REAL-TIME MONITORING OF DIOXIN PRECURSORS BY APCI-ITMS: CONTROL OF CATALYST INJECTION

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Introduction

Continuous real-time monitoring of flue gas is needed for properly controlling incinerator operation to reduce dioxin formation. However, the method for regular dioxin analysis may take several weeks due to the complicated cleanup and enrichment process. An alternative method for estimating the dioxin emission levels in a shorter time is to correlate them with measured dioxin precursor levels, such as chlorophenols and chlorobenzenes.[1] Hitachi has developed a dioxin precursor real-time monitor CP-2000 using atmospheric pressure chemical ionization (APCI) and ion trap mass spectrometry (ITMS).[2,3] The CP-2000 can measure chlorophenol[2] and chlorobenzene[3] in incinerator flue gas at one-minute time intervals and can operate continuously for two months without requiring any maintenance.

Among the methods for reducing dioxin emissions in incinerator flue gas, injecting a catalyst in the incinerator furnace or the flue gas piping is one of the most economical and effective methods. Toda Kogyo developed an iron oxide type catalyst (TIC) and reported that it suppresses dioxin formation well due to its oxidation catalysis.[4,5] The TIC accelerates the perfect combustion for hydrocarbons in the incinerator flue gas and thereby decomposes the dioxins and the dioxin precursors. In the experimental reactor, chlorobenzene was decomposed by TIC catalytic oxidation. The apparent decomposition rates can be expressed as the first order reaction.[6]

Conventionally, the injection rate of the TIC was sometimes excessive so as to suppress dioxin emissions lower than the regulation level. It caused the increase of both the running cost and the amount of ash from dust removal equipment. The rate was determined using the field test results of the varying dioxin concentrations with different TIC injection rates. Because dioxin emission fluctuates through changes in combustion condition, the fixed rate needed to be high enough to achieve the regulation level.

We used the CP-2000 to control the injection rate of the TIC. In this manner, the dioxin emission level would be continuously suppressed and the running cost could be reduced. In this paper, we investigated the relation between the injection rate and trichlorophenol (TCP) in flue gas. During a field test at a municipal waste incinerator, we monitored the TCP in flue gas using CP-2000 for the various injection rates of the TIC. We also investigated the dioxin concentration before and after the injection. The dioxin concentration was analyzed using HRGC/MS as per regular analyzing procedure.

Methods and Materials

Figure 1 shows the schematic flow of the incinerator that we tested using the CP-2000 and TIC. The incinerator was a stoker type and was capable of burning 300 tons/day of waste. The catalyst TIC was injected with air flow at the inlet of an electrostatic precipitator (EP). The injection rate could be

changed by adjusting TIC feed rate in the air. During our experiment, the TIC injection rate was varied in the range of 0-150 kg/hr. The CP-2000 monitored the TCP every minute at the outlet of the EP. In the CP-2000, the compounds in the flue gas were ionized using negative APCI. Ionized compounds that included TCP ions were carried to an ITMS and analyzed. To remove the chemical noise, collision-induced dissociation was used in the ITMS. For regular dioxin analysis, the flue gas was sampled for four hours upstream of the TIC injection point and downstream of the CP-2000 sampling point. The amount of dioxin on EP ash was also analyzed. The carbon monoxide (CO) level during the experiment was also measured by conventional procedure.

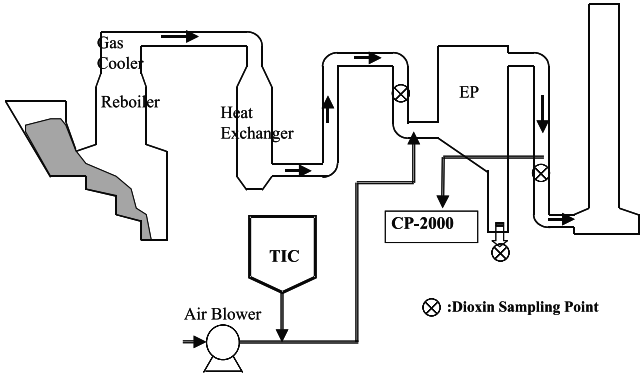

Figure 1. Schematic of experiment

Results and Discussion

Table 1 shows the comparison of the dioxin concentration before and after the TIC injection. The dioxin level upstream was the same between before and after the TIC injection. The dioxin level downstream of the EP, however, was drastically reduced after the TIC was injected at a rate of 130 kg/hr.

Figure 2 shows the dioxin mass balance at the EP. The value of the EP ash was calculated by dividing its dioxin amounts by the flue gas flow rate. Approximately half of the dioxin in the flue gas at the inlet of the EP is accumulated on the ash, and a very small amount of dioxin remained in the flue gas at the outlet. This result shows that the rest of the dioxin was decomposed by the TIC inside the EP.

Figure 3 shows the TCP response with different TIC injection rates. The TCP concentration shows the 5 minutes moving average value. Although the TCP fluctuates in the span of several tens of minutes, the averaged TCP concentration over several hours was decreased by increasing the TIC

Table 1. Comparasion of dioxin and TCP level before and after TIC injection.

	TIC injection rate [kg/hr]	EP inlet	EP outlet	
		dioxin ng-TEQ/Nm³n	dioxin ng-TEQ/Nm³n	TCP ng/Nm³n
Before TIC injection	0	3.1	1.8	3.2
After TIC injection	130	3.1	0.085	1.66

injection rate. The TCP level was also found to be not constant even if the injection rate was constant, due to the changes in the combustion condition or the compounds in the waste.

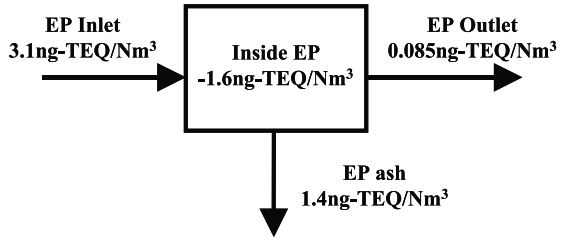

Figure 2. Mass balance of dioxin concentration at EP

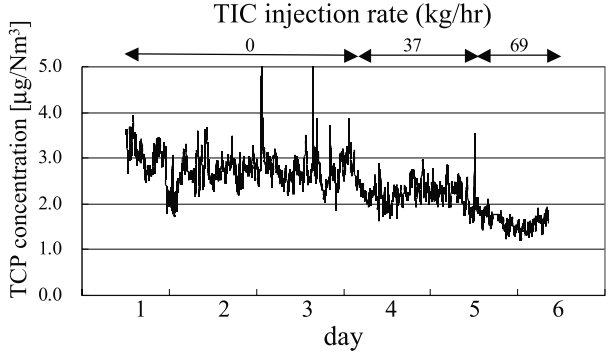

Figure 3. TCP response with different TIC injection

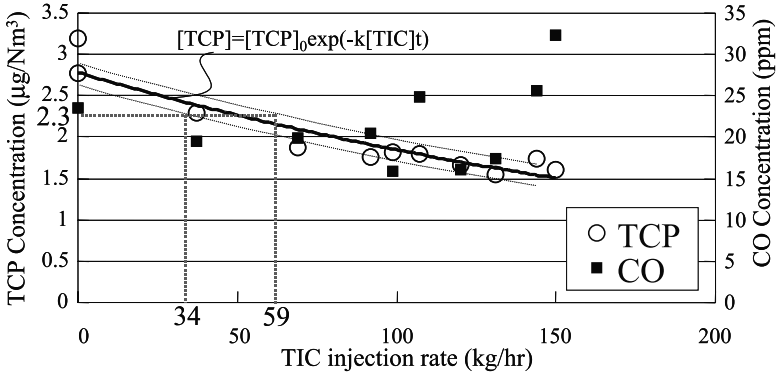

Figure 4. Relation between TIC injection rate and TCP concentration

Figure 4 shows the relation between the TIC injection rate and the TCP concentration. All of the TCP data shows more than five hours average of the one-minute interval data. The TCP emission was exponentially decreased with increasing the TIC injection. The bold line shows the exponential curve fitting using least-squares approximation of the TCP data. This result clearly shows the TCP in flue gas was decomposed by the TIC. Because the experimental data of the TCP agreed with the fitted exponential curve, the main mechanism of the TCP decomposition is consistent with the two-body collision between the TIC particulate and the TCP molecule, where the decomposition proceeds as the first order reaction, similar to the decomposition of chlorobenzene[6]. The dashed thin line shows the standard deviation of the TCP concentration from the bold fitted line, which is due to the changes in the combustion condition and the compounds in the waste.

The injection rate of the TIC can be controlled by the correlation between the TIC injection and the TCP concentration. The CP-2000 outputs the TCP concentration that is averaged for 20-30 minutes, and the injection rate of the TIC can be adjusted to achieve a target TCP concentration. The target TCP concentration can be determined by the correlation between the dioxin and the TCP. If the target TCP is 2.3 mg/Nm^3, which corresponds to 0.5 ng-TEQ/Nm^3 for dioxins in this incinerator, the TIC injection rate should be adjusted in the range of 34-59 kg/hr by monitoring TCP.

Figure 4 compared TCP with CO, which is used as a conventional monitoring index for the combustion condition. The results show no correlation with the TIC injection rate. Therefore, CO monitoring is not suitable for a TIC injection rate control, even though it is conventionally used for combustion control.

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References

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