

Reactions of PCDD/F in Waste Incineration Flyash

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Introduction

Emissions of PCDD/F 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 beneficial process changes or after disturbances to combustion conditions¹. This persistence of PCDD/F emissions has become known as the 'dioxin memory effect' and has been linked with slow formation of PCDD/F on the flyash coating the post-combustor plant walls by a *de-novo* reaction scheme or (more speculatively) by the adsorption of vapour phase PCDD/F onto the ash, followed by slow desorption back into the flue gas^{2,3}.

In this investigation, a flyash 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/F before and after treatment to establish the influence of temperature and soak time. This study forms the first part of a project that aims to investigate the memory effect in incineration systems more fully.

Methods and materials

The flyash used in these experiments was derived from a 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 presents the elemental composition and selected properties of the flyash. The carbon, hydrogen, nitrogen and sulphur contents were found using a CE Instruments Flash elemental analyser, while the concentration of the trace 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 was measured by nitrogen desorption using a Quantachrome Quantasorb instrument and the loss on ignition was determined by placing the flyash in a muffle furnace at 800°C for 30min.

Cadmium	243ppm	Nickel	<2ppm
Carbon	5.00wt %	Nitrogen	0.03wt %
Chlorine	11.44wt %	Oxygen	42.29wt %
Copper	0.12wt %	Sulphur	2.92wt %
Hydrogen	0.35wt %	Zinc	3.21wt %
Iron	0.95wt %		
Lead	0.87wt %	BET surface area	4.69m ² g ⁻¹
Mercury	<2ppm	Bulk density	0.50g cm ⁻³
		Loss on ignition	13.29wt %

The flyash (10g ±0.01g) was weighed in a vertical static-bed reactor of 50mm internal diameter, and placed in an electrical tube furnace. The flyash bed was purged with nitrogen via a gas inlet at the top of the reactor for 15min prior to heating to remove trapped air and was constantly purged with a metered flow of nitrogen throughout the experimental run. The run time, of 1, 2, 4 or 8 days duration, was started when the sample reached the desired final temperature of between 200 and 400°C. At the end of the run the sample was left to cool in the reactor under nitrogen until the ash could be safely recovered. Heating and cooling times were normally 40 and 60min respectively. The ashes were stored in amber glass bottles in a laboratory freezer until analysis.

The ashes were digested with cold HCl (37wt % solution) for 2hrs, spiked with ¹³C₁₂-labelled recovery standard and

extracted using a Dionex ASE-100 accelerated solvent extractor. Interfering species were removed by elution through an acidic/basic silica gel column and a basic alumina column, as described in US EPA Method 1613⁴. Analysis of the extract for all eight congener groups was performed using a Varian GC3800 gas chromatograph linked to a Varian Saturn 2200 ion trap detector operating in tandem mass spectrometry mode. Calibration and spiking mixtures containing native and ¹³C₁₂-labelled PCDD/F as described by Method 1613 were obtained from Cambridge Isotope Laboratories. In addition, prepared solutions of M₁-T₃CDD/F were purchased to quantify the lower chlorinated dioxins and furans. Labelled analogues were not purchased for these species. The extraction, cleanup and analysis methods employed are described in detail elsewhere, together with method validation data⁵.

Results and Discussion

The PCDD and PCDF contents of the ashes are given in Figures 1 and 2 respectively. The PCDD level increased by around 13% after 8 days at 200 and 250°C, while the furan content of the flyashes increased very markedly at temperatures up to and including 300°C. For example, the PCDF content of an ash maintained at 250°C for 4 days was 6.1 times that of the starting material. Small decreases in the dioxin content were seen at 250 and 275°C between four and eight days soak time. Substantial reductions in the PCDD content of the samples were seen after one day at temperatures of 300°C and above, indicating that dioxin formation under these conditions was considerably less important than losses through desorption, dechlorination and destruction. Higher temperatures and/or longer soak times were required for substantial furan losses to be observed.

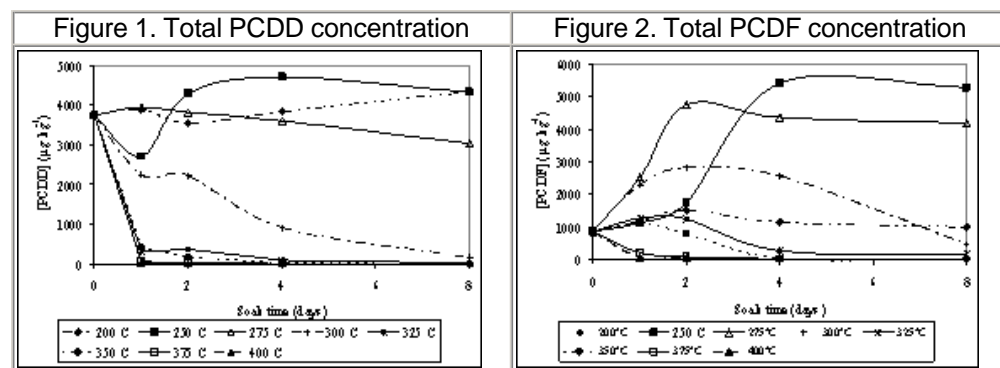
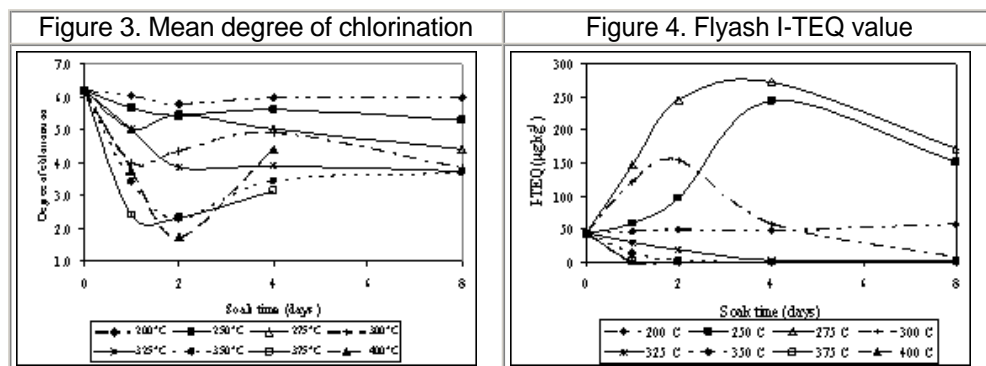


Figure 3 presents the average degree of chlorination of the PCDD/F found in each flyash sample. It may be seen that at 200°C, there was again no significant change in this property. There was a small change in the degree of chlorination of the ashes that had been heated to 250°C, indicating that the PCDD/F formed at this temperature were similarly distributed across the congener groups to those in the original flyash. As the temperature increased, the degree of chlorination reduced markedly, indicating that PCDD/F dechlorination was becoming increasingly important. The degree of chlorination of the PCDD and PCDF were found as a percentage of the degree of chlorination of the PCDD and PCDF in the initial flyash respectively. The percentage change obtained for the PCDF was then divided by the value for PCDD under the same conditions in order to investigate the relative changes in degree of chlorination for the furans in comparison to the dioxins. Up to 300°C, the PCDD and PCDF showed similar changes in degree of chlorination, as shown by the relative change being close to unity. However, at 325°C the relative decrease in the degree of chlorination of the dioxins in relation to the change in the degree of chlorination of the furans was 1.25, increasing to 1.70 at 375°C. The trends shown by the total PCDD content of the ash at 300-350°C in comparison to the total PCDF content in Figures 1 and 2 similarly suggest that the dioxins in the sample are susceptible to dechlorination at lower temperatures than the furans.

The I-TEQ value of the flyashes shown in Figure 4 followed similar trends in relation to temperature and soak time as the total PCDD/F content. However, it is worth noting that the maximum I-TEQ values obtained were around five times that of the starting material, whereas the total PCDD/F content of the ashes exposed to the same conditions were between two and three times that of the original flyash. This may indicate that prolonged exposure to temperatures between 200 and 300°C could favour the formation of 2378-substituted congeners in relation to congeners with different substitution patterns.



The results outlined above indicated that PCDF and to a much lesser extent PCDD can be formed in incinerator flyash at temperatures greater than 200°C and less than 325°C over the course of several days without the addition of reactants and in an inert atmosphere. Weber and co-workers noted that furans were formed during the dechlorination of OCDD on flyash under an inert atmosphere⁶. However, they showed that the PCDF were not directly formed from ¹³C₁₂-labelled OCDD or the other dioxin species subsequently generated from it. Instead, they suggested that the PCDF resulted from continuing de novo formation. To overcome the objection that this formation pathway is only available in the presence of oxygen, they suggested that some air was introduced during reactor loading^{7,8}. Both gaseous oxygen and solid-state oxygen present in the flyash can be involved in de novo synthesis⁹. Table 1 shows that the raw flyash sample contained the known de novo reaction catalysts copper and iron, together with a high amount of chlorine and carbon, so all the reactants required for de novo reactions were available in the flyash. In addition, the prolonged time scales and low temperatures found to result in PCDD/F formation in this work fit a de novo mechanism¹⁰. While atmospheric oxygen contamination remains a possibility in this study, the ash bed was subject to a constant through-flow of nitrogen before and during heating, so it seems more likely that a de novo formation route would use solid-state rather than gaseous oxygen in this case. Although no precursor species were artificially introduced into the ash during this study, the formation of PCDF from precursors previously adsorbed on the flyash is possible, especially as this route has been shown to operate in oxygen-deficient atmospheres¹¹.

Acknowledgements

This work was funded by UK EPSRC grant GR/R98549/01, Investigation of the Dioxin Memory Effect. The authors would like to thank Ed Woodhouse for technical assistance, Mick Daniel of the Environment Agency, Leeds, for his advice on reagents and methods for sample preparation and Varian Instruments (UK) for their support.

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