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Influence of residual carbon on the decomposition process of PCDD/Fs in MSWI fly ash

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Abstract

In heating treatment of fly ash to reduce PCDD/Fs, cooling process is important to inhibit de novo formation of PCDD/Fs. In this study, assuming that residual carbon is the dominant factor of de novo synthesis, the relation between PCDD/Fs and residual carbon was examined.

Firstly, by using MSWI fly ash which was treated in an actually operated facility, both the content of PCDD/Fs and residual carbon were decreased as heating temperature increased. At temperatures higher than 400 °C, the reduction rate of residual carbon was higher than 20% and more than 95% of PCDD/Fs was decomposed.

In order to simulate a heating treatment process, fly ash was heated at different temperatures and gas atmospheres, oxygen or nitrogen. Heated fly ash was placed for 2 h at 300 °C in oxygen to promote de novo synthesis, or cooled immediately. As a result, good correlation between PCDD/Fs and residual carbon was found, therefore it was shown experimentally that residual carbon was the main factor for PCDD/Fs formation by de novo synthesis in fly ash.

Keywords: PCDD/PCDFs; De novo synthesis; MSWI fly ash; Heating treatment; Residual carbon

1. Introduction

In Japan, since polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) released from municipal solid waste incinerators (MSWI) became a big concern in the early 1990s, considerable efforts have been put into emission control of flue gases. However, 80% of PCDD/Fs is contained in fly ash and is consequently disposed of in landfills. In order to reduce environmental risks, PCDD/Fs in fly ash should be decomposed before final disposal. The heating treatment system of PCDD/Fs in fly ash is a simple process, requiring low energy consumption, and was being operated in about 50 facilities in 2002. Their operating processes are about 40 facilities with nitrogen, and 10 with air. The treatment capacities of fly ash are 100–1300 kg/h for the former facility, and 100–1000 kg/h for the latter.

In this system, fly ash is heated either in a nitrogen or air atmosphere. The former method is called the "Hagenmaier type" after the name of the inventor, and the temperature of fly ash is lowered in a short time after heating treatment to prevent de novo synthesis of

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PCDD/Fs at around 300 °C. In the latter process in an air atmosphere, rapid cooling is also applied, but with gradual cooling there are contradictory reports; PCDD/Fs were formed in some studies (e.g. Itaya, 1997), and not formed in others (Okuyama et al., 1994; Masuda et al., 2001).

After Vogg and Stieglitz (1986) showed the formation of PCDD/Fs in MSWI fly ash, many studies on de novo synthesis of PCDD/Fs in fly ash were done, and the influence of various factors, such as residual carbon, temperature, metal catalysts, chlorine, oxygen concentration, were examined. Vogg et al. (1987) first mentioned the correlation between oxidation of carbon in fly ash and PCDD/Fs formation. Stieglitz et al. (1989) concluded that particulate organic carbon was the primary source for PCDD/Fs formation from experimental results using carbon of different origins in air.

Tanigawa et al. (2001) showed that the PCDD/Fs formation rate and carbon content in fly ash had a good correlation both in logarithmic scales. Milligan and Altwicker (1993) found the correlation between carbon gasification rates and PCDD/Fs formation rates for different fly ashes, and suggested that a similar catalytic mechanism might be involved in both cases. Stieglitz et al. (1997) investigated the reactions of precursors in de novo synthesis with thermal experiments using labeled carbon (^{12}C and ^{13}C), and demonstrated that PCDDs were formed partly via condensation of the precursor and PCDFs were formed directly from carbon structures.

Judging from the past studies described above, carbon is "the potential" which becomes a source of PCDD/Fs formation. Therefore, in the case of the heating treatment of fly ash, it was considered that the content of PCDD/Fs by de novo synthesis during gradual cooling would depend on the residual carbon contained in the fly ash. The main objectives in this study are, after confirming the measurement method of residual carbon in fly ash,

(i) to examine the relation between PCDD/Fs and residual carbon by using fly ash treated at an actually operated facility in an air atmosphere,
(ii) to examine the influence of residual carbon in fly ash on PCDD/Fs formation by de novo synthesis with an experiment in optimal conditions.

2. Experimental method

2.1. Experimental apparatus

Fly ash was heated in a silica tube reactor (56 mm in inner diameter, 1500 mm in length) as shown in Fig. 1. The furnace was divided into three parts, each of whose temperature could be controlled separately. A fly ash sample was put on a silica boat (150 mm length, 25 mm width, 15 mm depth) and was placed on a non-heated area in a tube reactor. Pure nitrogen or oxygen gas was introduced to the reactor and the flow rate was adjusted to 1.3 l/min. For measurement of the carbon content, the concentrations of CO and CO_2 were continuously monitored by non-dispersive infrared type gas analyzers, and data were recorded by a personal computer. When CO and CO_2 were not detected, the silica boat was moved to the middle part of the reactor and the measurement was begun. The experimental apparatus simulated the practical device where air flowed over the surface of fly ash as shown in Fig. 2. The maximum range of the gas analyzer was chosen as 100 ppm or 2000 ppm for CO, and 500 ppm or 1% for CO_2. The measurement accuracy of an integrating flow meter was checked by comparison with a water substitution method, and the measurement errors of flow rate at the inlet and outlet of the reactor were confirmed to be within 3%.

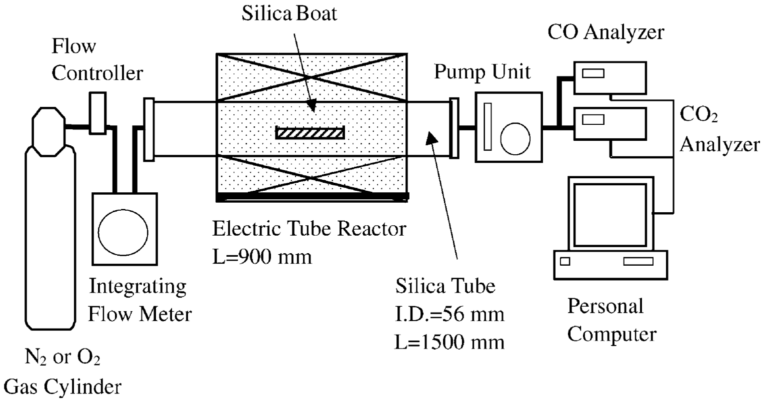

Fig. 1. Schematic of the experimental apparatus.