POPs FORMATION AT LOW TEMPERATURE IN FLY ASH COLLECTED FROM ALUMINUM ALLOY SMELTING PLANTS

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Introduction

Much effort has been made to reduce emissions of unintentionally produced persistent organic pollutants (POPs) from aluminum alloy smelting plants because itis the third largest source of dioxin emissions except from municipal waste incinerators in Japan[1]. Since these plants are mostly small-scale, it is difficult to reduce their emissions by installingadvanced gas cleaning processessuch as a post-combustor and a quenching chamber. Utilizing fabric filters of smelting furnaces is reasonable measures for reduction of POPs emissions by setting their operating conditions appropriate.

The emissions of these byproducts were investigated in recent research by using an experimental fabric filteradded to an aluminum alloy smelting plant in operation[2]. The results of the analysis for POPs in flue gas showed that removal efficiencies ofthese pollutants by the experimental fabric filterwere often lower than expected when the temperature was set to the value which was generally recognized to be low enough in case of waste incinerators. POPs were probably formed in the fabric filter at the sufficiently low temperature.It is important to find the temperature at which the expected removal efficienciescan be achievedsteadilyfor utilizing fabric filtersof smelting furnaces as the best available technology (BAT).

The aim of this study is to reveal the formation of unintentionally produced POPsat sufficiently low temperature in fly ash samples collected from fabric filters of aluminum alloy smelting plants by laboratory experiments. Heating experiments were performed in our laboratory using these fly ash samples. This paper describes the effects of the heating temperature of fly ash samples on the POPs formation. The target temperature range was below 200 ^{o}C in these experiments.

Materials and methods

The heating experiments were performed using fly ash collected from a fabric filter unit of an aluminum alloy smelting plant. Two types of experimental apparatus were applied to the experiments (Figure 1). At apparatus 1, 5 g of fly ash was put on a glass boat and it was inserted into a glass tube (40 mm diam., 300 mm length) to the position where the temperature measured by a thermocouple inserted into the tube was equal to the set value. The tube was heated by a horizontal electric heater. At apparatus 2, 5 g of fly ash was put on quartz wool supported by a sintered glass plate in a glass tube (30 mm diam., 180 mm length). The tube was heated by a vertical electric heater which was controlled by three separate sections. Simulated flue gas was supplied to the glass tube. The filtration rate was 1.2 m/min. 1 %vol moisture was supplied by bubbling air through a temperature-controlled water bath. These conditions were determined by measuring flue gas compositionsinthe fabric filter which fly ash samples were collected from. POPs in flue gas emitted from the tube were trapped in a sampling unit. This flue gas sample and the residue in the tube were analyzed for polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), penta- and hexa-chlorobenzene (CBzs), and polychlorinated naphthalenes (PCNs) [2]. The concentrations of CO, CO_2, and O_2 in flue gas were continuously measured by use of nondispersive infrared spectroscopy (NDIR) and paramagnetic oxygen analyzers.

It was reported in the previous experiments that POPs formation was not apparent in the experiments with keeping fly ash at 190 ^{o}C for 6 hours[3]. However, heating it at the same temperaturefor longer hours or temperature rise above the set valuewith naturally cooling fly ash to itbefore starting the experiment, i.e., preheating,remarkably increased the total amounts of POPs in fly ash and flue gasat 190^{o}C.It is probable that activation of chlorine sources or catalysts of their formation and chlorination in fly ash demands

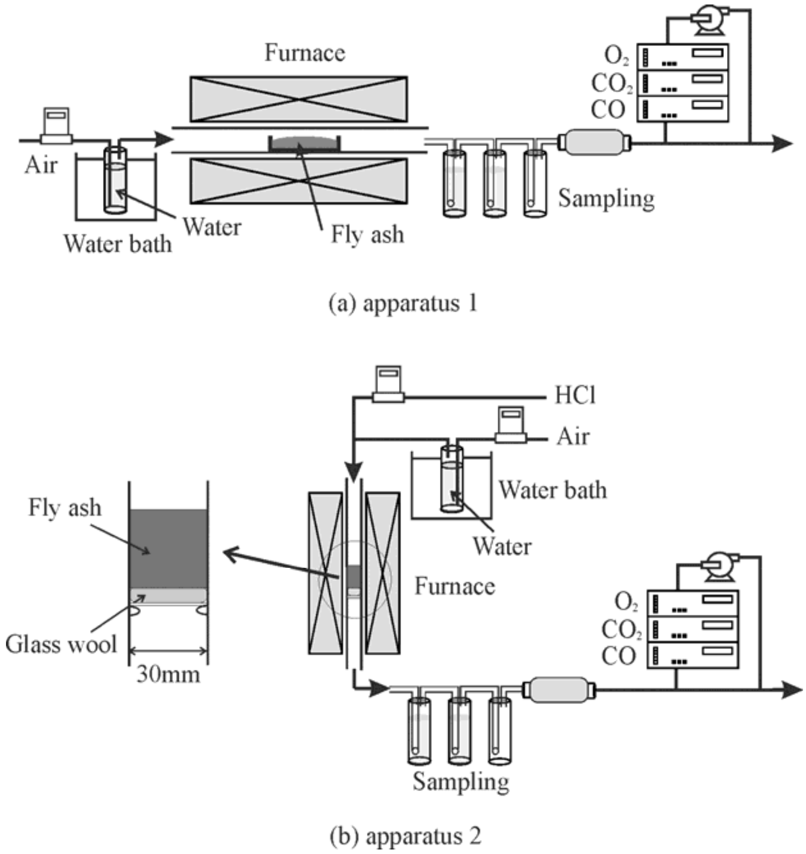

Figure 1. Schematic diagram of experimental apparatus.

high temperature or long heating period and the activated Cl sources or catalysts contribute to the formation of these byproducts. Preheating was done to simulate temperature changes of flue gas passing from furnaces through pipes to fabric filters in aluminum alloy smelting plants. However, physical properties and chemicalcompositions of fly ash would change when the temperature rose over it before keeping fly ash at the set value for hours. These changes affected the homologue profiles and the amounts of POPsformed in fly ashin the previous experiments. Therefore, at first, long heating period at the same temperature was applied to the experiments. The heating period was changed according to the set temperature. Lower temperature demanded longer heating period. It was confirmed by inserting a thermocouple into fly ash that it was not over the set value when raising the temperature of fly ash in the tube.

Results and discussion

Figure 2 shows the amounts of unintentionally produced POPsin flue gas trapped in the sampling unit and in the residue in the tube. The total amounts of POPs obtained in the heating experiments increased more than those of original fly ash at 110 ^{o}C for 70 hours and 190 ^{o}C for 18 hours. Short heating period probably caused their lower amounts at 150 ^{o}C for 25.5 hours than at 110 ^{o}C. The amounts of POPs in flue gasout of the tube decreased as the heating temperature was low, which corresponded to higher removal efficiencies of these byproducts at a lower temperature of a fabric filter.Higher chlorinated homologues of PCDD/Fs were formed more than lower chlorinated species (Figure 3). Especially, the higher temperature resulted in the larger increase of higher chlorinated species. Homologue profiles of PCBs were also shifted toward higherchlorinated compounds after the heating experiments. It is interesting that low chlorinated species of PCBs largely increased at 190 ^{o}C simultaneously with high chlorinated homologues. PeCBs had the lowest increase rate of the amounts formed in

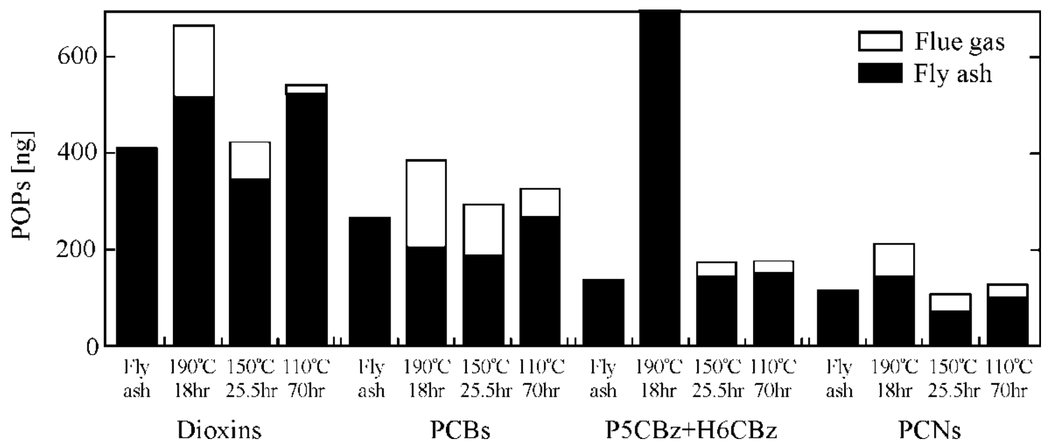

Figure 2. POPs formation at low temperature with long heating period.

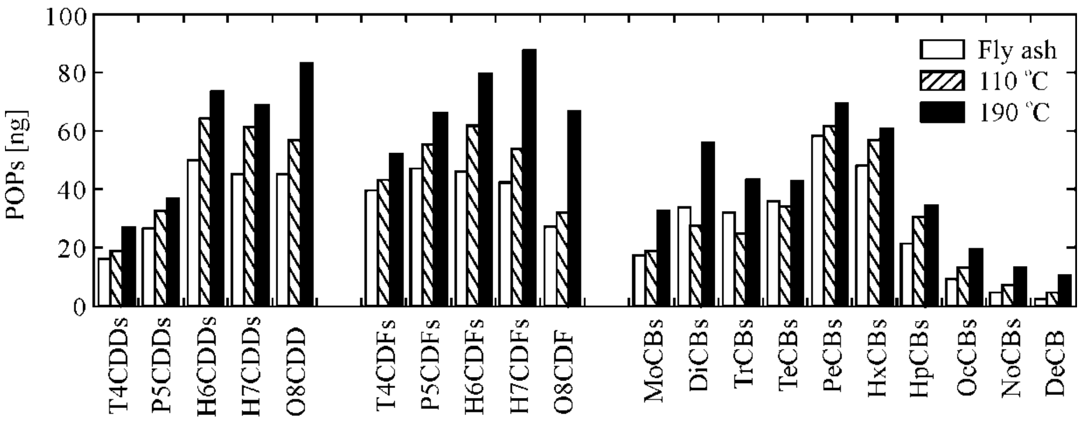

Figure 3. Effects of heating temperature of fly ash on homologue profiles of POPs.

the experiment at 190 °C in all PCB homologues. This trend was often observed in other experiments at comparatively high temperature in the range used in these experiments. The increases of both the high and low chlorinated speciesare probably related to more than two types of PCB formation mechanisms.One of these pathways is through oxidative decomposition and chlorination of carbon and polycyclic aromatic hydrocarbons (PAHs), so called de novo synthesis, in which higher chlorinated compounds are likely to be formed[4]. Another is through condensation reactions of chlorobenzenes and chlorophenols[5]. These reaction rates are dependent on experimental conditions such as heating temperature and catalyst activity levels. The increase rates of the amounts of the high and low chlorinated homologues of POPs formed should change according to the experimental conditions.

The POPs formation was observed in the experiment at 110 °C for 70 hours. If the heating experimentsareperformed at the temperature less than 110 °C by the same methods, it will demand much longer heating period more than 70 hours. It is a very difficult experiment. Instead of long heating period, preheating, i.e., temperature rise above it before keeping fly ash at the set value for hours, was applied to the experiments at the temperature less than 110 °C.Fly ash in the tube was heated to 190 °C, keeping it at the temperature for 12 hours. Then, it was naturally cooled to the set value, 90 or 70 °C, and the heating experiment at the temperature was started by supplying simulated flue gas to the tube after the temperature of fly ashwas stable, which was verified by inserting a thermocouple into it in the tube. The heating period was 12 hours. When the temperature for preheating was set to 500 °C for 10 minutes, the amounts of POPs in fly ash remarkably decreasedand their homologue profiles were shifted towards lower chlorinated speciesby decomposition and dechlorination in the previous experiments.Moreover, the lower chlorinated species were dominant in POPs formed and their amounts in flue gas out of the tube largely increased more than in fly ash during the heating period at 190 °C after preheating. This shows higher volatilityof components in fly ash such as chlorine and other byproducts than before preheating. The physical properties and chemical compositions of fly ashsignificantly changed by preheating, which affected their formation as mentioned above. To lower the effects of preheating on these changes of fly ash, the temperature of preheatingwas set to 190 °C for 12 hours in these experiments since POPs clearly formed in the experiments at 190 °C with long heating period.

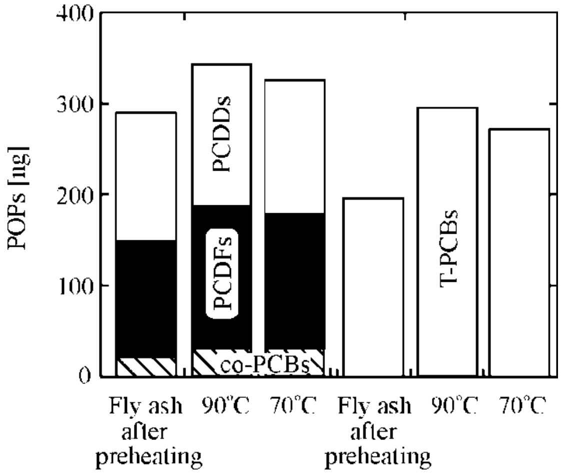

Figure 4. POPs formation at low temperature with preheating.

Figure 4 shows the amounts of POPs in fly ashafter preheating with cooling it to 90 °C and their total amounts in flue gas and in fly ash obtained in the heating experiments at 90 or 70 °C for 12 hours after preheating.The amounts of POPs formed exceeded those in fly ash just after preheating.The increases of PCBs weredefinite. Theseare consistent with the results obtained in the experimental fabric filter added to the aluminum alloy smelting plant[2].Furthermore, these are not contradictory to the POPs concentrations and the temperature of flue gas collected from the pipes just before and after the fabric filters in other aluminum alloy smelting plants in operation.These results indicate that it is necessary to set the temperature of fabric filters of furnaces quitelow when utilizing them forreduction of unintentionally produced POPs emissionsin aluminum alloy smelting plants.

References

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