Aerobic Treatment of PCDD/F in Fly Ash by Amine Compounds

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Introduction

The new guideline for PCDD/F control in municipal waste management was published in Japan on January 1997. This guideline not only provided PCDD/F emission standards in flue gas, but also set the target for the total amount of PCDD/F emission from an incinerator at below 5μg-TEQ/waste-ton[1]. According to the calculation from experimental data in a continuous combustion incinerator[2], PCDD/F in fly ash comprised 68.5-92.1% of total emission. Therefore, the development and application of PCDD/F control technology to fly ash will be essential in the very near future.

The available technologies at present are ash melting process[3] and anaerobic heat-dechlorination process[4]. The former is very effective to degrade PCDD/F, reduce ash volume and immobilize heavy metals contained in fly ash, but it needs much more energy, because melting temperature is over 1200°C. While the latter requires lower temperature of 280°C, it's necessary to heat for 2 hours under oxygen deficient conditions.

The authors have investigated the development of new treatment technology of fly ash and recently found that PCDD/F in fly ash was decreased markedly by amine compounds under mild and aerobic conditions. This paper describes basic characteristics of this reaction and the results obtained so far.

Materials and Methods

Experimental Method #1. Fig. 1 shows a schematic diagram of the experimental set-up. One gram of fly ash was put into the quartz column (20mm x 250mm) and 50mg of amine compounds attached to 1 g of glass beads was set before the fly ash. Glass wool separated these two layers. This column was heated at given temperature for given time with aeration of 15ml/min. PCDD/F in flue gas was trapped by an ice-cooled toluene impinger. PCDD/F concentration was determined by analyzing both fly ash and toluene. This Method #1 was applied mainly, unless otherwise stated.

Experimental Method #2. As shown in Fig-2, 7g of fly ash was put into 200ml of three-necked-flask and heated at given temperature. Then amine compound, 5% of fly ash by weight, was injected into the flask and kept for given minutes with stirring. After rapid cooling, PCDD/F conc. in fly ash was determined. All PCDD/F analyses were based on "Measuring Manual of Dioxins for Waste Treatment" published from the Japanese Ministry of Health and Welfare.

All the fly ash tested were collected from continuous combustion incinerators in Japan.

Results and Discussion

Table-1 shows the effect of amines at 250°C for 20 min. All of tested amines reduced PCDD/F conc. markedly in aerobic conditions. Especially, monoethanolamine(MEA), diethanolamine(DEA) and Triethanolamine(TEA) reduced PCDD/F conc. over 90%. Naikwadi *et al.* showed that amine compounds, such as TEA, MEA and monoisopropanolamine were strong inhibitor of catalytic PCDD/F formation on fly ash[5]. But, it became also clear that amine compounds acts not only as an inhibitor but also as a decomposer of PCDD/F. It was thought that amines reacted with heavy metals on the surface of fly ash when behaving as inhibitors and reacted with PCDD/F directly when behaving as decomposers.

Fig-3 shows PCDD/F reduction in various kinds of fly ash by TEA at 250°C for 20 min. Some fly ash contained calcium hydroxide for acidic gas treatment or powdered activated carbon for PCDD/F removal in flue gas. Fly ash of different origin, ESP or Fabric Filter (F.F), were also tested. PCDD/F in any types of fly ash was reduced well. These results indicated that the reaction between amine and PCDD/F wasn't inhibited by calcium hydroxide and that amines reacted PCDD/F absorbed to carbon particles. Different removal rates might be affected by channeling of air.

Table-2 shows the effect of temperature on PCDD/F removal. Added amines were 5% of fly ash and heating time was 20min. Lower limit of reaction temperature was quite different depending on the kinds of amines. For example, TEA didn't react with PCDD/F below 180°C, whereas

MEA, which has higher vapor pressure at lower temperature, reduced PCDD/F even at 100℃. This suggested that the reaction of amines and PCDD/F might be a gas-solid reaction. Therefore, it may be concluded that PCDD/F was reduced by MEA at a lower temperature and shorter time than any other PCDD/F treatment technology and that PCDD/F concentration of 0.1ng-TEQ/g-fly ash is attainable by optimization of reaction conditions.

Fig-4 shows isomer distribution pattern of PCDD/F before and after reaction for 3 min. by method #2. It is clear that the percentages of highly chlorinated H_7CDD/F and OCDD/F were greatly decreased and, instead, more lower chlorinated TCDD/F and PCDD/F comprised most of residual PCDD/F. These results suggested that dechlorination or replacement reaction was occurring. A detailed pathway is now under investigation. But anyway, it is thought that both reactions can decrease toxicity of PCDD/F markedly and the development of new technology for PCDD/F treatment in fly ash by amine compounds is quite possible.

References

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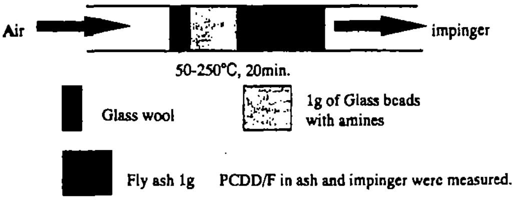


Fig-1. Schematic view of Experimental method #1

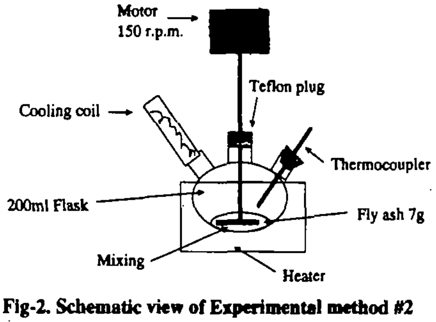
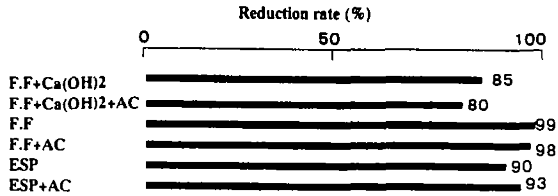


Fig-2. Schematic view of Experimental method #2

Table-1. PCDD/F decomposition by various amines

	PCDD/F (ng-TEQ/g)	% Reduced	PCDD/F (ng/g)	% Reduced
Blank	10.2	-	1335	-
Only heating	80	-	3800	-
Monoethanolamine	0.34	96.7	39	97.1
Diethanolamine	0.78	92.4	50	96.2
Triethanolamine	0.71	93.0	49	96.3
Aniline	2.4	76.5	210	84.2
n-Propylamine	3.0	70.6	350	73.8
Ethylenediamine	1.2	88.2	100	92.5
Aminomethylpropanol	2.3	77.4	300	77.5

amine conc. 5% of fly ash by weight.
heating temp. 250°C, reaction time 20min.



TEA conc. 5% of fly ash by weight.
heating temp. 250°C, reaction time 20min.

Fig-3 Reduction of PCDD/F in various fly ash by TEA

Table-2. Effect of temp. on PCDD/F decomposition by amines

	MEA		DEA		TEA	
	(ng/g)	% Reduced	(ng/g)	%Reduced	(ng/g)	% Reduced
Blank	1335	-	1335	-	1335	-
100°C	120	91	1328	0.5	-	-
150°C	97	93	245	82	-	-
180°C	54	96	178	87	2303	-
200°C	90	93	100	92	726	66
250°C	39	97	50	96	7	99

amine conc. 5% of fly ash by weight.
reaction time 20min.

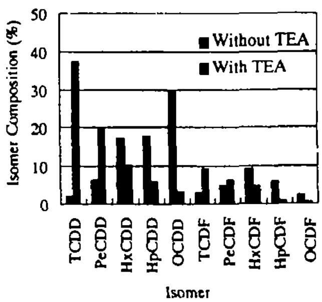


Fig-4. Comparison of isomer distribution pattern by TEA traetment at 250 for 3 min.