LABORATORY STUDIES OF INHIBITION TECHNOLOGY FOR REDUCTION OF PCDD/PCDF IN A SWISS MUNICIPAL SOLID WASTE INCINERATOR

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1. Abstract

The release of polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and other organohalogen compounds (OHC) by municipal solid waste incinerators (MSWI) through the stack emissions and flyash is of great public concern. Our laboratory studies have shown that the formation of PCDD from a typical precursor such as pentachlorophenol (PCP) by catalytic activity of flyash can be reduced by using various inhibitors. Using specific inhibitor mixtures 99 % prevention of formation of PCDD on flyash from potential precursor PCP has been achieved. Inhibitor/destroyer mixtures also have shown destruction of native PCDD/PCDF on flyash when flyash was heated at 300- 350°C. A plant test conducted at Swiss incinerator at Bazenheid using specific inhibitor/destroyer mixtures has shown the reduction of PCDD/PCDF in flyash and stack emissions.

2. Introduction

Many studies on the mechanism of formation of PCDD/PCDF in MSWI have been reported during the past several years[1-3]. There are two generally accepted mechanisms of formation of PCDD/PCDF in MSWI, which can provide concrete evidence to explain the amounts of PCDD/PCDF produced in MSWI. The first was proposed by Karasek and co-workers at the University of Waterloo. It involved the isomerization and condensation of chemically related precursors via the catalytic reactions on the flyash and has been supported by laboratory experimental data[1-3]. Another is the de-novo synthesis from unrelated species proposed by Stieglitz. The laboratory work only suggest its validity and does not definitely prove it[4].

Once the concept of catalytic formation of PCDD/PCDF on the surface of flyash has been shown, a method of blocking this formation is then apparent. It was observed that the effectiveness of a specific inhibitor in prevention of dioxin formation depends on the type and the reactivity of the flyash sample[5-8]. Each incinerator appears to produce a flyash of specific activity. A significant difference in the effect of the same inhibitor on different flyash samples has been observed. Hence, prior to conducting plant tests several laboratory tests experiments are recommended to assess the suitability of the inhibitor technology to a

particular incinerator.

This paper contains a description of the evaluation of the Swiss MSW incinerator chosen for a PCDD/F inhibitor/destroyer testing program. It describes:

1. The analytical results of PCDD/F in the flyash samples from the Swiss MSWI.
2. The results of catalytic activity tests performed on the Swiss incinerator flyash in the formation of ^{13}C-labelled PCDD from ^{13}C-PCP at 300°C and 350°C.
3. The results of the catalytic activity tests after application of the two most effective inhibitor/destroyer mixtures and observed destruction of native PCDD/PCDF originally present on the flyash .
4. The results of the effect of heat on native PCDD/PCDF on Swiss incinerator flyash with and without inhibitors at 350°C.

A description of experimental procedures used for catalytic activity, inhibition tests and results of effect of heating on amount of PCDD/PCDF on fly ash have been previously described[5,6]. Effective inhibitors have been monoethanol amine and triethanol amines and mixtures of these amines with alkaline hydroxides.

3. Results and discussions

Catalytic activity tests were conducted on the flyash sample from Bazenheid incinerator at 300°C and 350°C using ^{13}C-PCP as precursor. The distinction of Bazenheid flyash from our previously studied flyash samples from various incinerators is that the Bazenheid flyash sample produced all congeners (tetra- to octa-) of PCDD, however other flyash samples from different MSWI had produced mainly Oct- and Hepta-CDDs. For comparison the amount of ^{13}C-PCDD produced by catalytic activity of Canadian, USA and Japanese (Machida) MSW incinerator flyash samples are shown in **Figure 1**.

It is observed that there is a trend in the amounts of PCDD produced in the incineration process and the amounts of PCDD produced in the laboratory tests from ^{13}C-PCP. The flyash samples showing high levels of native PCDD produced in the incineration process also produced high levels of PCDD in the catalytic activity tests in the laboratory. The amount of PCDD detected on the Swiss incinerator flyash compared to that on other flyash samples from different incinerators as well as a plots of amount of PCDD produced in the incineration process and amount of ^{13}C-PCDD produced in the laboratory tests of catalytic activity of flyash samples from various incinerators are shown in Figure 1. It is surprising that Swiss flyash shows very high catalytic activity in spite of comparatively lower levels of native PCDD detected on the flyash which were produced in the incineration process.

The effect of heat treatment on Swiss flyash at 300°C and 350°C was determined by analysing flyash extracts for native PCDD/PCDF. The amount of native PCDD/PCDF formed in the incineration process (BG) and formed after heat treatment are shown in **Table 1 (columns a & b)**. There was tremendous increase in levels of PCDD/PCDF on flyash samples when they were heated. This increase can be attributed to the catalytic activity of the flyash and the native precursors present on the flyash. Determination of these increased levels of PCDD/PCDF by heating the flyash samples is very important to find out the effectiveness of the inhibitor/destroyer mixtures. In another set of experiments flyash

FIGURE 1. COMPARISON OF PCDD PRODUCED IN MSWI PROCESS AND IN CATALYTIC ACTIVITY TESTS

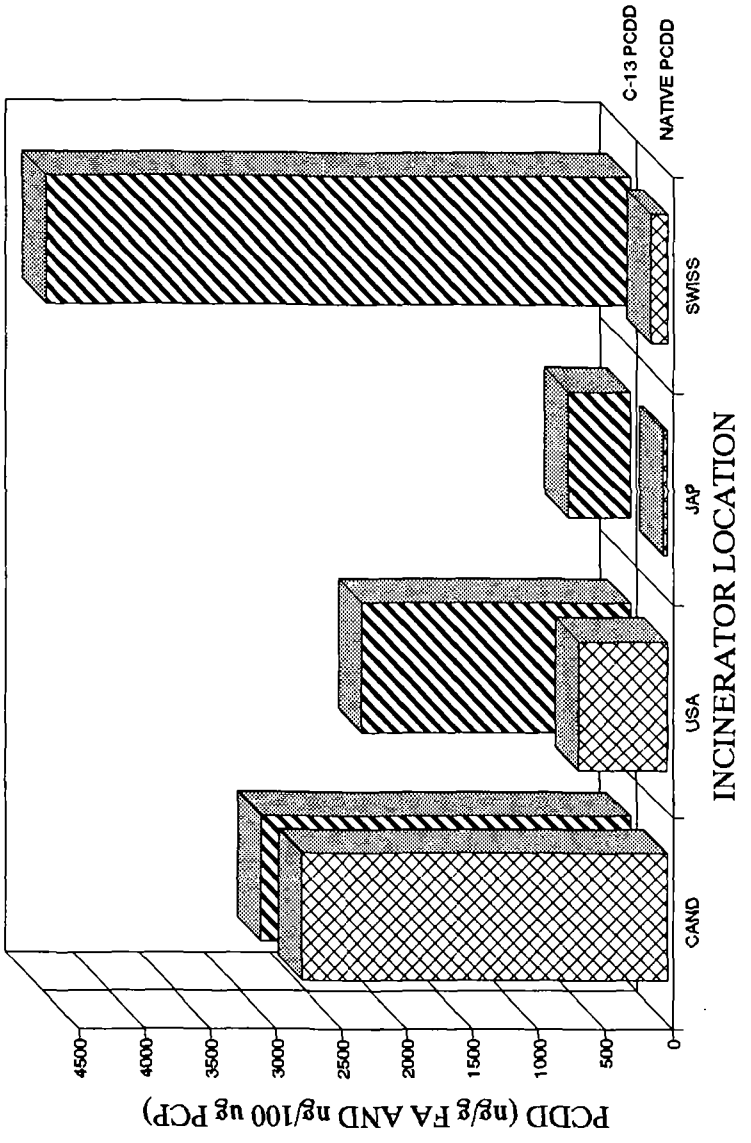

TABLE 1. NATIVE PCDD/PCDF (ng/g FLYASH) ON SWISS FLYASH PRODUCED IN INCINERATION, WHEN FLYASH HEATED AT 300°C AND 350°C AND WHEN FLYASH HEATED WITH THE INHIBITORS AT 350°C

PCDD/F CONGENER	(a) PRODUCED IN MSWI PROCESS	(b) PRODUCED WHEN FLYASH HEATED AT 300°C	(b) PRODUCED WHEN FLYASH HEATED AT 350°C (X)	(c) PRODUCED WHEN FLYASH HEATED WITH **PSEGC** AT 350°C (% reduction of X)	(c) PRODUCED WHEN FLYASH HEATED WITH **SMEGC** AT 350°C (% reduction of X)
TCDD	NC	9	53	10	19
P5CDD	7	83	268	ND	4
H6CDD	21	210	316	ND	ND
H7CDD	40	217	158	ND	ND
OCDD	52	89	40	ND	ND
TOTAL	120	608	834	10 (99)	23 (97)
TCDF	NC	56	330	154	265
P5CDF	18	154	465	62	119
H6CDF	13	179	323	12	15
H7CDF	17	119	126	ND	ND
OCDF	6	24	16	ND	ND
TOTAL	54	532	1265	238 (82)	399 (68)

NC= NOT CONFIRMED , ND = NOT DETECTED

coated with the inhibitor/destroyer mixtures were heated at 350°C. The amount of PCDD/PCDF detected in inhibitor/destroyer treated flyash are also shown in **Table 1 (column c).** It can be seen that there is tremendous decrease in levels of PCDD/PCDF when flyash was heated with the /inhibitor/destroyer mixtures. Also, complete prevention of formation of ^{13}C-PCDD from ^{13}C-PCP precursor was observed on inhibitor/destroyer coated flyash at 300 and 350°C.

4. Conclusions

1. The Swiss incinerator flyash shows the highest catalytic activity for producing PCDD among all the flyash samples we have studied from different incinerators around the world.
2. Formation of ^{13}C-PCDD by catalytic activity of the Swiss flyash and ^{13}C-PCP was completely prevented using both PSEGC and SMEGC inhibitor/destroyer mixtures.
3. More than 99% destruction of PCDD on the flyash can be achieved using PSEGC inhibitor/destroyer mixture at 350°C.

5. REFERENCES

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