

## PRIMARY AND SECONDARY PCDD/F FORMATIONS IN A MUNICIPAL SOLID WASTE INCINERATOR

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### Introduction

In this study, the primary and secondary PCDD/F formations from municipal solid waste incineration are discussed based on the experimental results obtained at a laboratory-scale fluidized-bed incinerator (LSFBI)<sup>1</sup>. To reproduce the PCDD/F formation along the gas cooling process in the LSFBI in detail, simple flow reactor experiments were conducted using the fly ash collected from the LSFBI experiments and the flue gas, also from the LSFBI, was passed through an electrically heated flow reactor. It is suggested that the secondary formation or *de novo* formation along the cooling process takes place at temperatures of around 300 °C and it doesn't proceed at all at around 200 °C. It is also noted that secondary formation depends on the HCl concentration and is independent of the concentrations of CO and hydrocarbons. On the contrary, primary formation or formation in the combustive fields is in proportion to the concentrations of CO and hydrocarbons and it is promoted due to insufficient mixing with air.

### Experimental Method

Figure 1 is a schematic of the LSFBI<sup>1</sup> used in the experiments. The primary and secondary combustors were made of a quartz tube and a high-alumina tube, respectively. The temperatures of the primary and secondary combustor were controlled using an electric heater, maintained at 800 °C and 900 °C, respectively. The excess air ratio  $\lambda = 2.0$  yielded neither CO nor hydrocarbons, and several peaks attributable to CO and hydrocarbons were observed in combustion at  $\lambda = 1.6$ <sup>1</sup>. Flue gas was cooled by passage through a connection duct and a gas cooling tube, and these parts were made of stainless steel. The temperatures of the connection duct and the top part of the gas cooling tube were roughly controlled by choosing the duct and tube for either water-cooled or air-cooled. The temperature at the bottom part of the gas cooling tube was controlled by an electric heater. PCDD/F sampling was conducted over 2 hours at locations S3 and S6 (see Figure 1). The main components used for the base ASW were unbleached paper powder (45 %), pine wood powder (20 %), salt-free flour (15 %) and virgin resin PE powder (20 %). To adjust the Cl contents and change the Cl compounds, PVC, PVdC or NaCl powders were added to the base ASW. In order to prevent influence from a previous experiment, between each experiment, the quartz tube and the high-alumina tube of the combustors and the fluidized-bed sand were renewed, and the inner surface of the connection duct and the gas cooling tube were washed out using the hydrogen fluoride.

## FORMATION AND SOURCES

To examine the PCDD/F formation during the gas cooling process in detail, the flue gas from the LSFBI was extracted at the outlet of the secondary combustor and was led to the electrically heated flow reactor, which was filled with fly ash obtained from the same LSFBI experiments. The flow reactor tube had an internal diameter of 30 mm and a length of 650 mm. The flow rate of the flue gas was 4L/min, and the layer thickness of the fly ash was 20 mm. The temperature of the reactor was monitored by the thermocouple. The time required for the reactor to reach the setting temperature was about 10 min. Both the gas and solid phase of PCDD/Fs were measured. The PCDD/F concentration in the flue gas was also measured and taken into account as the blank level. To decompose the PCDD/Fs in fly ash, the original fly ash was heated at 500 °C for 5 hr under a nitrogen circumstance.

### Results and Discussion

Figure 2 shows the effects of the flue gas cooling conditions on PCDD/F formation for PVC 4 %-ASW incineration at  $l = 2.0$ . It is noted that the amount of PCDD/Fs became significantly low with the decrease of the cooling temperatures. The result also suggests that PCDD/Fs is formed mainly from the ash deposited in the top part of the gas cooling tube during the gas cooling process because of the larger difference in PCDD/F concentration with cooling conditions between I and II than that between II and III. The flue gas was contacted with the inner surface of the top part of the gas cooling tube, and the temperature of the flue gas (about 400 °C) was higher than the wall surface of the top part of the gas cooling tube (Air-cooled: 300 °C, Water-cooled: 200 °C); therefore, the fly ash in the flue gas was easily deposited by the inertial force and the thermo-phoresis. On the other hand, in the bottom of the gas cooling tube, the temperature of the flue gas (300 °C) was the same as the wall surface. Thus, PCDD/Fs formed in the top part of the gas cooling tube, where a large amount of fly ash was deposited.

PCDD/F concentrations at the outlet of the secondary combustor (sampling location at S6, see Figure 1) and the outlet of the gas cooling tube (S3) during PVC 4 %-ASW incineration under the cooling conditions of I and II are shown in Figure 3. At location S6, the PCDD/F concentration at  $l = 1.6$  exceeded that at  $l = 2.0$ , suggesting that primary PCDD/F formation is due to the imperfect mixing of air and reactants in the combustion fields. In the case of cooling condition I, the PCDD/F concentration at location S3 shows a higher level than that at S6. The difference in PCDD/F concentrations between locations S3 and S6 indicates the amount of secondary PCDD/F formation in the gas cooling process. On the contrary, PCDD/F decreases along the flow from S3 to S6 in the case of cooling condition II. This suggests that no secondary formation takes place along the flue gas flow from the combustor outlet to the cooling section under the cooling condition of II. This is also confirmed from the flow reactor experiments as shown in Figure 4. It is noted that PCDD/F is not formed in temperatures of around 200 °C but significant PCDD/F formation was observed at around 300 °C.

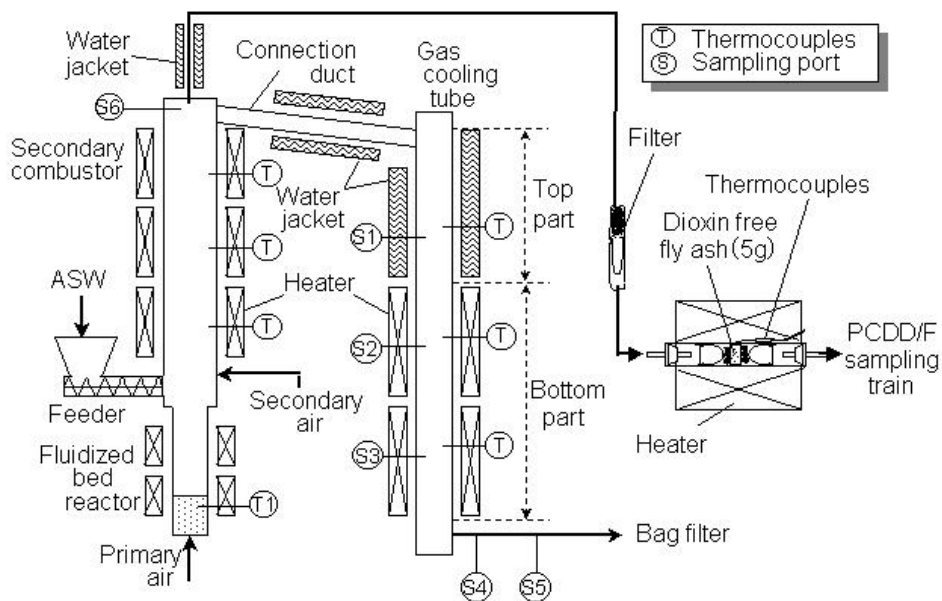
Figure 5 shows PCDD/F concentrations under the cooling conditions of I and II at the incinerations of Base-, PVC 4 %-, PVdC 3 %- and NaCl 4 %-ASW. Besides Base-ASW incineration, the cooling condition of I shows higher PCDD/F concentrations than condition II by one order of magnitude for both cases of  $l = 2.0$  and 1.6. On the other hand, PCDD/F concentrations are independent of the cooling conditions for Base-ASW. Figures 6 and 7 show the effects of the excess air ratio and HCl concentration on the primary PCDD/F formation, respectively. These results suggest that PCDD/F concentration is not proportional to HCl concentration, but inversely proportional to the excess air ratio. Insufficient mixing during combustion, which yields CO and hydrocarbon peaks, will be the origin of the primary generation as mentioned in a previous paper<sup>1)</sup>. Figure 8 shows the effects of HCl concentration on the secondary PCDD/F formation. In the case of the secondary formation, PCDD/F concentration is proportional to the HCl concentration in the flue gas. These results show that the dependent factors of primary and secondary PCDD/F formation are different from each other.

## Acknowledgements

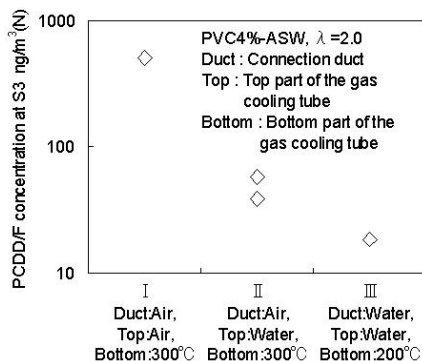
This study was supported by the Ministry of Economy, Trade and Industry (METI) and the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

## References

1. N. Ishibashi, Y. Yoshihara, et. al., *Organohalogen Compounds*, Vol. 50, 284-287 (2001).

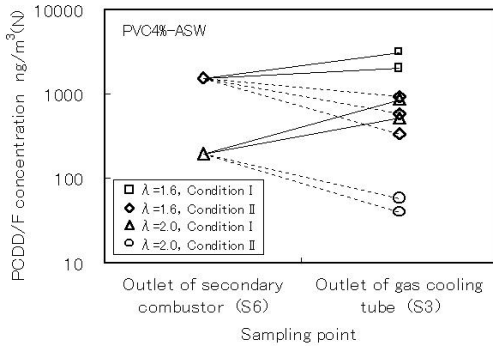


**Figure 1.** Schematic of a laboratory-scale fluidized-bed Incinerator

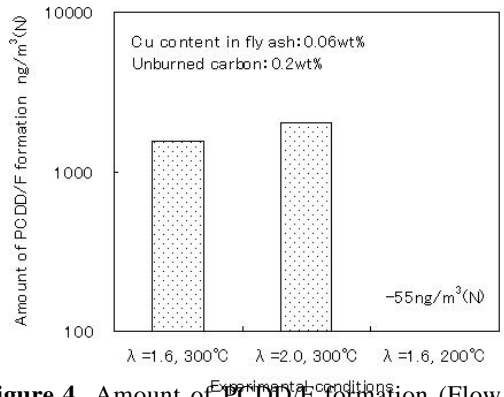


**Figure 2.** Effects of flue gas cooling conditions on PCDD/F formation

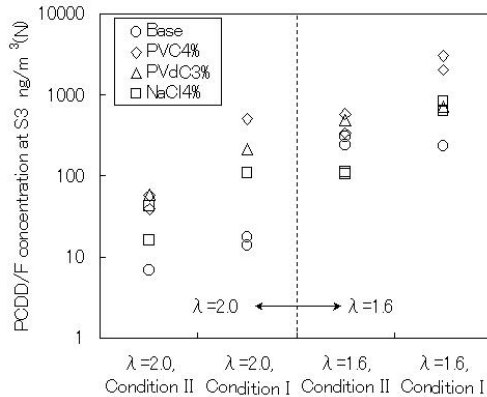
# FORMATION AND SOURCES



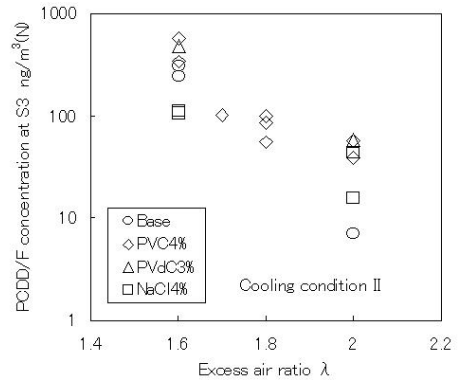
**Figure 3.** Effects of the excess air ratio  $\lambda$  and gas cooling condition on PCDD/F formation



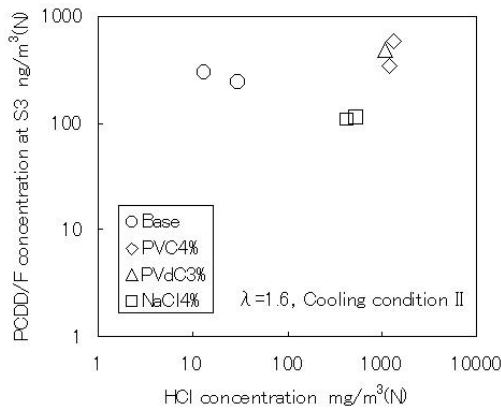
**Figure 4.** Amount of PCDD/F formation (Flow reactor)



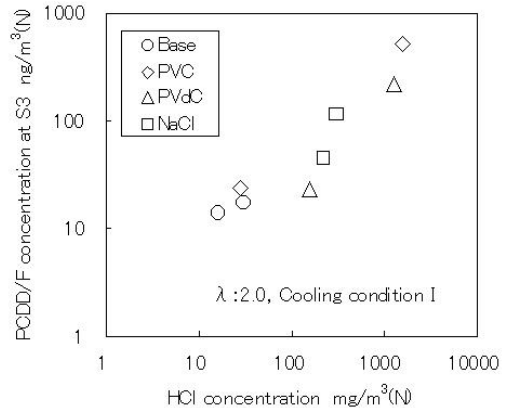
**Figure 5.** Effects of the excess air ratio  $\lambda$  and gas cooling condition on PCDD/F formation



**Figure 6.** Effects of the excess air ratio  $\lambda$  on primary PCDD/F formation



**Figure 7.** Effects of HCl concentration on primary PCDD/F formation



**Figure 8.** Effects of HCl concentration on secondary PCDD/F formation