# Removal OF Vapour Phase PCDD/F in Electric Arc Furnace Steelmaking Emissions by Adsorption on Polypropylene

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## Introduction

Dioxins (PCDD/F) are highly stable organic compounds that are emitted during waste incineration and other high-temperature processes. Emissions of PCDD/Fs from steel industry processes in the UK have been discussed by Anderson and Fisher (2002)[1] who reported that sintering is the only noteworthy source in the integrated steel route. Electric arc furnace (EAF) steelmaking is also a source of PCDD/Fs and the best available technology for pollution control in this process includes the use of fabric filters for removal of particulates from the waste gas stream[2] The removal of PCDD/Fs by fabric filtration is dependent on the waste gas temperature, since there is a greater tendency for PCDD/Fs to partition to the dust particles as the waste gas temperature is reduced. However, it is difficult to control precisely the waste gas temperature and, therefore several end-of-pipe methods, which include activated carbon adsorption (injection, fixed-bed carbon filters or carbon-impregnated bag filters), SCR (selective catalytic reduction) and catalytic oxidation have been used[3] to effect further reductions in PCDD/F emissions. Injection of activated carbon into the waste gas upstream of a bag filter is currently regarded as best available technology for achieving very low concentrations of PCDD/Fs from EAF steelmaking plants. Catalytic oxidation is less effective than carbon adsorption, while catalysts used in SCR can be expensive depending on the operating conditions. It has been reported in the literature that polymers and other standard plastics are capable of PCDD/F removal[4,5]. These plastics, e.g. polypropylene and polyethylene, are commonly used as the wall coating material in wet scrubbers due to their capacity to prevent corrosion. The interaction between PCDD/F and plastics occurs via an absorption mechanism[6]. This bond is thought to be weak and its capacity for PCDD/F absorption is governed by the equilibrium load on the plastics, which changes with temperature and PCDD/F concentration in gas phase. This paper presents the results of laboratory studies that were conducted to determine the capacity of plastics for reducing emissions of PCDD/Fs. The optimum operating temperature of polypropylene for PCDD/F removal was investigated and the interaction between PCDD/F and the polymer surface was studied. Additionally, a method is described for the extraction of PCDD/Fs from plastics for the quantification of these species trapped on the polypropylene adsorbent.

## Experimental

Experimental apparatus

The experimental system used for studying the adsorption/desorption of PCDD/Fs on plastics is shown in Fig 1. The system comprised essentially five parts: a regulated supply of high-purity nitrogen as carrier gas, two modified gas chromatography (GC) ovens that contained, respectively, the PCDD/F source and the plastic adsorbent, a polyurethane foam plug (ORBO-1000, Supelco) to trap PCDD/Fs remaining in the gas phase leaving the adsorber and a gas cooler and flowmeter to measure and set the gas flow rate. Glass was used for all parts of the system in contact with PCDD/Fs. In all experiments, the heating time was 8 h and the weight of plastics used was 18 g. The carrier gas, nitrogen (BOC), was supplied into the system at a regulated flowrate of 2.0 l/min.

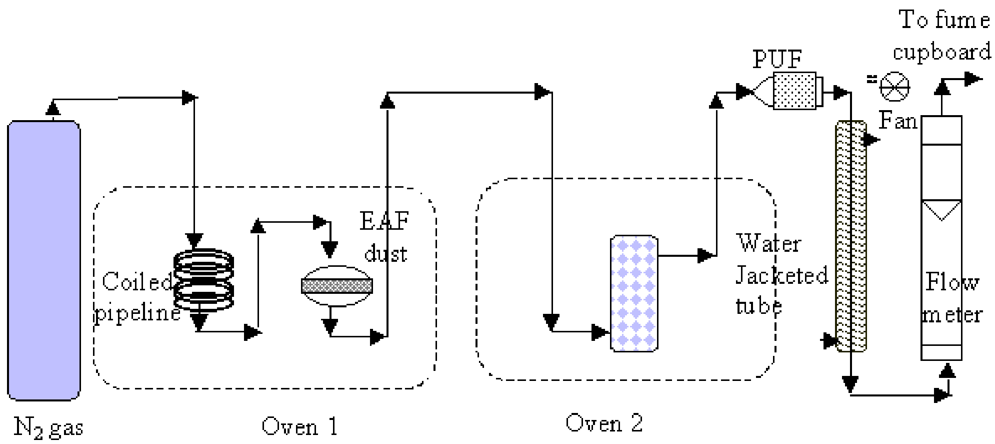


Figure 1. The schematic diagram of the plastic absorption experiment

PCDD/F source EAF steelmaking dust was used as a source of PCDD/Fs. A weighed portion of EAF dust was spread on a filter paper (Whatman GFA) that was supported on a sintered glass disc. The dust was heated at a constant temperature of 150°C to release the PCDD/Fs into the carrier gas.

Adsorbents

Two different types of polystyrene polymers were tested: these were polypropylene BE170MO (Borealis A/S, Denmark) and polypropylene in the form of 5 mm spheres (The Precision Plastic Ball Co. Ltd., UK). The optimum absorption temperature was determined by performing adsorption experiments when the adsorbent was heated in the range of 60 to 120°C, which represents the normal operating temperature range for a bag filter equipped with economic fabric sleeves. PCDD/F desorption studies were performed by heating polypropylene containing a fixed amount of PCDD/F at either 120 or 130°C.

Analytical methods

The PCDD/F source, the PUF and the plastic adsorber were analysed for PCDD/F using USEPA Method 23 isotope dilution technique, as described by Wang et. al. (2003)[7]. Extraction of PCDD/F from plastics was conducted using a modified USEPA Method 23 procedure, wherein the polypropylene adsorbent was immersed in toluene for two days, followed by titration of the extract with hexane to precipitate soluble polypropylene. The precipitate was removed using a quantitative filter (Whatman No.4). The polypropylene-free extract containing the PCDD/Fs was then submitted to standard clean-up procedures prior to analysis by HRGC-HRMS.

## Results and Discussion

### Comparison of plastic adsorbers

The concentrations of PCDD/F adsorbed on polypropylene (BE170MO) and polypropylene (sphere, d=5mm) at a temperature of 80°C are shown in Table 1. PCDD/F removal efficiencies were similar and were high for both forms of polymer. This is attributed to the similar porosity of both types of polypropylene used (polypropylene spheres, 6.21% and polypropylene plain, 5.14%). Removal efficiencies for all homologue groups of PCDD/Fs in the vapour phase averaged 98.1% and 97.8% for polypropylene BE170MO and polypropylene spheres, respectively. Due to the capacity of the commercial polypropylene BE170MO for PCDD/F absorption and also to the lower cost, polypropylene BE170MO would be the preferred material for a full-scale implementation. All the remaining experiments were performed using this material as adsorbent.

Table 1. PCDD/F adsorbed on polypropylene BE170MO and polypropylene sphere

| Totals | PCDD/F concentration (ng/kg) | | |
|---|---|---|---|
| | No adsorber | polypropylene (BE170MO) | polypropylene (sphere, d=5mm) |
| TeCDDs | 2320 | 2240. | 2229 |
| PeCDDs | 3045 | 3029 | 3031 |
| HxCDDs | 1593 | 1588 | 1591 |
| HpCDDs | 295 | 290 | 293 |
| OCDDs | 38 | 37 | 37 |
| TeCDFs | 16606 | 16071 | 15933 |
| PeCDFs | 9355 | 9299 | 9309 |
| HxCDFs | 4159 | 4151 | 4156 |
| HpCDFs | 748 | 745 | 746 |
| OCDDs | 56 | 55 | 55 |
| sum | **38215** | **37505** | **37380** |

**2) Determination of the optimum adsorption temperature**

Figure 2 shows the effect of temperature on the adsorption of PCDD/Fs on polypropylene BE170MO in the range 60 to 110°C. The PCDD/F removal efficiency was effectively constant at >99.5% over the temperature range 60 to 90° C, but fell to 61% when the temperature was increased to 110°C. Maximum removal efficiency was achieved at a gas temperature of 75°C.

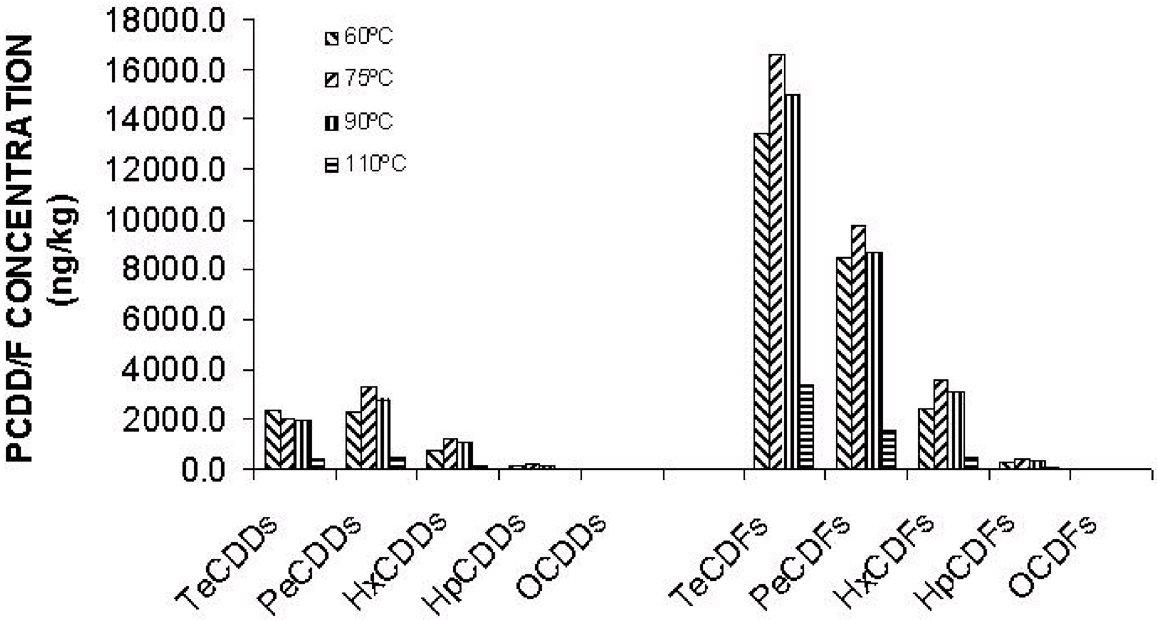


Figure 2. PCDD/F absorption on polypropylene (BE170MO)

**3) Desorption studies**

The effect of temperature on the desorption of PCDD/Fs from polypropylene BE170MO was studied at 120 and 130°C and the results are shown in Fig 3. On average 64% of the adsorbed PCDD/Fs was desorbed at 130°C. Based on I-TEQ values, 16% of the total adsorbed PCDD/Fs was desorbed into the vapour phase at 120°C, and this increased to 61% at 130°C. Furthermore, the extent of desorption was constant for all homologue groups. Desorption of PCDD/F from polypropylene (BE170MO) could not be increased by raising the temperature above

130°C because this would cause the softening point of the polymer to be exceeded, and would limit the reuse of the material.

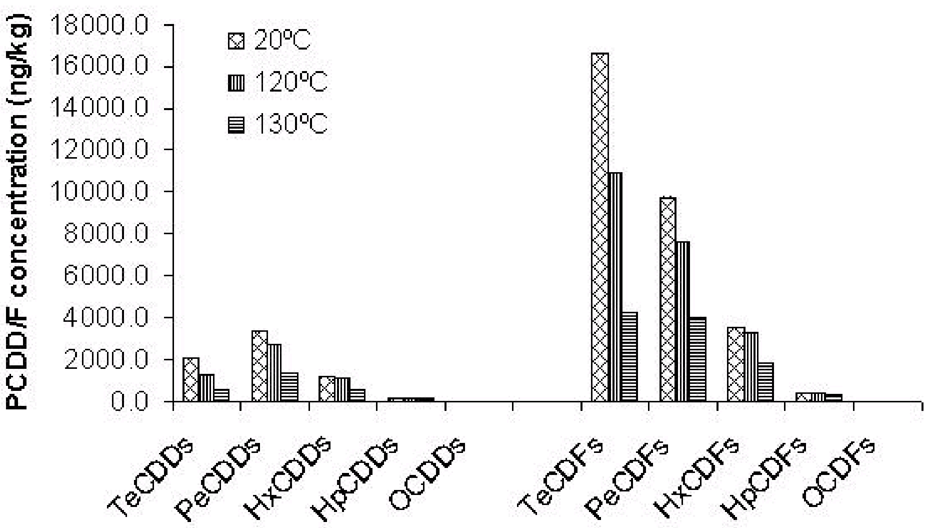


Figure 3. PCDD/F desorption from polypropylene (BE170MO)

**Conclusion**

This study suggests that polypropylene is a potential absorption material for removal of vapour phase PCDD/F from waste gas streams. Polypropylene BE170MO and polypropylene spheres (d=5mm) exhibited essentially the same efficiency for PCDD/F absorption, i.e. ~ 98%. However, polypropylene BE170MO is less expensive than polypropylene spheres. An adsorber consisting of polypropylene BE170MO could be operated in the temperature range of 60 to 90°C with removal efficiency above 99.5%. The maximum PCDD/F desorption temperature was determined to be 130°C, which was close to the softening point of the polymer. At this temperature 61% of adsorbed PCDD/Fs was desorbed based on I-TEQ values was observed.

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