MECHANISM OF FORMATION OF PCDD/PCDF IN INDUSTRIAL WASTE INCINERATION AND A METHOD OF PREVENTION OF THEIR FORMATION

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There are very few studies on the mechanism of formation of PCDD/PCDF and related compounds in industrial waste incinerators (IWIs) and possible techniques to prevent their formation. There are several industrial waste sites in the U.S.A., where waste containing organohalogen compounds is treated for decontamination by subjecting to incineration technology at temperatures above 1100°C. During incineration the formation of hydrochloric acid occurs, which is neutralized using caustic soda (NaOH). The chemical reaction results in the formation of sodium chloride and water. Sodium chloride along with dust particles are recycled to a spray dryer and then passed on to the filters used in the bag-house. The bag-house particulate samples consisted mainly of sodium chloride and possibly fine metallic dust from the waste feed. It has been observed that, in spite of the high temperatures (1100°C) used during incineration, dioxins are detected in the bag-house dust samples and the stack emissions. To determine the possible mechanism or explanation concerning the occurrence of dioxins in the bag-house filter samples, it was decided to test the catalytic activity of both the particulate at the bag-house and bottom ash towards the formation of dioxins.

Industrial waste incinerators are highly efficient for destruction of hazardous waste. In particular, incinerators used in decontamination of soils and destruction of organohalogen compounds in the waste are usually operated at temperatures above 1100°C. It has been shown in several studies that the organic waste including halogenated organic compounds decompose above 900°C. Industrial waste incinerators are significantly different than that of municipal solid waste incinerators (MSWI) with respect to the operating conditions in that IWIs are operated at higher temperatures to destroy organic waste. The similarity between these incinerators is the formation of PCDD/PCDF.

It has been shown in our laboratories that fly ash from MSWI catalyzes the reactions leading to the formation of PCDD/PCDF under mild conditions[1]. Studies by others have shown that the formation of PCDD/PCDF occurs by de-novo synthesis in MSWI[2]. Both mechanisms show the formation of PCDD/PCDF at 200 to 400°C. The catalytic activity of fly ash is dependent on metallic sites or metal content of the fly ash. De-novo synthesis depends on the presence of particulate carbon and specific metals such as copper.

In the current investigation several samples of particulates collected at the bag-house filters and bottom ash were tested for the catalytic activity towards the formation of dioxins. In each experiment 2 g of powdered sample was placed in a glass tube (30 cm X 9 mm I.D.). A volume of 80 micro-litres (µl) of 5 µg/µl ^{13}C-PCP (carbon 13 labelled pentachlorophenol) solution in methanol was deposited on the glass wool on the top of the sample and the solvent allowed to evaporate. The section of the tube containing sample and PCP was heated in a vertically oriented oven at 300°C for 60 minutes using 12 ml/minute flow of dry air going down stream. The end of the tubing was connected to an impinger containing toluene. The exit of the impinger was connected to a florisil trap. The exit of the florisil trap leads to the fume hood. After completing the experiment, the sample was extracted by eluting with 220 ml toluene, and the toluene in the impinger was mixed with the column eluent. The extract was concentrated by rotary evaporation to a few ml and finally concentrated in a sample vial to 200 µl under a gentle stream of N_2. All experiments conducted using these samples are designated as IWIE# 1, 2, etc. In experiment #6 (IWIE#6) a bag-house sample was coated with 5% destroyer/inhibitor mixture and then catalytic activity test was conducted. Sample used and the amount of ^{13}C dioxins formed by catalytic active are shown in Table 1.

From these results it can be seen that the IWI samples are catalytically active towards the formation of dioxins at 300°C (IWIE#1 and 2, Table 1). The mechanism of the formation of dioxins seems analogous to MSWI fly ash in which dioxins are formed by catalytic activity of fly ash (IWIE#3). The blank experiments IWIE # 4 and 5 using sodium chloride and empty column respectively shows that the formation of dioxins in IWIE # 1-3 is due to the catalytic activity of the samples and not by pyrolysis of the PCP. The IWIE#6 shows that it is possible to prevent the formation of dioxins in IWIs using specific destroyer compound or mixtures. A possible location to add the destroyer can be in stream of recycled brine solution.

TABLE 1. AMOUNT OF ^{13}C-LABELLED DIOXINS (ng/100 μg PCP) PRODUCED BY CATALYTIC ACTIVITY OF IWI SAMPLES AND MSWI FLY ASH

EXPERIMENT #	H6CDD	H7CDD	OCDD	TOTAL
IWIE#1, Bag-house Sample	13	394	543	950
IWIE#2, Bottom ash sample	ND	32	800	832
IWIE#3, MSWI fly ash sample	28	369	1662	2059
IWIE#4, NaCl, blank run	ND	ND	ND	ND
IWIE#5, Empty tubing, blank run	ND	ND	ND	ND
IWIE#6, Bag house sample+destroyer	ND	ND	ND	ND

ND= not detected

1. Naikwadi K P, Karasek F W,"Formation of highly toxic polychlorinated dibenzo-p-dioxins by catalytic activity of metallic compounds in fly ash", in *Emission from combustion processes*, R. Clement and R. Kagel Eds. Lewis Publishers Boca Raton, Ann Arbor and Boston, 1990, 57.
2. Stieglitz L, Zwick G, Beck H, Roth W, Voog H, "On the De-Novo synthesis of PCDD/PCDF on fly ash of municipal waste incinerators", *Chemosphere*, 1989, 18:1219.