Formation of PCDDs, PCDFs and PCBz during high temperature filtration of flue gases in a pilot incinerator.

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A pilot fluidized bed reactor and a synthetic fuel has been used to study the formation of chlorinated aromatic compounds during incineration. The results show that polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), polychlorinated benzenes (PCBzs), and non-ortho polychlorinated biphenyls are all formed during cooling of the flue gases within a temperature interval around 340°C, (1). All of the studied compound were found to be affected in the same way by the temperature and residence time in the cooling section of the reactor. When most of the fly ash load was removed by a cyclone placed at the inlet to the cooling section there was no significant decrease in fly ash levels of the above chlorinated aromatics, (1). From these results it was suggested that the small particles, which contain most of the available surface area, are the main contributors to the formation of chlorinated aromatics in flue gases.

The purpose of the present study is to investigate the influence of fly ash particles on the formation of chlorinated aromatics during cooling of the flue gases.

MATERIALS AND METHODS

The laboratory scale pilot fluidized bed reactor was used to simulate municipal solid waste (MSW) incinerators, Figure 1. It has a high freeboard connected to a cooling section, which simulates the boiler in a full scale incinerator, (1). By using one of the four sampling ports, SP1 - SP4, in the cooling section it is possible to collect samples with different flue gas residence times. A large number of temperatures are monitored in the reactor, in the freeboard and in the cooling section (Tf1-Tf3, and Tk1 - Tk7). A synthetic fuel was used in order to overcome variations associated with fuel inhomogenities (1). A high temperature filter (Cerafil S) from aluminasilicate was introduced after the cyclone in order to remove fly ash particles from the cooler parts of the reactor.

FORM

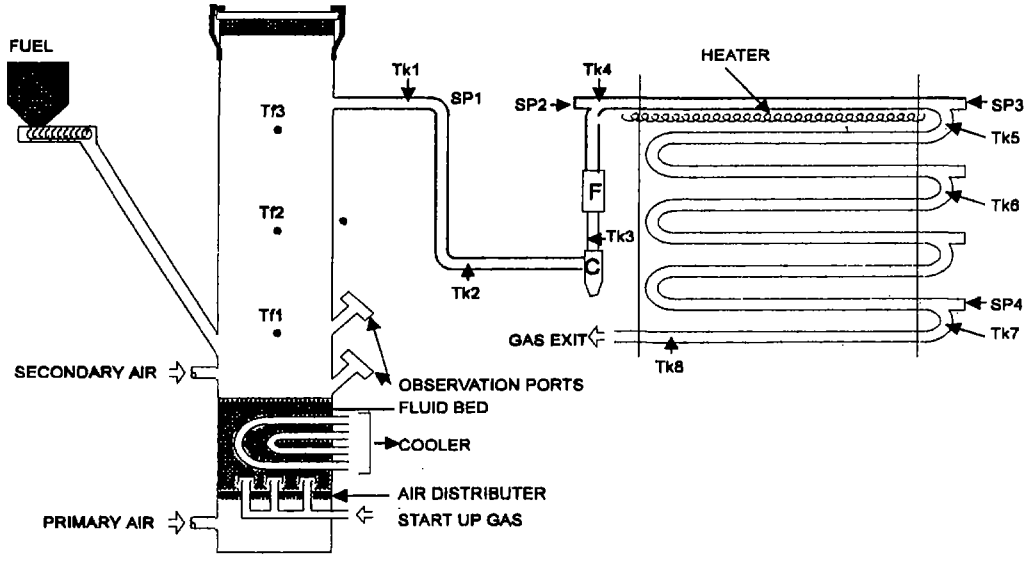

Figure 1. The pilot fluidized bed reactor (C = cyclone, F = filter).

An experimental plan of full factorial design in the variables sampling temperature and residence time in the cooling section, Table 1, was used for the experiments. In order to ensure that there were no fly ash deposits in the cooling section during the experimental runs, the cooling section was by-passed during the time needed for stability. The reactor was also cleaned between experiments and the sand bed replaced. Parallel samples were collected in two of the sampling ports in most experiments. In total 16 flue gas samples were collected and analyzed for toxic isomers of PCDDs and PCDFs on HRGC/HRMS and for PCBzs on HRGC/LRMS.

Table 1. Variables and levels used in a full factorial experimental design.

Variable	Level		
	Low (-)	Middle (0)	High (+)
Time (sec)	0.9	1.4	2.9
Temp (°C)	260	345	430 (510)*

*) 430° C at 0.9 and 2.9 sec residence time, 510° C at 0.9 and 1.4 seconds.

RESULTS AND DISCUSSION

During the experiments the filter temperatures varied between 335 - 501°C and the cyclone temperature between 540 - 630°C. The resulting flue gas levels of TCDDs and TCDFs, varied between 7 and 600 ng/Nm^3, expressed as toxic equivalents according to the international scale (I-TEQ). There are at least three possible explanations for these results: 1) Chlorinated aromatics are formed from reactions occurring during passage of the filter or the ash filter cake, 2) The walls of the cooling section catalyze formation of chlorinated aromatics, or 3) Gas phase formation occurs. These possibilities were investigated by primcipal components analysis (PCA), (2). Combustion conditions, temperatures in the freeboard and cooling section and the resulting flue gas levels expressed as the total sum of PCDDs, PCDFs, the I-TEQs and the tri-hexachloro-PCBzs, were used as variables. Three significant PCs were calculated describing a total of 76 % (36 + 28 + 13 %) of the total variance in the data set. A plot of the first two PC scores and loadings are shown in Figure 2. The data points for the samples collected in parallel, during the same experimental run, at two different sampling ports are close to each other in the score plot and will thus have similar levels. Apparently, chlorinated aromatics are not formed in the cooling section when no fly ash particles are present. Thus, formation of chlorinated aromatics seem to occure from reactions taking place during passage of the ash filter cake.

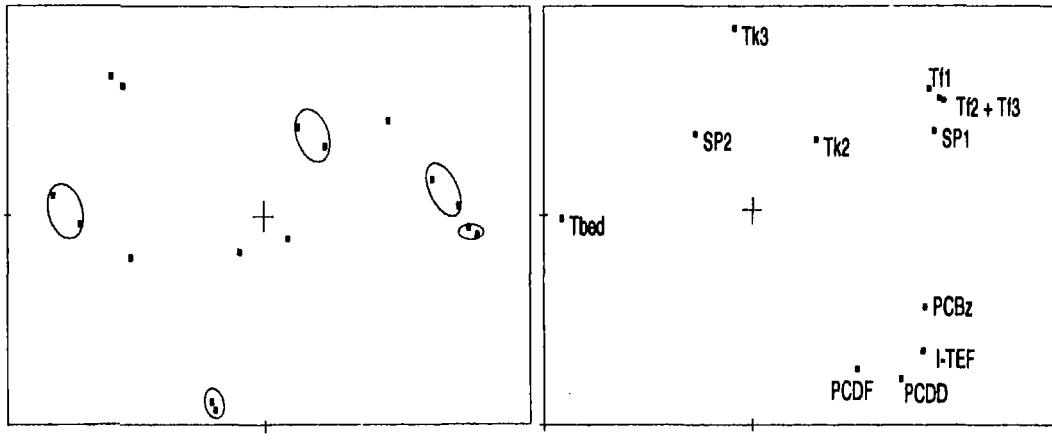

Figure 2. To the left: plot of second score vector versus the first . Samples collected in parallel marked with circles. To the right the corresponding plot of the second loading vector versus the first. (Tbed, Tf, Tk and SP = temperature measuring points according to Figure 1).

FORM

The opposite position of the variables Tk2 (filter temperature), the temperature at SP2 and the levels of PCDDs, PCDFs and PCBz in the loading plot (Figure 2) shows that the filter temperature is negatively correlated with the levels of chlorinated aromatics. Within the above temperature interval, a low filter temperature yields high levels of chlorinated aromatics. This result demonstrates the importance of fly ash particle surfaces in the formation reactions. It also verifies the importance of the small particles in the formation reactions. Upon passing the filter cake formed by the small fly ash particles, formation of chlorinated aromatics occurred momentarily.

The isomeric pattern of the PCDFs in some of these samples are atypical for incinerator flue gases and contain a higher proportion of 3,4,6,7-substituted congeners. The 3,4,6,7-substituted congeners of PCDFs seem to be those formed most rapidly while the other isomers of the "combustion pattern" may be formed by a slower reaction mechanism, by rearrangements or by chlorination/dechlorination reactions. On a weight basis an average of 97% of the total fly ash weight was removed by the cyclone and the remaining 3 % by the filter. The fly ash particles collected by the cyclone has a number median diameter of 5.4 μm and the particles collected by the cyclone 2.2 μm. Analysis of the fly ash composition revealed that elements such as Cu, Zn, Ni and Cr are enriched on thee small particles collected by the filter. That elements volatized in MSW incinerators due to the prescence of HCl will be enriched in the small particle size fraction has been reported by Fernandez et al, (3). They concluded that formation-volatilization-condensation of chlorides play an important role in the transport of heavy metals by the combustion gas stream.

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