Removal of PCDD/PCDF and Polyaromatic Hydrocarbons (PAHs) by Catalytic Filters

Remedia™
CATALYTIC FILTER SYSTEM

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Introduction

To minimize the emissions into the air, stringent limiting values for PCDD/PCDF of 0.1 ng TEQ/Nm^3 for some emission sources (e.g., municipal and hazardous waste incinerators) have been in effect in several European countries, and also for new municipal waste incinerators (MWIs) in Japan[1-3].

Catalytic oxidation with direct destruction of PCDD/PCDF in the flue gas is a proven technology to reduce PCDD/PCDF. It has been shown by Hagenmaier and co-workers that the TiO_2-based V_2O_5/WO_3 catalysts are very effective in the decomposition of PCDD/PCDF at the same temperatures used for the DeNO$_x$-reaction[4,5]. This technology enables stack gas concentrations below 0.1 ng TEQ/Nm^3.

During the last five years it has been demonstrated that a catalytic filter system can also destroy PCDD/PCDF below the regulatory limit of 0.1 ng/Nm^3 TEQ[6]. Field measurements and laboratory experiments were in good agreement and showed removal efficiencies for PCDD/PCDF of more than 99%[7].
Beneath the PCDD/PCDF, polyaromatic hydrocarbons (PAHs) are toxic compounds of ecotoxicological relevance and generated from incomplete combustion. PAHs are generally among the most abundant organic micro-pollutants in incineration processes, and present in considerably higher concentrations as compared to PCDD/PCDF[8-10]. Due to their high concentrations, the PAHs cause an even higher carcinogenic risk in flue gases from thermal processes compared to PCDD/PCDF[11,12]. Therefore, we wanted to investigate the removal efficiency of catalytic filters for PAHs and compare it with the removal of PCDD/ PCDF.

Materials and Methods

Catalytic Filtration Product Information: The REMEDIA^{TM*} catalytic filter system is manufactured by W. L. Gore & Associates, Inc. (Gore) and is described elsewhere[6].

Laboratory experiments: Catalytic filters were tested in a stainless steel reactor. First, a filter was loaded into the stainless steel reactor. Then the reactor was surrounded by a heating mantel, which maintained the reactor temperature within of ± 2°C. Heating tape was used to maintain all ancillary tubing at the same temperature as the reactor. A temperature of 200°C was chosen since most actual plants are operated at this temperature. Before closing the reactor, the PAHs, or the PCDD/PCDF mixture, were placed in the evaporating zone. The volumetric flow through the catalytic filter was 300 cm^3/min (20% O_2, 80% N_2), and corresponded to a face velocity of about 1 m/min. When equilibrium was reached, the experiment began by heating the evaporation zone for 10 minutes and continuing the flow through the filter for 30 minutes.

The catalysts are extracted by 12 hours Soxleth extraction. The catalyst and impinger are analyzed separately for PCDD/PCDF.

Results and Discussion

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Destruction of PAHs

Four representative PAHs commonly found in incineration processes were chosen for this study: naphthalene, phenanthrene and pyrene (some of the most abundant PAHs[8-10]) and benzo[*a*]pyrene, due to its elevated carcinogenic potential and its high toxic equivalence factor[13]. A second criteria for choosing these four compounds was to compare PAHs that contain two-, three-, four-, and five-rings and, therefore, have differences in volatility.

The PAHs are removed effectively by the catalytic filter. The highest removal was detected for the low volatile benzo[*a*]pyrene (boiling point 495°C) with a RE above 99.9%. The RE decreased with increasing volatility (Figure 1). For both pyrene (99.8%) and phenanthrene (98%) the RE was very high. Only for the highly volatile naphthalene (boiling point 217°C), was the removal efficiency as low as 75% (Figure 1). Therefore, for PAHs, the volatility is the main determining factor for removal efficiency. After the experiment, no PAHs were detected on the catalyst.
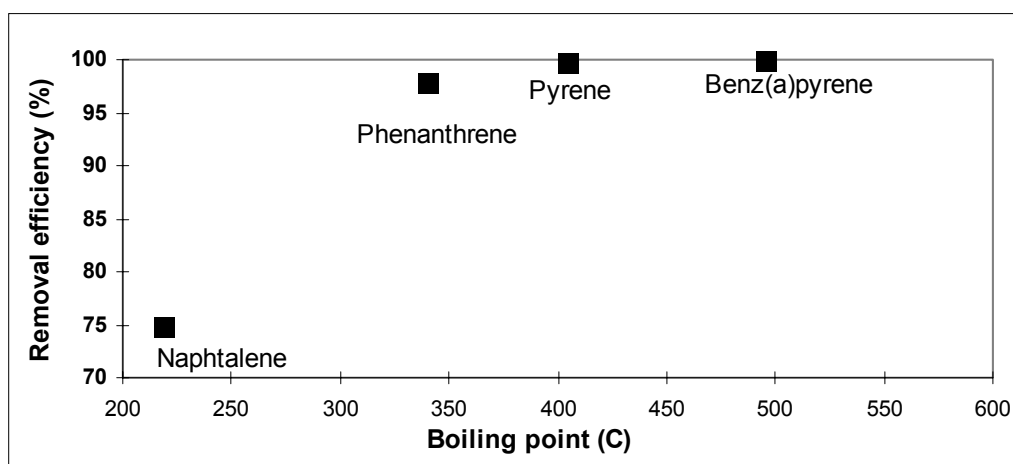

Figure 1: Removal efficiency of the catalytic filter for PAHs

Removal of PCDD/PCDF in dependence of chlorination degree

The removal efficiency of PCDD/PCDF showed a dependence on the degree of chlorination. Starting with OCDF/OCDD, the removal efficiency decreased with decreasing chlorination degree. However, with PCDF it reached a minimum for P_5CDF/T_4CDF, and then the removal efficiency increases with decreasing chlorination degree (Figure 2). This increase of removal efficiency with decreasing chlorination degree was less pronounced for the PCDD. The dependence of the removal efficiency on chlorination degree of PCDF is similar between the laboratory tests and the field studies (Figure 2).

The observed dependence of the removal efficiency from chlorination degree can be explained by two competing effects on the removal efficiency with each other depending on the chlorination degree:

The first effect is due to the change of the volatility of the PCDD/PCDF with chlorination degree. The volatility of PCDD/PCDF decreases with increasing chlorination degree as can be derived from the boiling points of the PCDD/PCDF[14]. This is analogous to the observed effect for the PAHs. Higher chlorinated PCDD/PCDFs are retained on the catalyst surface longer (as can be

derived from the small amount of only H_6CDD/F to $OCDD/F$ adsorbed on the catalyst[7]), increasing the chance of oxidation (and therefore for removal).

The opposing effect results from decreasing oxidation rates with increasing chlorination degree. This was demonstrated in a former study[15], investigating the isolated effect of chlorination degree on destruction rates by applying stationary conditions. Under these circumstances, interfering adsorption and desorption effects were eliminated. According to this effect, lower chlorinated PCDD/PCDF are better destroyed than higher chlorinated PCDD/PCDF during the same residence time on the catalyst surface.

Overlaying both effects (residence time due - redox potential) leads under the applied conditions to maximum removal efficiency for octa/hepta- and monochlorinated congeners, and a minimum for the tetra- to hexachlorinated furans (Figure 2).

In former studies using honeycomb catalysts, these competing effects were discussed for the chlorobenzenes[15,16]. However, with chlorobenzenes the effect of lowering the volatility with increasing chlorine substitution overcompensated the effect of an increasing "redox potential". This resulted in a decreasing removal efficiency with decreasing chlorine degree only[15,16].
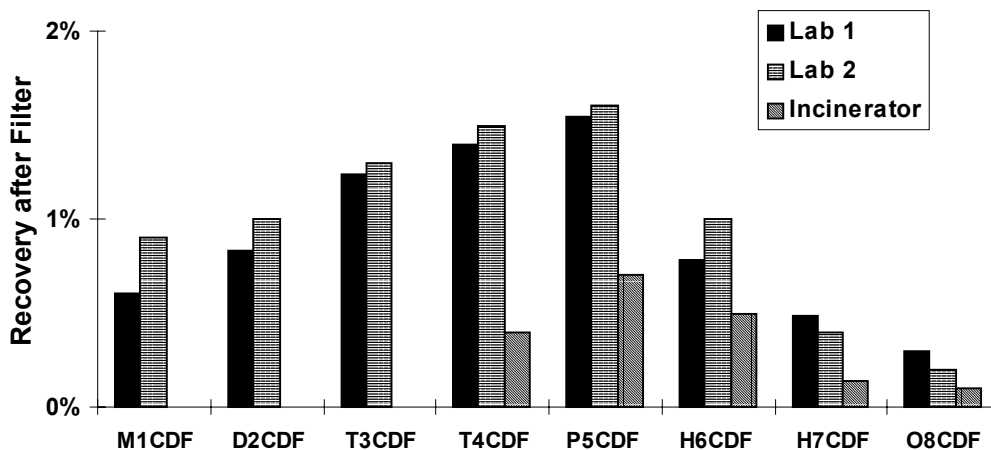

Figure 2: Recovery of PCDF after the catalytic filter (1-removal efficiency)

Conclusions

This study has shown that the catalytic decomposition and the removal of semivolatile compounds strongly depends on volatility and oxidative behavior of the compounds. Both factors are related to the degree of chlorination.

For PAHs (containing no chlorine substituent), the volatility is the main determining factor in respect to removal efficiency. The catalytic filter effectively removes PAHs with an high efficiency including the carcinogenic Benz(a)pyrene with a removal efficiency of more than 99%. Therefore, the catalytic filter should be useful not only for removal of PCDD/PCDF in municipal waste incinerators and other applications, but also in processes where semivolatile compounds such as PAHs must be removed.

Acknowledgments

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