FORMATION OF DIOXINS FROM RAW SINTERING MIXTURE HEATED IN A PACKED BED REACTOR

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Introduction

Total dioxins emission from waste treatment processes and sintering processes in 1999 were estimated to be 2521g-TEQ and 101 g-TEQ respectively, or about 90 and 4 percent of total emissions in Japan. The ratio may increase as reduction in emissions from waste treatment processes makes progress. A research project named SDD Project conducted experimental studies on the issues, and a result was reported[1]. Based on fundamental research and measured data, the project came to an assumption that drying zone of sintering processes played an important role in formation of dioxins. It was assumed that so-called de novo synthesis occurred in the zone when some carbon and chlorine materials and further catalytic metals existed.
This study investigates formation behavior of dioxins with sintering mixture heated in a packed bed reactor. Effects of some factors on dioxin formation were tested and discussed.

Materials and Methods

Raw mixture samples were basically prepared with fine ore, powdered coke, limestone, return ore, serpentine and iron bearing residue. Because the mixture showed very low formation potential in a preliminary test, copper compound, EP dust and blast furnace ash were added to promote dioxins formation. Composition of these samples is shown in Table1. The mixtures were mixed mechanically in a pelletizing machine with water, methanol and liquid glass and

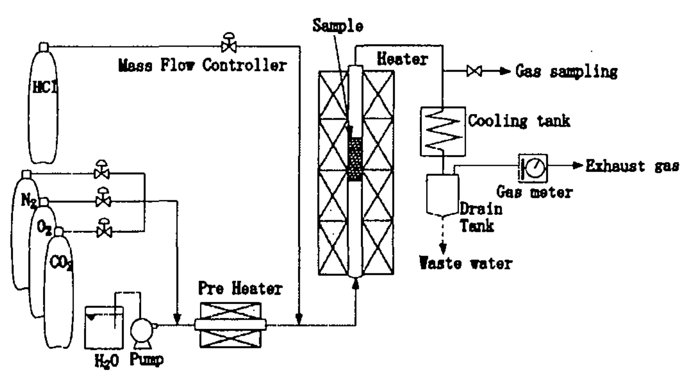

Fig.1 Experimental apparatus

were pelletized. The pellets were then soaked in copper (II) chloride solution or mixed with copper (II) oxide powder. Figure 1 shows the experimental apparatus used. A sample of 600 g was packed into a quartz tube (1300 mm × 50 mm internal diameter), and gas was introduced into the tube at a constant flow rate of 20 l/min. Gas composition was set at N_2:80%; O_2:10%; CO_2:10%; HCl:100 ppm in a dry base; and H_2O 10% in a wet base.

Experiments were conducted in a temperature range of 300° -550℃. Gas sampling was done at the outlet of the tube. After dioxin measurement was completed, the sintered sample was cooled and taken out from the reactor and a part of the solids was tested to determine dioxins. Analyses of PCDDs, PCDFs and Co-PCBs for the samples were carried out based JIS K 0311 and 0301 using a gas chromatography/high-resolution mass spectrometry.

Results are discussed based on total amounts of dioxins: summation of the amount flowed out in flue gas during 4 hours of an experiment and the amount in a solid sample.

Table 1 Composition of raw sintering materials (%)

Sample	Iron ore	Serpentine	Lime Stone	Coke	Return Ore	EP Dust	Copper ($CuCl_2$)
Sinter mixture A	69.5	1.67	12.6	3.77	12.6	–	–
Sinter mixture B	69.5	1.67	12.6	3.77	12.6	–	0.1
Sinter mixture C	68.8	1.66	12.4	3.73	12.4	0.994	0.1

Results and Discussion

Effects of copper on dioxins formation

Figure 2 shows effects of copper addition on total amount of dioxins. In case of sinter mixture A, the total amount of dioxins was only 0.026 ng/g. The value was considerably low compared to that in a case of employing fly ash from a gasification-melting process[2]. Adding copper oxide (CuO) or copper chloride ($CuCl_2$) to sinter mixtures at 0.1wt% dramatically increased dioxins formation, 21 and 470 times with addition of CuO and $CuCl_2$, respectively, in case sinter mixture A. This fact suggests that *catalyst copper in sinter mixture* catalyzed formation of dioxins to the same level fly ash samples produced. Copper chloride

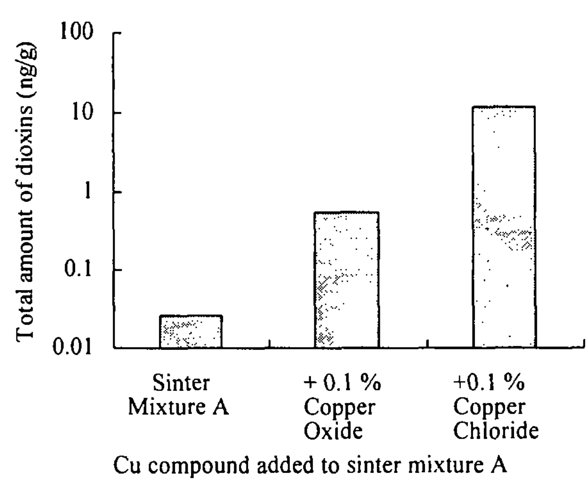

Fig.2 Effect of copper compound addition on dioxins formation

promoted the formation much stronger than copper oxide probably because the chloride also acted as a chlorine source in the experimental system and was more volatile than oxide. In other words, copper chloride would make a more active reactant than copper oxide.

Temperature dependence

Figure 3 shows temperature dependence of total amount of formed dioxins in case of sinter mixture B. The amount of dioxins decreased with an increase of temperature between 300° to 550 ℃. This dependence is similar to typical dependence of total dioxins amount on the temperature for fly ash from an incineration plant of municipal solid waste[3]. Figure 4 shows a temperature dependence of dioxins concentration in flue gas in the same experimental condition. The concentration increased with an increase of temperature unlike the case of the total amount. These results may show two things, namely, that sintering at 300℃ gives higher formation and that the formed dioxins will be adsorbed on carbonaceous materials, which result in higher concentration in flue gas at high temperatures with dioxins desorbed from the surface of the material.

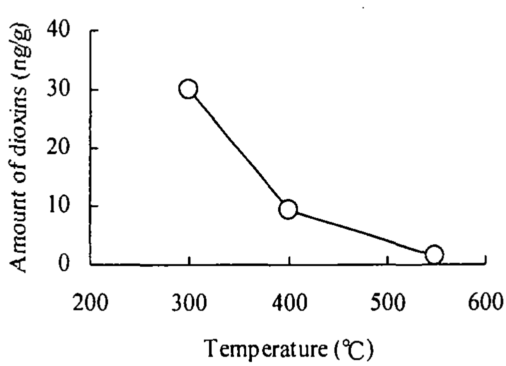

Fig.3 Temperature dependence of total amount of formed dioxins in sinter mixture B

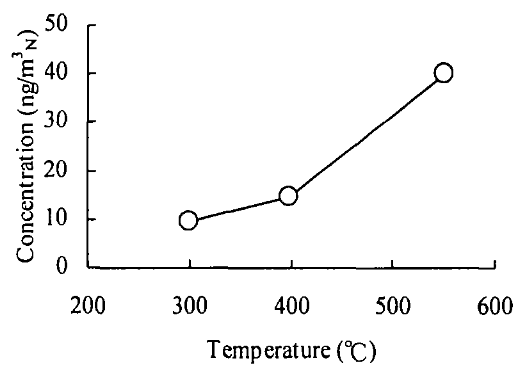

Fig.4 Temperature dependence of dioxins concentration in flue gas

Influence of carbon material in sinter mixture

Carbon material seemed to be an important source for dioxins formation and influence of it in a sinter material was observed in an experiment using a process simulator. Table 2 summarizes the results that investigated effects of some parameters. First, there is a noticeable difference between coke (Run 1) and activated coke (Run 2). Dioxins concentration in Run 2 flue gas was lower than that of Run 1, whereas the amounts retained in sintered mixtures were nearly equal. This fact again suggests that the formed dioxins are adsorbed in micro pores of activated coke. Figure 5 shows difference in homologue distribution of dioxins in flue gas. It is obvious that the decrease of PCDFs contributed the reduction in flue gas concentration.

Table 2 also shows influence of EP dust addition. The dust was introduced to be a possible carbon source for dioxin formation. However, the comparison between Run 1 and 4 shows that the addition had no effect on dioxins concentrations in neither flue gas nor sinter mixture.

Table 2 Influences of carbon material, HCl and H_2O to dioxins formation

Run	Sample*1	HCl (ppm)	H_2O (%)	Coke	Dioxins in flue gas (ng/m^3_N)	Dioxins in flue gas (TEQ)	Dioxins in sinter mixture*2 (ng/g)	Dioxins in sinter mixture*2 (TEQ)
1	B	100	10	Coke	4.5	0.085	30	0.60
2	B	100	10	Activated coke	0.79	0.0083	19	0.39
3	C	0	10	Coke	0.66	0.0066	3.6	0.085
4	C	100	10	Coke	7.7	0.097	24	0.48
5	C	100	0	Coke	0.49	0.0044	20	0.19
6	C	100	40	Coke	24	0.31	15	0.34

*1 This means the kind of sinter mixture
*2 Sample after experiment

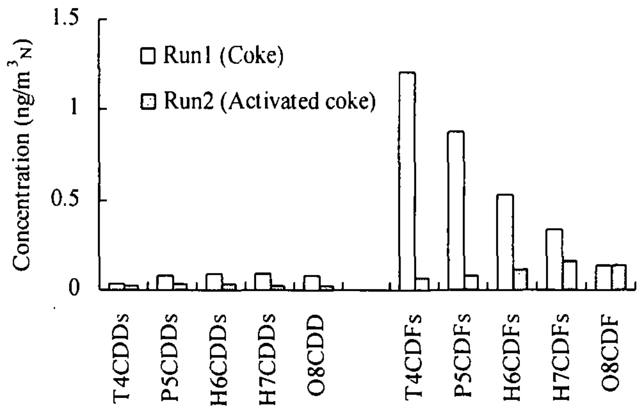

Fig.5 Homologue pattern of PCDDs/DFs in flue gas in runs 1 and 2

Influence of hydrogen chloride and moisture content in atmosphere

Characteristic influences were observed for dioxins in flue gas and sinter mixture concerning hydrogen chloride (HCl) and moisture content in flue gas. As for HCl, dioxins in flue gas as well as in sinter mixture in a run with no HCl supply (Run3) were fairly low compared to Run 4 with 100 ppm of HCl. Restricting HCl supply, therefore, may reduce dioxins formation. Effects of moisture can be seen in Runs 4, 5 and 6 in Table 2. Amounts of dioxins were similar in the three runs, though, higher moisture content result in rather high dioxins concentrations. This fact suggests that dioxin molecules tend to be ejected from the surface of sinter mixture due to competitive adsorption with abundant water molecules.

Acknowledgements

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