# Dioxin decomposition by the application of alkanolamine to various fly ashes

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## Introduction

In Japan, regulation of dioxin concentrations in fly ash was published first in the world on January 2000 and newly constructed incinerators had to discharge fly ash below 3ng-TEQ/g. As dioxin emissions through fly ash occupies most part of total emissions from MSW incinerators[1)], fly ash treatment becomes more important to reduce total emissions.

The authors already reported that amine compounds, such as alkylamines, alkanolamines and aromatic amines, could decompose dioxins effectively by dechlorination at lower temperature and shorter time[2)] than those of traditional heat dechlorination process[3)] and thermal decompsition[4)]. However, information was limited to several kinds of fly ash derived from municipal solid waste incinerators with continuous operation.

This paper describes the application of alkanolamine to various fly ashes under mild and aerobic conditions and the examination on inhibitory factors contained in fly ash.

## Materials and Methods

**Fly ash samples:** As shown in Table-1, ten kinds of fly ash samples were collected from different incinerators in Japan with continuous, semi-continuous, or batch operation. Among them, two samples didn't contain calcium hydroxide nor activated carbon. Calcium hydroxide was included in eight samples and activated carbon in two samples. The eight samples were derived from an electrostatic precipitator (ESP) and two samples were from a fabric filter (FF). The highest dioxin concentration was 52ng-TEQ/g and the lowest was 0.8ng-TEQ/g.

**Alkanolamine treatment:** Alkanolamine was added to 20g of fly ash by 0-5% and mixed well before heating. This mixture was put into 200ml of pre-heated glass flask shown in Fig.-1, and heated for 10-20 minutes at 250-350□ with agitation. After rapid cooling, the dioxin concentration in the treated fly ash was measured according to Japanese analysis method[5)] using GC/MS. As the flask was opened to ambient air through a cooling coil, the oxygen concentration in the flask after treatment was about 9-12%.

**Analysis of heavy metals:** Heavy metals contained in fly ash were measured by the atomic absorption analysis after acid extraction according to JIS-K-0102[6)].

**Results and Discussion**

Dioxin decomposition by alkanolamine: **The results are shown in Table-2. The increase of dioxin concentration was observed in 5 of 6 samples at 250 , 4 of 5 samples at 300 , and 1 of 2 samples at 350 without alkanolamine. These phenomena are well explained by the fact that dioxin formation temperature is about at 200-400 [7)]. On the other hand, high dioxin decomposition rate over 90% was performed in fly ash A, B, C, D, and I by the addition of 5% of alkanolamine. It is thought that this chemical accelerates heat dechlorination by its reductivity and inhibits the activity of $CuCl_2$ which is known as a strong dioxin formation catalyst[8)].**

**However, it was also found that alkanolamine wasn't so effective in fly ash E, F and J. Especially, the dioxin concentration in fly ash J increased by 1.1 times. In these cases, increasing the heating temperature from 250 to 300 improved decomposition rate markedly even with the lower additional volume of alkanolamine. Fly ash G that had high dioxin formation potential was the most difficult sample to be treated. The decomposition rate at 300C with 2% addition was 61.3%, but it increased to 98.5% at 350 . As a conclusion, alkanolamine can be applied to any kind of fly ash at 250-350 . Alkanolamine is decomposed quickly during heat treatment, and finally treated fly ashes can be landfilled after the heavy metals immobilization process.**

Inhibitory factor: **From the above data, the relationship between dioxin decomposition rate and each component of fly ash was investigated. Figure-2 shows plots of dioxin decomposition versus chlorine content of the fly ash samples at different temperatures and amounts of alkanolamine addition. It can be seen that when the chlorine content was over 15% at 250 and 20% at 300–350 in a given fly ash, the dioxin decomposition rate was well decreased. Other factors such as heavy metals, acid-insoluble fraction, chlorobenzene and chlorophenol had no relationship. The reason why chlorine compounds, mainly calcium chloride, inhibit the decomposition reaction isn't clear at present. However, estimation of optimum treatment temperature and alkanolamine concentration is possible by measuring chlorine content in the fly ash.**

**References**


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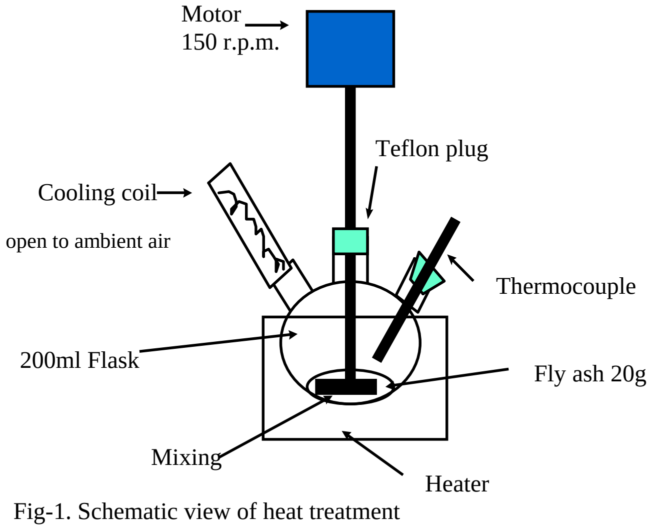


Fig-1. Schematic view of heat treatment

Table-1 Characteristics of fly ash samples

| Fly ash | | A | B | C | D | E | F | G | H | I | J |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Operation | | C | C | C | C | C | SC | C | B | SC | C |
| Dust collector | | ESP | ESP | ESP | ESP | ESP | FF | FF | ESP | ESP | ESP |
| Calcium hydroxide | | × | × | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| Activated carbon | | × | × | × | × | × | × | × | × | ○ | ○ |
| Dioxin | ng-TEQ/g | 10 | 1.9 | 2.6 | 52 | 0.95 | 6.2 | 0.80 | 1.1 | 13 | 3.6 |
| Cu | mg/kg | 2300 | 1910 | 840 | 860 | 500 | 420 | 680 | 1280 | 690 | 230 |
| Ca | mg/kg | 4300 | 94100 | 248000 | 152000 | 210000 | 205000 | 244000 | 156000 | 222000 | 422000 |
| Pb | mg/kg | — | 6040 | 4280 | 2490 | 1560 | 1080 | 2770 | — | 3100 | 840 |
| Fe | mg/kg | 14000 | 5940 | 13100 | 9620 | 8200 | 20500 | 4170 | 15600 | 8640 | 2730 |
| Zn | mg/kg | 33000 | 26700 | 14000 | 8730 | 4400 | 4600 | 6800 | — | 7750 | 2190 |
| Al | mg/kg | 52000 | 37700 | 22600 | 53200 | 32000 | 39400 | 18200 | 80200 | 37400 | 13700 |
| Na | mg/kg | 39300 | 110000 | 40500 | 35600 | 48100 | 44300 | 39400 | 42300 | 38300 | 9570 |
| K | mg/kg | 39600 | 84600 | 44100 | 34800 | 62000 | 43000 | 39500 | 38400 | 42000 | 9380 |
| Cl | wt% | — | 16.4 | 12.5 | 6.2 | 15.5 | 17.6 | 28 | 7.6 | 8.9 | 3.4 |
| CB | μg/kg | — | 272 | 394 | 2147 | 267 | 1155 | 573 | 1063 | 1670 | 928 |
| CP | μg/kg | — | 5675 | 1193 | 2718 | 359 | 2512 | 704 | 3398 | 2306 | 1859 |
| AIF | wt% | — | 17.0 | 9.7 | 23.7 | 15.6 | 17.3 | 8.5 | 34.2 | 17.5 | 5.9 |

C: Continuous, SC: Semi-Continuous, B: Batch, ESP: Electrostatic Preciptator, FF: Fabric Filter, AIF: Acid Insoluble Fraction, —: No data

## Table-2. Dioxin decomposition by alkanolamine (ng-TEQ/g)

| | Original | 250□ | 250□ | 300□ | 300□ | 300□ | 350□ | 350□ |
|---|---|---|---|---|---|---|---|---|
| Amine conc. | 0% | 0% | 5% | 0% | 2% | 5% | 0% | 2% |
| A | 10 | □ | 0.13 | □ | □ | 0.14 | □ | □ |
| B | 1.9 | 3.6 | 0.067 | □ | □ | □ | □ | □ |
| C | 2.6 | 3.1 | 0.11 | □ | □ | □ | □ | □ |
| D | 52 | 52 | 0.78 | □ | 1.5 | 0.57 | □ | □ |
| E | 0.95 | 1.8 | 0.14 | 0.30 | 0.014 | □ | □ | □ |
| F | 6.2 | 11 | 3.4 | 11 | 0.28 | 0.050 | 8.3 | 0.019 |
| G | 0.80 | □ | □ | 11 | 0.31 | 0.15 | 0.24 | 0.012 |
| H | 1.1 | □ | □ | 1.7 | 0.043 | □ | □ | □ |
| I | 13 | □ | 1.0 | □ | □ | □ | □ | □ |
| J | 2.6 | 4.7 | 4.0 | 6.1 | 0.079 | 0.018 | □ | □ |

— □ No data

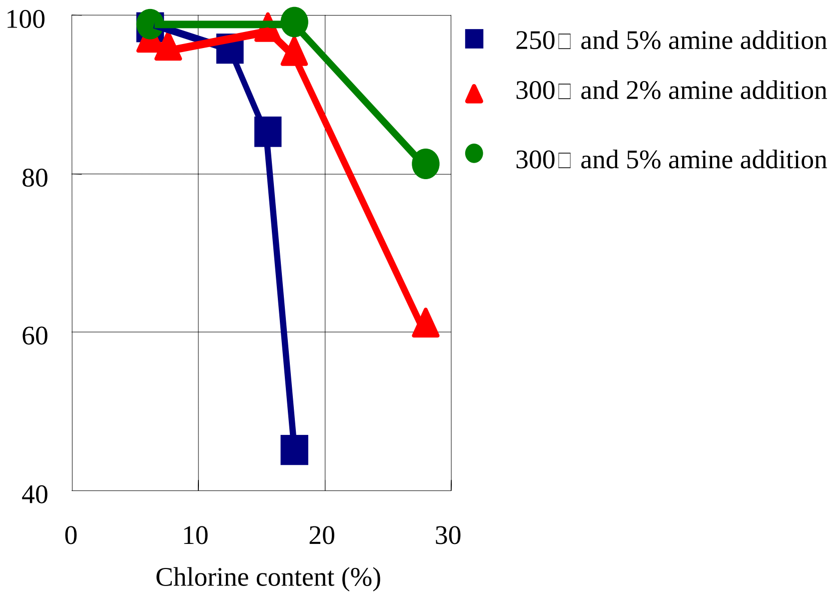


**Fig-2. The effect of chlorine content of a fly ash on efficiency of dioxin decomposition by alkanolamine.**