the PCDD/Fs formation catalyst. All ingredients were ground separately and mixed mechanically, and then pelletized into particles in the range of 1 to 3 mm in diameter. Analyzed Cl contents were 0.97% (Fuel 1) and 1.24% (Fuel 2). Copper was not detected in Fuel 1.

The setup was assembled with new sand for the fluidized material. After each experiment, the 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. Actually, the reactor was remade after the experiment of Fuel 2 because Cu compounds adhered to it by reacting with the quartz surface of the reactor. The experimental conditions are listed in Table 1. The excess air ratio (λ) is set to 2.0 in total. Sampling was carried out for 4 hours or more at the middle of the post combustion section (indicated as point X). Analysis methods are the same in our previous paper⁶.

Results and discussion

Figure 2 shows the homologue profile obtained in the experiment of Fuel 1 containing no copper. PCDFs were formed about 6 times as much as PCDDs. In both of PCDD/Fs, pentachlorinated compounds are the main homologues. From hexa- to octa-chlorinated compounds, the formation decreases rapidly. The ratio of octa-chlorinated dibenzofuran (O8CDF) in the total PCDFs is only 0.3%. The homologue profile in Fuel 2 containing CuCl_2 is shown in Fig. 3. PCDFs were also predominant in this case. However, there is a large difference in the homologue profile between Fuels 1 and 2. The result in Fuel 2 shows that the homologue distribution is shifted towards the more highly chlorinated species in both of PCDD/Fs. O8CDD/F are the dominant products. O8CDF amounts to about 60% in the total PCDFs.

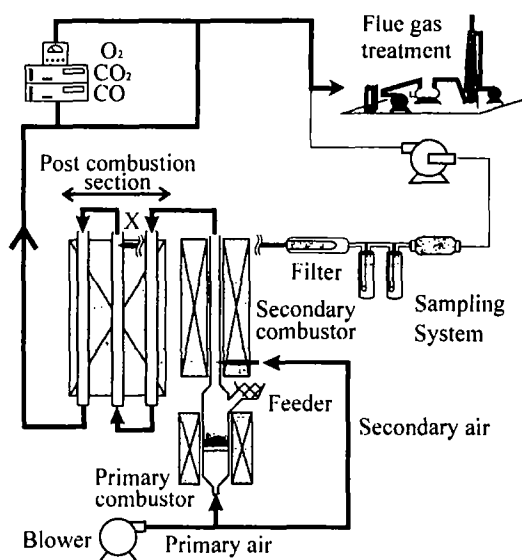


Figure 1. Schematic diagram of experimental setup.

Table 1 Experimental conditions.

temperature	
primary combustor	900 °C
secondary combustor	900 °C
cooling 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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Figure 3 definitely indicates that copper chloride acts as a chlorination catalyst of various compounds related to PCDD/Fs formation during incineration. The role of copper chloride on chlorination of the various compounds is considered to be (a) Cl_2 formation via Deacon reaction and decomposition of copper chloride (b) direct chlorination by copper chloride and chlorinated compounds related to Deacon reaction. Deacon reaction and decomposition of copper chloride are the matter of Cl_2 concentration in flue gas. Direct chlorination is connected to chlorination kinetics in addition to Cl_2 concentration. All of these reactions could be seen in the combustion chamber. However, direct chlorination might have a large contribution to chlorination of the various compounds related to PCDD/Fs formation because the chlorination rate is estimated to be very fast owing to the large differences in the homologue profiles of Fuels 1 and 2. There could be (a) non-chlorinated dibenzo-*p*-dioxin/furan and PCDD/Fs except O8CDD/F, (b) precursors such as chlorophenols and chlorobenzenes, and (c) carbon to be chlorinated. Probably chlorination occurs for all of these compounds. It is unclear what reactions are predominant in the process of chlorination.

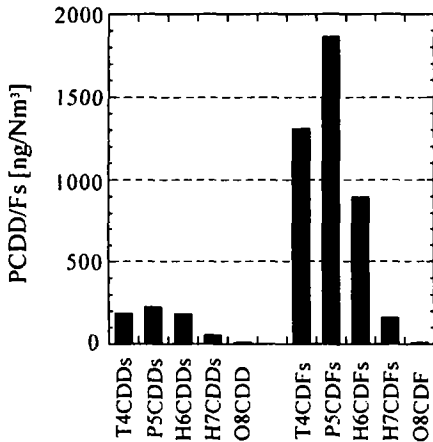


Figure 2. Homologue profiles of PCDD/Fs in the experiment of Fuel 1.

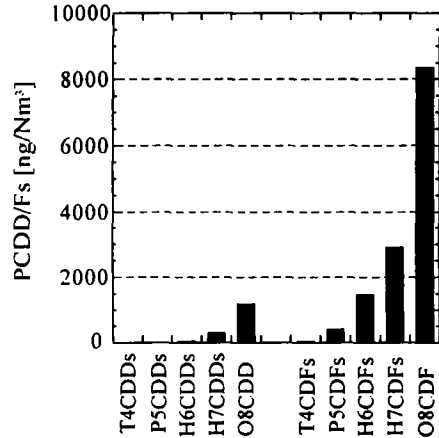


Figure 3. Homologue profiles of PCDD/Fs in the experiment of Fuel 2.

It is clarified in our previous paper that there is a good correlation between Cl content in waste and the amount of PCDD/Fs formed in the combustion experiments of the wastes containing PVC as a Cl source and copper chloride as a catalyst⁶. Figure 4 shows the relation between the amount of PCDFs formed and Cl content in waste. The result in Fuel 1 is also plotted in this figure. The amount of PCDFs formed in Fuel 1 cannot be directly compared with that in Fuel 2 from the viewpoint of Cl content in waste. However, it is definite in Fig. 4 that PCDFs

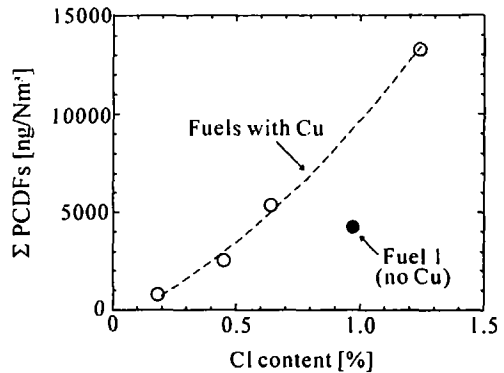


Figure 4. Effect of copper in waste to total concentrations of tetra to octa-chlorinated dibenzofurans.

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are more formed in the combustion of waste with copper than without copper. This is also observed in the case of PCDDs.

It is unclear whether the increased PCDD/Fs in the combustion of wastes containing copper as a catalyst can be explained only by chlorination of the compounds related to their formation or by other formation mechanisms in addition to chlorination. Further investigations are needed to clarify these points.

References

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