Inhibition of PCDD/Fs formation from dioxin precursors by calcium oxide

Wenbin Liu, Minghui Zheng ^{*}, Bing Zhang, Yong Qian,
Xiaodong Ma, Wenxia Liu

*State Key laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, PR China*

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Abstract

Research aimed at understanding the inhibition effect of CaO on polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) formation from dioxins precursors, such as chlorophenols (CPs) and chlorobenzenes (CBs). The results indicated that a clear dioxin inhibition effect occurred both in open and sealed system when CaO was used. In the open system, PCDDs were the main congeners and the inhibition efficiency was all over 99% in the experiments. In the experiments with CaO, less than 0.1% of the initial PCP was detected in the absorption tube and only about 1% of the initial PCP was examined as calcium pentachlorophenate in the reaction tube. In the sealed system, the inhibition efficiency was over 90% at temperature range between 280 and 450 °C when PCP was used as model precursor. When HCB and 2,3,4,5-T₄CP replaced PCP, significant inhibition effect was also observed. As CaO has the advantageous properties of non-toxicity and non-volatile nature, it is our hope that the result will contribute to the development of a new technique to cope with the problem of dioxin pollution in MWIs.

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1. Introduction

The presence of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in the effluents of incinerators was widely recognized as a major source of dioxins in the environment. PCDD/Fs were always detected in stack gas and fly ash from municipal waste incinerators (MWIs) (Olie et al., 1977). As a result of many investigations, the theories of precursor formation and

de novo formation have been developed to describe the pathways and mechanisms of PCDD/Fs formation in stack gas of incinerators.

The decisive role of chlorophenols (CPs) and chlorobenzenes (CBs) could hardly be challenged in PCDD/Fs formation (Altwicker, 1996; Milligan and Altwicker, 1996; Weber and Hagenmaier, 1999; Iino et al., 2000; Catherine and Dellinger, 2003). These classes of compounds were always found together with PCDD/Fs in the effluents of incinerators and have been suggested as indicator compounds. Concentrations of CBs and CPs could be correlated with that of PCDD/Fs in stack gas of incinerators (Kaune et al., 1998; Lenoir et al., 2001). CBs concentrations were typically about three orders of

^{*} Corresponding author. Tel.: +86 10 6284 9172; fax: +86 10 6292 3563.

E-mail address: zhengmh@mail.rcees.ac.cn (M. Zheng).

magnitude greater than PCDD/Fs in incinerator effluents and CPs concentrations were a factor of 5 larger than PCDD/Fs, although yields varied from incinerator to incinerator. In addition, PCDDs formation was strongly related to CPs concentration (Tuppurainen et al., 2000; Stanmore, 2002). Dickson et al. (1992) found that PCDD/Fs formation from model precursor compound pentachlorophenol (PCP) was 72–99000 times greater than that from carbon via de novo mechanism. Altwicker concluded from his kinetic calculations that PCDD/Fs were formed much faster from precursors than from carbon in fly ash and that chlorophenols therefore represented key molecules in PCDD/Fs formation in combustion processes (Weber and Hagenmaier, 1999).

A large number of dioxin emission control techniques in MWIs were concerned mainly with the “end of pipe” or secondary measures such as wet/dry scrubbing, fabric filtration, active carbon adsorption and so on. These approaches were focused on the project by means of gas cleaning devices, increasing the installation and operation costs. The best way, however, is to block PCDD/Fs formation in stack gas and mitigate the dioxins pollution in MWIs.

Various chemical inhibitors have been tested to reduce PCDD/Fs formation both in the laboratories and pilot plants. Several alkali chemicals were reported to suppress the formation of PCDD/Fs (Karasek et al., 1992). Different studies revealed the inhibition ability of some basic compounds such as NH_3 (Ruokojärvi et al., 1998), CaO (Naikwadi and Karasek, 1989), NaOH and KOH (Naikwadi et al., 1993). The presence of compounds containing sulfur and nitrogen affected PCDD/Fs formation pathways, as it was observed from the ratios and the homologue profiles of PCDDs and PCDFs (Xhrouet et al., 2002; Samaras et al., 2000; Raghunathan and Gullett, 1996). Tuppurainen et al. (1999) studied the effect of two liquid inhibitors, sodium ammonium hydrogen phosphate and urea, on PCDD/Fs formation in the combustion of liquid fuel doped with copper and chlorine at a pilot-scale plant. It should be emphasized that the use of inhibitors has been limited so far to the laboratory only and few were on the practice application.

Calcium oxide has been used mainly as a good absorber of HCl and SO_2 in the low temperature zone of an incinerator for a long time, where the temperature of the flue gas scrubber system was commonly below 250 °C. Though Naikwadi and Karasek (1989) reported PCDD/Fs formation by catalysis of fly ash from PCP at 300 °C can be reduced by CaO, there is no further research to disclose the influence of CaO on dioxin formation from dioxin precursors. In this paper, pentachlorophenol (PCP), hexachlorobenzene (HCB) and 2,3,4,5-tetrachlorophenol (2,3,4,5- T_4CP) were selected as model dioxin precursors to investigate the inhibition effect of CaO. As CaO has the advantageous properties

of non-toxicity and non-volatile nature, it is our hope that the result will contribute to the development of a new technique to cope with the problem of dioxin pollution in MWIs.

2. Experimental section

A schematic of experimental apparatus used in this study is shown in Fig. 1. Simulate experiments were carried out in it to estimate inhibition effect of CaO. The length and inner diameter of quartz glass reaction tube were 250 and 10 mm, respectively. Quartz grain with diameter 1 mm was used as additive. Two absorption tubes with 80 ml toluene were placed into ice water. Before being passed through the reaction tube, 5 mg PCP was pre-heated in the pre-heater at 250 °C and evaporated into the reaction tube slowly under the air flow of 10 ml/min. The oven temperature was set at 350 °C and the reaction time lasted 2 h. 0.8 g CaO and 15.2 g quartz grain were mixed manually and placed into the reaction tube in the experiment of 5% CaO, while 3.2 g CaO and 12.8 g quartz grain in the experiment of 20% CaO. Other experiments were carried out in sealed glass tube with diameter 8 mm and length 100 mm.

The samples were extracted with 5% toluene/n-hexane by ultrasonic extraction and cleaned with alkali Al_2O_3 column. PCDD/Fs analysis was carried out by isotope dilution method with Agilent 6890 GC/5973N MS using a 30-m DB-5 fused-silica column. The quantification analysis of PCDD/Fs was performed in selected ion monitoring (SIM) mode. 2,3,7,8-Cl-substituted PCDD/Fs and total PCDD/Fs were analyzed. No analyses of the species without chlorine or less than four chlorines were performed. Polychlorophenols were also analyzed to investigate the PCDD/Fs formation. Polychlorophenols were derivatized with pentafluorobenzoyl chloride as a derivatizing reagent and analyzed by GC/ECD (Bao and Dong, 1990).

3. Results and discussion

Calcium oxide was tested to study its effect towards the prevention of PCDD/Fs formation. The inhibition

Fig. 1. Schematic of the experimental apparatus.

tests were compared to reference experiments, which consist of thermal experiments performed without CaO. Inhibition efficiency of CaO was calculated from the reference tests. Some experiments were carried out in the experimental apparatus, while others were done in the sealed glass tube. The results indicated that a clear dioxin inhibition effect occurred both in open and sealed systems when CaO was used.

The analytical results of dioxins obtained from the experimental apparatus are shown in Fig. 2. In this open system, PCDDs were the main congeners and the inhibition efficiency was all over 99% in the experiments. T₄CDD to OCDD, T₄CDF and OCDF were detected in the reference experiment in which only quartz grain was used as the additive, while OCDD and T₄CDF were detected in the experiment of 5% CaO and only OCDD were detected in the experiment of 20% CaO. The conversion from CPs to PCDDs at about 300 °C has been verified experimentally and the most abundant PCDD congeners have been obtained in the previous works (Born et al., 1993; Tuppurainen et al., 1998). These condensation reactions are postulated to take place via Smiles rearrangement with a dioxaspiro-type compound as an intermediate.

Remainder PCP in the pre-heater, reaction tube and absorption tube was also analyzed. The reaction time was determined by the amount of the remainder PCP in the pre-heater, and it lasted 2 h until the remainder PCP was less than 0.1% of the initial PCP. In the reference test, 75.4% of the initial PCP was detected in the absorption tube and less than 0.5% of the initial PCP was detected in the reaction tube. As a contrast, in the experiments with CaO, less than 0.1% of the initial PCP was detected in the absorption tube and only about 1% of the initial PCP was examined as calcium pentachlorophenate in the reaction tube, which means that PCP was absorbed by CaO and decomposed in the reac-

tion tube. The inhibition effects obtained from some experiments as a function of the reaction times in the sealed glass tubes are listed in Fig. 3. PCP was used as the model precursor and mixed manually with 20 times of CaO. CaO suppressed the dioxins formation so that

Fig. 3. Inhibition effect of CaO on the dioxins formation from PCP at different reaction times (1 mg PCP, 20 mg CaO, reaction temperature 280 °C).

Fig. 4. Inhibition efficiency of CaO at different temperatures (1 mg PCP, reaction time 2 h, 1#: 280 °C, 20 mg CaO; 2#: 280 °C, 50 mg CaO; 3#: 280 °C, 100 mg CaO; 4#: 350 °C, 20 mg CaO; 5#: 350 °C, 150 mg CaO; 6#: 450 °C, 20 mg CaO; 7#: 450 °C, 150 mg CaO).

Fig. 2. Inhibition effect of CaO on dioxins formation from PCP in the experimental apparatus (reaction temperature 350 °C, reaction time 2 h, air flow 10 ml/min, 5 mg PCP, 0.8 g CaO and 15.2 quartz grain in 5% CaO; 3.2 g CaO and 12.8 quartz grain in 20% CaO).

the concentrations of dioxins could be maintained in a relatively low level.

A comparison of the inhibition efficiency obtained at the different reaction temperature and the ratio of CaO to PCP is presented in Fig. 4. In the sealed glass tubes, the reaction lasted 2 h in order that chemical reaction equilibrium could be achieved. It can be observed that

the inhibition efficiency increased when more amount of CaO was added. The inhibition efficiency was over 90% at temperature range between 280 and 450 °C. Increasing the amount of CaO to 150 times of PCP, the inhibition efficiency could reach 99%.

The homologue profiles and inhibition yields at target temperatures in the sealed glass tubes are given in

Table 1

The homologue profiles of PCDD/Fs at various temperatures (ng/mg PCP)

Congeners	8#	9#	10#	11#	12#	13#	14#	15#
1,2,3,4,7,8-H ₆ CDD	1.6	ND	ND	ND	ND	ND	ND	ND
1,2,3,6,7,8-H ₆ CDD	2.7	ND	ND	ND	3.6	3.1	ND	6.6
1,2,3,7,8,9-H ₆ CDD	8.2	ND	ND	ND	6.0	5.5	ND	ND
∑H ₆ CDDs	33	ND	ND	ND	50	19	ND	6.6
1,2,3,4,6,7,8-H ₇ CDD	320	8.9	181	191	280	25	64	60
∑H ₇ CDDs	750	16	595	234	600	100	134	92
OCDD	80040	4243	91330	897	104400	3050	22500	1610
∑PCDDs	80823	4259	91925	1131	105050	3169	22634	1709
∑PCDFs	ND	ND	ND	ND	ND	ND	ND	ND
Inhibition efficiency of total PCDD/Fs	94.7%		98.8%		97.0%		92.4%	

1 mg PCP, reaction time 2 h, 8#: 280 °C, without CaO; 9#: 280 °C, 20 mg CaO; 10#: 300 °C, without CaO; 11#: 300 °C, 20 mg CaO; 12#: 350 °C, without CaO; 13#: 350 °C, 20 mg CaO; 14#: 450 °C, without CaO; 15#: 450 °C, 20 mg CaO.

Table 2

The homologue profiles of PCDD/Fs with various precursors (ng/mg precursor)

Congeners	16#	17#	18#	19#	20#	21#
∑TCDD	ND	ND	ND	ND	1.7	ND
∑TCDF	ND	ND	ND	0.022	ND	ND
∑P ₅ CDF	ND	ND	ND	ND	ND	ND
1,2,3,7,8-P ₅ CDD	ND	ND	ND	ND	1.6	1.0
∑P ₅ CDD	ND	ND	ND	ND	11.8	6.6
1,2,3,6,7,8-H ₆ CDF	ND	ND	ND	ND	0.57	0.64
1,2,3,7,8,9-H ₆ CDF	ND	ND	ND	ND	2.1	1.29
∑H ₆ CDF	ND	ND	ND	ND	51.9	27.3
1,2,3,4,7,8-H ₆ CDD	ND	ND	ND	0.0091	ND	ND
1,2,3,6,7,8-H ₆ CDD	ND	ND	ND	0.010	1235	133
1,2,3,7,8,9-H ₆ CDD	ND	ND	ND	0.0068	765	73
∑H ₆ CDD	ND	ND	ND	0.059	6862	918
1,2,3,4,6,7,8-H ₇ CDF	ND	ND	ND	0.056	41	19
1,2,3,4,7,8,9-H ₇ CDF	ND	ND	ND	ND	2.9	ND
∑H ₇ CDF	ND	ND	ND	0.066	130	63
1,2,3,4,6,7,8-H ₇ CDD	23	1.5	0.082	0.021	1135	200
∑H ₇ CDD	43	2.0	0.13	0.024	2036	382
OCDD	20600	120	10.0	1.08	128	34
OCDF	23	0.48	11.0	0.71	37	18
∑TCDD to OCDD	20643	122	10.3	1.4	9039	1340
∑TCDF to OCDF	23	0.48	11.0	0.79	220	109
∑PCDD/Fs	20666	122	21.3	2.2	9058	1449
I-TEQ	21	0.14	0.022	0.0052	213	24
Inhibition efficiency of total PCDD/Fs	99.4%		89.8%		84.3%	
Inhibition efficiency of I-TEQ	99.4%		76.4%		89.0%	

Reaction time 5 min, reaction temperature 350 °C, 16#: 1 mg PCP, without CaO; 17#: 1 mg PCP, 20 mg CaO; 18#: 1 mg HCB, without CaO; 19#: 1 mg HCB, 20 mg CaO; 20#: 1 mg 2,3,4,5-T₄CP, without CaO; 21#: 1 mg 2,3,4,5-T₄CP, 20 mg CaO.

Table 1. These tests of PCP with 20 times CaO were carried out at temperature range between 280 and 450 °C and the reaction lasted 2 h. It can be seen from Table 1, the maximum of dioxins formation from PCP without CaO was achieved at 350 °C. The best inhibition efficiency was 98.8% at 300 °C and all others exceeded 90% at other temperatures. OCDD were formed preferentially and the amount of all other congeners was as little as 2% of OCDD.

Further experiments were designed to study the inhibition effect of CaO when PCP was replaced by other dioxin precursor, such as HCB and 2,3,4,5-T₄CP, in the sealed glass tubes. The results are given in Table 2. Although the reaction time only lasted 5 min at 350 °C, the significant inhibition effect was also found. This result was different from the reaction at 280 °C, which no inhibition effect was observed when reaction time was 5 min. The probable reason was that the reaction rate in 350 °C is far faster than in 280 °C. The best inhibition efficiency of total PCDD/Fs achieved at 99.4% in the experiment of PCP with CaO, while the lowest inhibition efficiency was 84.3% when the precursor was 2,3,4,5-T₄CP. It was also observed that the amount of PCDD/Fs synthesized from PCP was more than that from 2,3,4,5-T₄CP and HCB. The amount of PCDD/Fs resulting from 2,3,4,5-T₄CP and HCB was 43.8% and 0.1% of which from PCP in the reference experiments, respectively.

When the flue gas leaves the primary combustion chamber, some organic materials, particularly the dioxin precursors, cool down from high temperature and subsequently condense, and it is during this molecular rearrangement that PCDD/Fs are formed, commonly in the temperature range between 650 and 250 °C (Tuppurainen et al., 1998). According to this study, CaO may be applied in the post-combustion zone of MWIs in the temperature range between 650 and 250 °C. CaO powder could be sprayed into the post-combustion zone of incinerator at 650 °C, and then the cooling process of flue gas occurs in the presence of CaO. The dioxin precursors are absorbed and decomposed by CaO and thus the PCDD/Fs formation from dioxin precursors is inhibited by CaO. In addition, CaO could also absorb HCl and prevent the formation of Cl₂ from HCl. In a word, CaO serves multiple goals, such as reducing PCDD/F formation, attacking precursors and also reducing HCl, that would provide an effective method of control of PCDD/Fs and acidic gases in MWIs.

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