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SUPPRESSION OF PCDD/F DURING THERMAL DESORPTION OF PCB-CONTAMINATED SOIL

Z. Zhao¹, M. Ni¹, X. Li¹, A. Buekens¹

¹*Institute for Thermal Power Engineering, Zhejiang University, Hangzhou, 310027, China*

Introduction

Thermal desorption is an effective technique to remediate soil contaminated by volatile or semi-volatile organic pollutants such as PCDD/F, PCB, Polycyclic Aromatic Hydrocarbons, pesticides, petroleum (Kunkel et al., 2006; Ji et al., 2012). However, formation of PCDD and PCDF in many PCB destruction processes has been reported, which leads to higher toxic equivalency, especially in the presence of oxygen (Weber, 2007).

Chemical inhibition has emerged as a popular option since it can efficiently prevent PCDD/F formation at the source (Wu et al., 2012). Previous study in laboratory-scale experiments (Pandelova et al., 2005) indicated that both sulphur- and nitrogen-containing compounds show high inhibition efficiency (more than 95%), based on the original PCDD/F concentration. Reducing the ability of catalytic metals to catalyse PCDD/F formation has been proposed as the main mechanism of inhibition by these sulphur or nitrogen containing compounds (Ruokojärvi et al., 2001). As a good absorber of HCl and SO₂, alkaline substances such as calcium oxide was also proposed as an inhibitor in the low temperature zone of an incinerator (Liu et al., 2005) and alkaline substances is a viable alternative, remarkably promoting the decomposition of PCB, PCDD/F, chlorobenzene, and other POPs (Xiao and Jiang, 2014).

However, until now, no experiments were conducted with these compounds in a thermal desorption system. In this study, three different suppressants, including ammonium sulphate ((NH₄)₂SO₄), urea (CO(NH₂)₂) and calcium oxide (CaO), were tested in attempts to reduce PCDD/F formation during thermal desorption of PCB-contaminated soil. The objective of this work was to investigate the effect of inhibitor addition on PCDD/F reduction during thermal desorption at 400 °C.

Materials and Methods

Materials

The PCB-contaminated soil originated from Zhejiang Province, China. It was contaminated due to actual leakage of discarded capacitors and transformers. The soil was collected, air dried, and homogenised after removal of stones and plant debris. It was stored in the refrigerator until testing.

Methods

The contaminated soil was mixed with an inhibitor before starting the experiment. Magnetic stirring was employed to thoroughly homogenise the samples. The amounts added are listed in Table 1.

A schematic diagram of the experimental apparatus employed in the test is shown in Fig. 1. It consists of three major parts, a carrier gas flow system, a horizontal tubular reactor and electric furnace and a trap for collecting PCDD/F from the exhaust gas. The PCDD/F evaporated from soil was carried by N₂ flow and then captured by the trap system. After the experiment, both the thermally treated soil and the trap are collected to analyse the concentration of PCDD/F in soil and gas.

Results and Discussion

Total emission of PCDD/F

The total concentration of PCDD/F both in flue gas and the soil, thermally treated without and with inhibitor addition, is shown in Fig. 2. A total amount of 9346 pg/g PCDD/F was detected in the flue gas without inhibitor, with mainly PCDF. Their concentration was remarkably reduced when inhibitors were introduced and the efficiency of PCDD/F suppression by CaO, CO(NH₂)₂ and (NH₄)₂SO₄ reached 94.3 %, 93.7 % and 73.2 %, respectively.

Fig. 2b show the PCDD/F concentration in the treated soil. The PCDD/F concentration decreased from 1314.9 pg/g to 300, 627.4 and 976.9 pg/g after addition of inhibitors, respectively, with reduction efficiency of 77.2, 52.3 and 25.1 %, which are much lower than that in flue gas. Thus, the addition of inhibitors effectively suppressed PCDD/F formation during thermal desorption.

PCDF isomer distribution

Fig. 3 shows the congener profiles of all PCDF in the flue gas and soil. PCDF contribute more than 85% to the total concentration of PCDD/F.

CaO and CO(NH₂)₂ share some common suppression characteristics. Both addition of CaO and CO(NH₂)₂ lead to a lower proportion of high-chlorinated PCDF and increase the relative amount of TCDF. This profile is consistent with some previous studies (Samaras, et al., 2001). After reaction, the ratio of TCDF increased from 20.32 % in blank soil to 81.25 % and 85.39 % in CaO and CO(NH₂)₂

adding soil, respectively. In the off-gas, the ratio increased from 63.3 % to 89.3 % and 77.9 %, indicating a stronger capability of CaO and CO(NH₂)₂ in inhibiting high-chlorinated PCDF. However, no significant changes in the homologue patterns by (NH₄)₂SO₄ addition were observed compared to the blank experiments.

Toxic PCDD/F concentration and TEQ

Table 2 shows the concentration of the 2,3,7,8-substituted PCDD/F. Their amount are much higher in the tests without inhibitor than in those with inhibitor.

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Table 1. Experimental test design conditions: inhibitor amount, based on 2 g soil.

No.	Inhibitor	Amount	No.	Inhibitor	Amount
S1	None	—	S3	(NH ₄) ₂ SO ₄	0.02 g
S2	CO(NH ₂) ₂	0.02 g	S4	CaO	0.02 g

Table 2. Concentration of 2,3,7,8-substituted PCDD/F in soil and gas

	Blank soil		CaO		CO(NH ₂) ₂		(NH ₄) ₂ SO ₄	
	S	G	S	G	S	G	S	G
Σ PCDD, pg/g	79.97	220.26	2.99	3.36	6.46	7.67	62.00	181.31
Σ PCDF, pg/g	538.12	1710.51	53.00	30.57	101.38	46.09	407.87	1007.56
Σ PCDD/F, pg/g	618.10	1930.79	56.00	33.94	107.85	53.77	469.88	1188.88
TEQ, I-TEQ pg/g	26.96	194.78	6.22	3.52	13.48	3.78	20.29	47.10

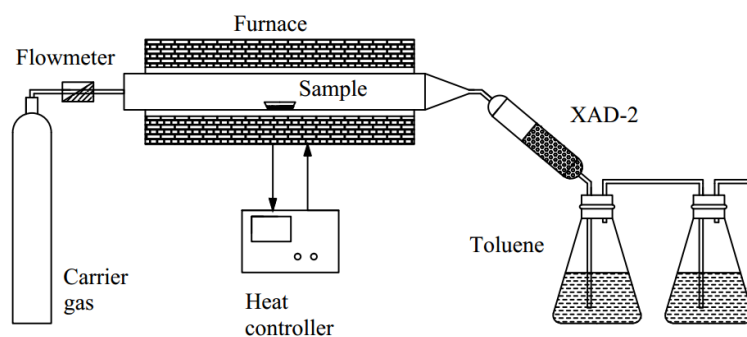


Fig. 1. Schematic diagram of the experiment apparatus.

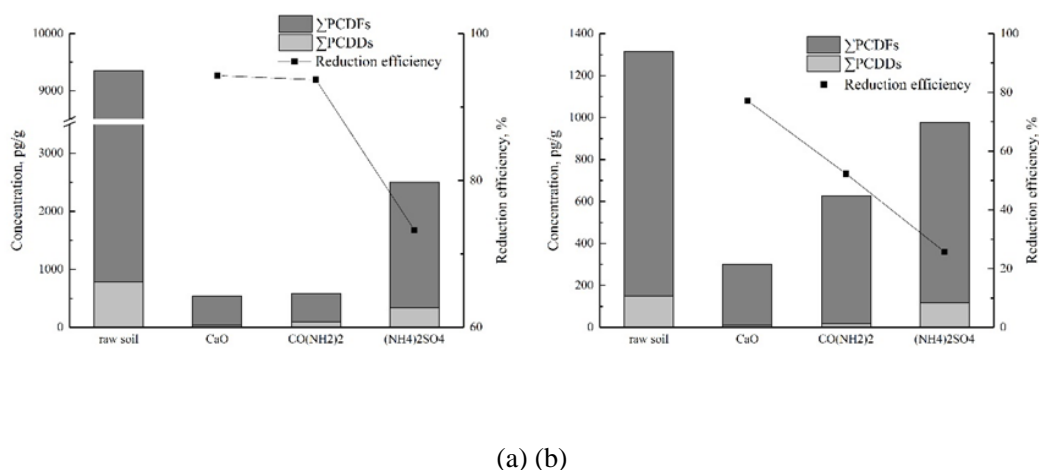
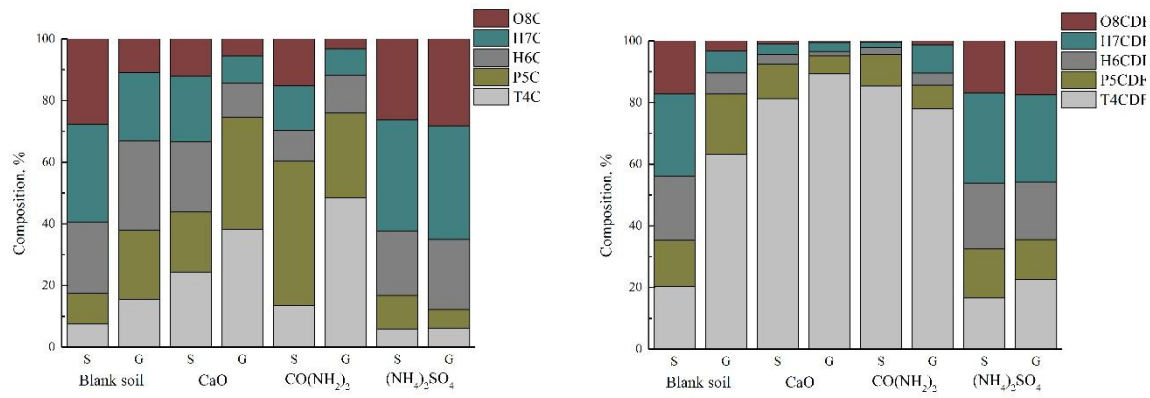


Fig. 2. Total concentration of PCDD/F in the flue gas and soil.



(a) (b)

Fig. 3. Distribution of PCDF in soil and off-gas.