THE ASSESSMENT OF A THERMAL ASH DETOXIFICATION PROCESS USING ION-TRAP GC-MS/MS ANALYSIS

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Introduction

Dioxins and associated furans (PCDD/F) are toxic micropollutants created as unwanted by-products from numerous combustion and chemical manufacturing processes [1]. In particular, MSW incineration has gained a reputation in the public eye as a major source of PCDD/F in the environment. Current UK Environment Agency Guidance Notes set a limit of 0.1 ng/Nm^3 ITEQ for atmospheric emission from MSW incinerators[2].

In order to comply with strict emission limits, most modern flue gas cleaning plants employ a combination of sorbent injection and bag filtration[3] before the atmospheric discharge. Hence PCDD/Fs and other pollutants, such as heavy metals, are collected as components of a solid toxic filter residue, requiring some further means of safe disposal.

Approximately 100,000 tonnes of toxic fly ash is produced each year by the UK MSW incineration industry alone [4]. With landfill being the preferred route of disposal, costs can be as high as £100 per tonne due to the strict measures demanded to ensure adequate containment. However, if converted to a non-toxic product, then conceivably less stringent handling would be necessary, reducing landfill costs to around £30 per tonne. Fly ash detoxification would provide a major financial benefit to the industry. Also, detoxified fly ash may have applications in the construction industry, becoming a potential resource rather than a waste product.

In response to demand for cheap, reliable technologies for the detoxification of fly ash, we have developed a novel, efficient process to meet this criteria. In order to promote high-energy efficiency, our proposed treatment process operates at ash sintering temperatures (850-900°C) using a natural gas burner and incorporates a novel application of pebble bed heat regeneration. In addition to the regeneration of waste heat, the pebble beds are also intended to both prevent the escape of volatile metals and the reformation of PCDD/F. Exhaust gases experience considerable and rapid cooling (approximately 850-150°C) whilst transiting the relevant bed. Such cooling should encourage the removal of vapour phase metals by precipitation to pebble surfaces, thereby allowing scope for possible recovery. In addition, cooling the gases rapidly through the PCDD/F formation window should also inhibit re-occurrence in the exiting. Further PCDD/F inhibition is also intended by the removal of particulates before gas cooling.

This study has focused on the PCDD/F content of the raw and treated material in an attempt to determine whether the proposed thermal process is capable of reducing the PCDD/F content of the

material. Using GC-MS/MS with simple quantitation, it is possible to examine the different parameters that are required in assessing the viability of this technique.

Experimental

Raw fly ash used in this study was collected from two typical MSW incinerators operating in the UK (plants A and B). Using a pilot test rig, (figure 1), a fraction of each collected raw material was processed to provide treated ash for comparison. In order to assess the effectiveness of the proposed ash detoxification process concerning PCDD/F, samples before and after the sintering process were analyzed.

A 10g sample of fly ash was extracted using accelerated solvent extraction with toluene (Fisher Scientific, Loughbrough, UK) as the extraction solvent. The extraction conditions used were as follows: Temperature 150°C, pressure 1500psi, static time 8 minutes with 3 static cycles.

The extracts were cleaned up on a combined acid silica/basic silica gel column and a aluminium oxide column as described by Horstmann[5]. The dichloromethane from the final fraction is removed using a rotary evaporator and the sample is reconstituted using 150µL of nonane (Fisher Scientific, Loughbrough, UK) containing 50pg mL^{-1} of 1,5-dichloroanthraquinone as an internal standard.

Varian 3800 gas chromatograph with Varian Saturn 2000 ion trap mass spectrometer in EI/MS/MS mode was used. The GC column was a 30m x 0.25mm ID x 0.25µm film DBX 5. Using helium as a carrier gas, the GC oven temperature was programmed from 155°C (3.5 mins) to 235°C at 25°C min^{-1}, followed by 10 minutes at 235°C, then to 275°C at 5°C min^{-1}, then to 320°C at 10°C min^{-1}; the final temperature being held for 3 minutes.

Using 1,5-dichloranthraquinone as an internal standard calibrated against 2,3,7,8-tetrachlorinated dibenzo-p-dioxin it was possible to produce a calibration chart that was linear between 1.15 pg μL^{-1} and 300 pg μL^{-1}. Quantitation was of the 2,3,7,8-substituted congeners was achieved by measuring peak area relative to 2,3,7,8-TCDD and the internal standard. The results obtained by the screening method of quantitation were compared to those obtain using enzyme linked immunoassay technologies and showed >90% confidence. This level of accuracy was decided to be fit for the purpose required..

Results and Discussion

The results obtained from the GC-MS/MS have shown that it is possible to efficiently destroy the PCDD/Fs that are present in fly ash using our process. It can be seen in Figure 2 that there is considerable differences before and after the treatment.

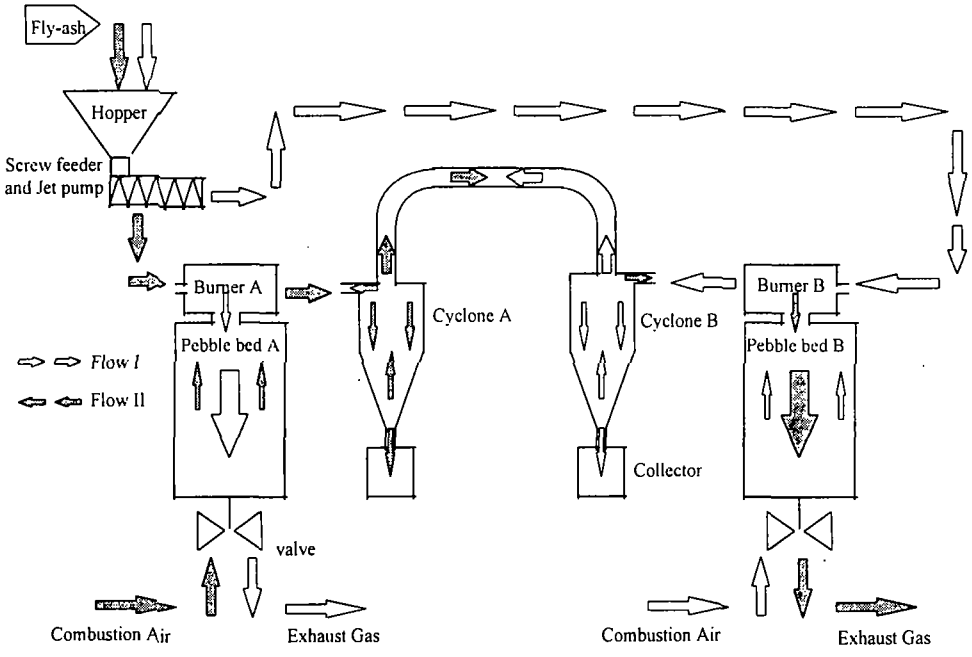

Figure 1. Schematic Diagram of Ash Detoxification Rig

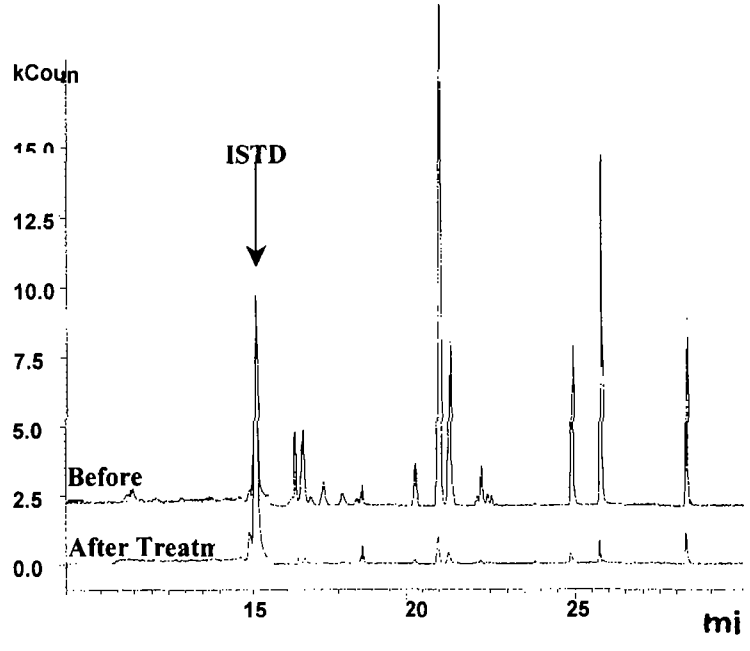

Figure 2: Diagram showing chromatograms of PCDD/F in fly ash before and after the *Thermal Decomposition Process.*

Using a simple quantitation technique it is possible to obtain ng/kg iTEQ results for the ash samples, these are shown in Table 1.

Table 1: Table showing iTEQ values for the Ash Samples Investigated

Sample ID	Σ PCDD (ng/kg iTEQ)	Σ PCDF (ng/kg iTEQ)	Σ PCDD/F (ng/kg iTEQ)
A1	120	160	280
A1.1	5	5	10
A2	60	270	330
A2.1	5	5	10
B1	530	800	1330
B1.1	<0.2	<1.0	<1.2

The percentage destruction of the PCDD/Fs in the ash samples as 96%, 97% and 99% for samples A1, A2 and B1 respectively.

Conclusions

In this work, we have shown that the process is viable on a pilot scale and our investigation into the proposed ash sintering process has so far demonstrated it to be an effective technique for the detoxification of MSW incinerator fly ash. The treated product has been shown to contain drastically reduced levels of both leachable heavy metals and PCDD/F contamination. As such, the material poses much less risk to public health and environment, enabling potential for safer, cheaper landfilling, or re-use by the construction industry. Although so far only applied to the MSW incineration material, the process has the potential to be used for energy-efficient detoxification of other hazardous wastes. Further research work is underway in order to investigate the energy efficiency of the process. Preliminary calculation of less than £10 per tonne shows much promise and suggests the process to offer major financial benefits to the future waste incineration industry. Furthermore, this would enable the industry to reduce the environmental burden of its activities and thereby enhance its reputation in the future eyes of the public.

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