

Influence of temperature on PCDD/PCDF desorption from waste incineration flyash under nitrogen

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Abstract

A municipal solid waste incinerator flyash was heated to between 200 and 400 °C under nitrogen in a bench-scale, static bed reactor for 4 days soak time. The influence of temperature on the levels of PCDD and PCDF remaining in and desorbed from the ash were investigated using GC-MS/MS. PCDD and especially PCDF formation was seen on the flyash between 225 and 300 °C. Large increases in the I-TEQ of the treated ash relative to the increase in its overall PCDD/PCDF content indicated that the formation of 2378-substituted congeners was favoured over that of other substitution patterns. In the absence of a source of gaseous oxygen, formation was mainly attributed to de novo reactions involving solid phase oxygen. Dechlorination of the PCDD/PCDF in flyash became increasingly important above 275 °C. Maximum desorption was seen at 325 °C, with the equivalent of 35 wt% of the PCDD/F in the original flyash being recovered from the exhaust traps at this temperature. The desorbed species were mainly M₁CDD/CDDF-T₃CDD/CDDF resulting from dechlorination of higher chlorinated PCDD/PCDF, with consequently low I-TEQ values.
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1. Introduction

Emissions of PCDD/PCDF from waste incineration processes have been reported to exhibit a significant time lag in relation to changes in incineration plant operational conditions, with higher emissions than expected being logged for prolonged periods after the implementation of operational changes or after disturbances in combustion (Chang and Lin, 2001; Zimmermann et al., 2001; Weber et al., 2002a). This persistence of PCDD/F emissions has become known as the ‘dioxin memory effect’. Flyash has been shown to play an important part in the formation of PCDD/PCDF in the relatively low temperatures of post-combustor waste incineration plant. Over time, flyash deposits build up on the walls of the flue and other post-combustor-plant associated with municipal solid waste incinerators. It has been suggested that slow de novo syn-

thesis in the ash deposits generates PCDD/PCDF, which then slowly desorb into the flue gas (Weber et al., 2002a). Another distinct type of memory effect postulated, involves the adsorption of PCDD/PCDF from the flue gas onto plastic scrubber components, followed by slow desorption (Hunsinger et al., 1998). Removing flyash deposits from the flue duct walls has been shown to reduce the emissions of PCDD/PCDF (Wevers and de Fre, 1998). Addink et al. (1995) performed desorption experiments on flyash in an 8.8% O₂/91.2% N₂ mixture at 398 °C. After 50 min the PCDD content of the flyash was 1.4% of the original level, but the PCDF content represented 10.7% of the original PCDF content. Similarly, a cold-trap fitted to the exhaust of their reactor contained the equivalent of 0.7% of the initial PCDD and 4.1% of the raw ash PCDF.

There are a range of control and monitoring strategies being developed to minimise or eliminate PCDD/PCDF from waste incinerator flue gas emissions. However, the influence of the ‘memory effect’ associated with PCDD/PCDF where desorption of previously adsorbed or newly

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formed PCDD/PCDF from flyash in the incinerator system which can take place over several days may lead to difficulties in determining the effects of such control strategies. Therefore a better understanding of the desorption of PCDD/PCDF from flyash over long time scales would be of great benefit to those involved with waste incineration and other combustion processes. In this investigation, a waste incinerator flyash sample was subjected to thermal treatment in a static-bed reactor under nitrogen at a range of temperatures typical of those found in post-combustor plant. The ash was analysed for PCDD/PCDF before and after treatment to establish to influence of temperature. In addition, PCDD/PCDF that had been desorbed from the ash were trapped and analysed. This study forms part of a project that aims to investigate the memory effect in incineration systems more fully.

2. Methods and materials

2.1. Flyash sample

The flyash used in these experiments was derived from a UK mid-1970s design incinerator that could not meet the 1989 EC Directive emissions legislation and was subsequently decommissioned. The ash sample was stored in glass bottles, in the dark under ambient conditions. Table 1 gives the elemental composition and other characteristics of the flyash sample. The carbon, hydrogen, nitrogen and sulphur contents were found using a CE Instruments Flash elemental analyser, while the concentration of the metals was found by acid digestion followed by inductively coupled plasma spectrometry. The relative concentration of the other elements given was determined by energy dispersive X-ray analysis on a semi-quantitative basis. The BET surface area, mesopore surface area and volume and the micropore volume were measured by nitrogen desorption using a Quantachrome Quantasorb instrument. The loss on ignition was determined by placing the flyash in a muffle furnace at 800 °C for 30 min.

Table 1
Flyash properties and elemental composition

Al (wt%)	3.84	N (wt%)	0.03
Ba (ppm)	320	Na (wt%)	4.39
Be (ppm)	<10	Ni (ppm)	50
Bi (ppm)	<10	O (wt%)	41.93
C (wt%)	4.96	P (wt%)	0.77
Ca (wt%)	13.01	Pb (wt%)	1.22
Cd (ppm)	390	S (wt%)	2.90
Cl (wt%)	11.35	Se (ppm)	20
Co (ppm)	30	Si (wt%)	5.01
Cr (ppm)	200	Sr (ppm)	270
Cu (ppm)	1580	Zn (wt%)	3.77
Fe (wt%)	1.68	BET surface area (m ² g ⁻¹)	4.69
Ga (ppm)	20	Mesopore surface area (m ² g ⁻¹)	3.56
H (wt%)	0.35	Mesopore volume (cm ³ g ⁻¹)	0.0114
K (wt%)	3.56	Mean mesopore radius (Å)	64
Li (ppm)	<10	Micropore volume (cm ³ g ⁻¹)	0.0001
Mg (wt%)	0.86	Bulk density (g cm ⁻³)	0.50
Mn (ppm)	820	Loss on ignition (wt%)	13.29

2.2. Desorption reactor and adsorption system

A quartz-lined static-bed reactor was used to process the flyash, as shown in Fig. 1. The reactor was of 45 mm inner diameter, with a purge gas inlet at the top. The ash (5.00 g ± 0.01 g) was supported by a Whatman GF/A glass fibre filter, held on a glass frit. A pair of glass traps were attached to the reactor exhaust, as shown in Fig. 1. The first trap contained Supelco Amberlite XAD-2 resin, held in place with Orbo pre-cleaned PUF plugs. A Dionex ASE-100 accelerated solvent extractor was employed to clean the XAD-2 resin before use by sequentially extracting it with acetone, 75/25 acetone/hexane and 50/50 acetone/hexane at 75 °C (Dionex Corp., 2002). The resin was spiked with ¹³C₁₂-labelled PCDD/PCDF. The second trap was an empty Dreschel bottle. Both the traps and their connections were covered with aluminium foil to prevent UV degradation of the trapped species.

The reactor was constantly purged with a metered flow of nitrogen. When the sample temperature reached the desired final temperature of 200–400 °C, the run soak time

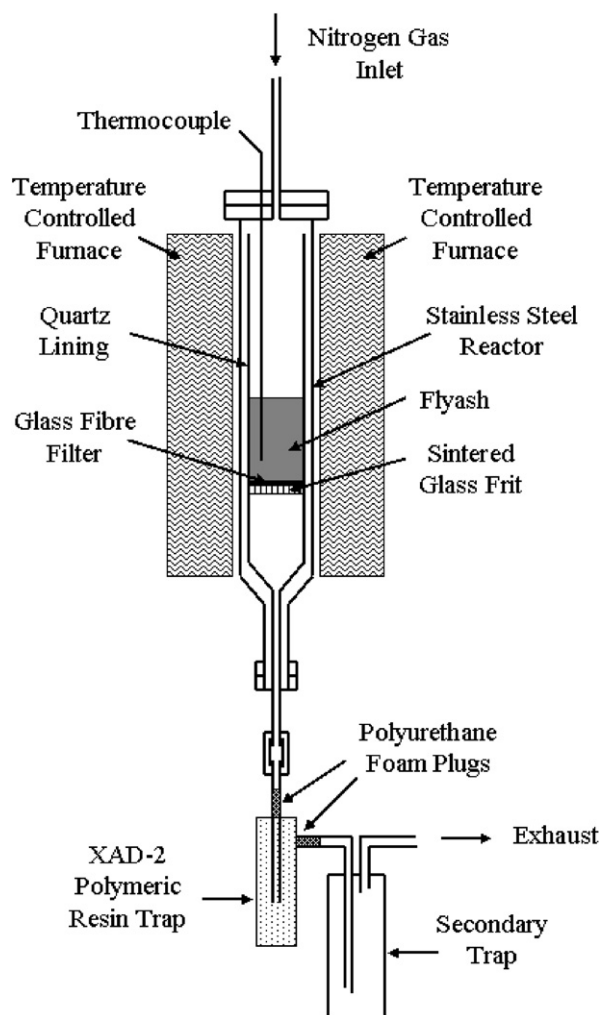


Fig. 1. Schematic diagram of the quartz lined, flyash PCDD/PCDF desorption reactor and adsorption system.

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