

## STUDIES OF FORMATION AND DESTRUCTION OF PCDD AND PCDF ON MSW INCINERATOR FLY ASH

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### ABSTRACT

It has been observed that the catalytic activity of fly ash to produce PCDD from the precursor pentachlorophenol is enhanced by the addition of certain metal/metal oxides. Enhanced catalytic activity of the fly ash was suppressed by addition of inhibitor/s. Both organic and inorganic inhibitors studied were found to be highly effective, resulting in greater than 95 % reduction in the formation of PCDD. MSW incinerators are big contributors of environmental pollution by PCDD, PCDF and other compounds. PCDD/PCDF have been detected in the stacks and fly ash of all incinerators around the world. Present studies show that more than 86% destruction of PCDD on the fly ash can be achieved by addition of specific compound (as destructor) to the fly ash prior to the heat treatment at 300 - 400°C.

### INTRODUCTION

Previous investigations have shown that polychlorinated dibenzo-p-dioxins (PCDD) and dibenzo furans (PCDF) formation in municipal solid waste (MSW) incinerators occurs in the post-combustion zone at temperatures between 200 and 400°C [1]. Laboratory studies show that incineration condition can be simulated and the congener pattern of PCDD observed on the MSW incinerator fly ash can be produced [2]. It has been shown that copper chloride is the most important ingredient in fly ash to produce PCDD [3]. Studies in our laboratory and others have shown that other metals and chlorine sources can contribute to form PCDD/PCDF under various conditions [4]. In the present investigation fly ash was spiked by various metal/ metal oxides and tested for catalytic activity to form PCDD/PCDF at 300°C. All metal/metal oxides studied enhanced the catalytic activity of fly ash. It has been shown that the PCDD/PCDF concentration on fly ash samples from various

incinerators differs depending on the amount of metal/metal oxides present in the fly ash. Previous studies show that catalytic formation of PCDD/PCDF can be suppressed by the use of certain inhibitors [5]. In this study mixtures of new inhibitors containing inorganic and organic compounds were used to deactivate the fly ash spiked with metal/metal oxides. Suppression of PCDD/PCDF formation depends upon the amount of inhibitor used and the temperature. Currently, attempts are being made to develop the techniques to destroy PCDD on MSW incinerator fly ash [6,7]. Our laboratory studies show that the addition of a small amount of specific compounds (1-2 % to fly ash) and heating at 200-400°C destroys more than 86 % PCDD on the fly ash.

## EXPERIMENTAL

Previously described apparatus was modified where a glass column (25 X 1 cm I.D.) was used in the vertically oriented oven (Thermercraft, Winston-Salem, U.S.A.) [5]. The modification allowed the use of 1 to 2 grams of fly ash instead of 20 to 25 g needed in the previously used apparatus. In a particular experiment the catalytic activity of Soxhlet extracted fly ash was determined for the formation of PCDD/PCDF using C-13 labelled pentachlorophenol (PCP) at 300°C. In another set of experiments fly ash was spiked with 2% Fe, MnO<sub>2</sub>, Zn and Cu and catalytic activity of mixture of fly ash and metal/metal oxide were determined separately. Fly ash and the mixture of fly ash and metal/metal oxide was then coated by different inhibitor mixtures and amount of PCDD/F formed from PCP at 300°C were determined. Selected samples were spiked by phenanthrene-D10 chrysene-D14 prior to extraction for recovery estimates. To study the destruction of PCDD/F and other compounds present on the fly ash various experiments were performed using specific compounds to coat on the fly ash prior to heating. All reaction products were analyzed for PCDD/PCDF using a Hewlett Packard 5890/5970 GC-MSD system operated in electron impact selected ion monitoring mode. The GC conditions were: a DB-5 fused silica capillary column (30 m X 0.25 mm i.d.), initial temperature 100°C, held for 1 minute then programmed to 230°C at 15° C/minute, finally programmed to 300°C at 3°C/minute.

## RESULTS AND DISCUSSION

The amounts of PCDD formed from PCP and fly ash, and fly ash spiked with different metal/metal oxides and inhibitors at 300°C are shown in Table 1. All experiments reported in Table 1 were repeated once and highly reproducible results were obtained for experiments # 1, 5 and 6. Poor reproducibility for experiments in the formation of PCDD in the experiments # 2-4 may be due to in-homogeneous mixing of fly ash with metal/metal oxides. However, it was noticed that in all experiments with metal/metal oxides and fly ash the PCDD formed were always higher than that produced using unspiked fly ash. These results show that fly ash is catalytically active at 300°C in the production of PCDD from PCP. Addition of metal/metal oxides enhances

the catalytic activity of fly ash in the formation of PCDD from PCP. The mixtures of organic and inorganic inhibitors are highly effective to suppress PCDD formation by highly active fly ash and PCP. It has been reported previously that heat treatment of MSW incinerator fly ash results in an increase of PCDD/PCDF [3]. However, it is found in our studies that addition of small amount of specific compounds (2% to fly ash) and heat treatment at 200-400°C results in more than 86% destruction of PCDD in the laboratory experiments. Results of these laboratory tests are shown in Table 1, experiments 7-9.

#### REFERENCES

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EXPERIMENT #	EXPERIMENTAL CONDITIONS, TEMPERATURE 300 C, FLY ASH 1.5g	PCDD FORMED (ng/100 ug PCP) FOR EXPER.#1-6. PCDD DETECTED ON FLY ASH (ng/g) FOR EXPER.# 7-9					
		T4CDD	P5CDD	H6CDD	H7CDD	OxCDD	TOTAL
1	PRE CLEANED FLY ASH + PCP	ND	6	68	270	470	813
2	PRE-CLEANED FLY ASH + Cu + PCP	ND	ND	19	149	1182	1350
3	PRECLEANED FLY ASH + Fe + PCP	ND	ND	15	193	1116	1324
4	PRE-CLEANED FLY ASH + Zn + PCP	ND	ND	9	148	1249	1406
5	PRECLEANED FLY ASH + Cu + INHIBITOR #1 (2%) + PCP	ND	ND	1	1	4	6
6	PRECLEANED FLY ASH + Fe + INHIBITOR #1 (2%) + PCP	ND	ND	1	6	10	17
7	FLY ASH FROM MSWI NO TREATMENT: NATIVE PCDD	66	304	728	837	368	2303
8	FLY ASH FROM MSWI WITH NATIVE PCDD AS IN 7, HEATED AT 300 IN AIR	105	395	711	638	225	2074
9	FLY ASH FROM MSWI WITH NATIVE PCDD AS IN 7 + DESTROYER (2%), AT 300 IN AIR	87	155	122	50	12	323

EXPER.# 1-6 SHOWS THE CATALYTIC ACTIVITY OF FLY ASH ONLY (EXPER.#1), FLY ASH + METALS (EXPER.#2-4), AND INHIBITOR EFFECT TO PREVENT THE FORMATION OF PCDD (EXPER.# 5,6).

EXPER.# 7 SHOWS AMOUNT OF NATIVE PCDD PRESENT IN THE FLY ASH SAMPLE, EXPER.# 8 SHOW THE EFFECT OF HEAT ON THE NATIVE PCDD ON THE FLY ASH AND EXPER.#9 SHOWS EFFECTIVE DESTRUCTION OF NATIVE PCDD ON THE FLY ASH DUE TO ADDITION OF DESTROYER COMPOUND AND THEN HEAT TREATMENT.

PCP- PENTACHLOROPHENOL, ND- NOT DETECTED