INHIBITION OF PCDD/F 'DE NOVO' FORMATION BY ADDITION OF BASIC COMPOUNDS TO DUST FROM METALLURGICAL PLANTS (I) EXPERIMENTAL RESULTS

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Introduction

Polychlorinated dibenzodioxins and –furans (PCDD/F) and a variety of other chlorinated aromatic compounds are formed 'de novo' by thermal treatment in air of dust from different origins, e.g. municipal solid waste incinerators (MSWI), iron ore sintering plants (ISP), etc.[2, 4, 5]. Probably they are formed 'de-novo' by incomplete combustion of residual carbon[1, 3]. Inhibition of PCDD/F formation was intensively studied on fly ashes from MSWI and also achieved in an oxygen free atmosphere[10] or by addition of basic compounds e.g. triethanolamine[7, 9], or of sulfur dioxide[8] or other sulfur compounds. The goal of our study was to investigate the inhibition of the PCDD/F formation, by testing 'de novo' formation under standardized laboratory conditions in dust collected in an iron ore sintering plant (ISP) or from the evaporative cooler of a Waelz process zinc recycling plant (ZRP) after addition of various amounts of some basic inhibitors.

Materials and Methods

Materials: The experiments were conducted in a tubular glass reactor (1.5 cm diameter x 50 cm length) mounted vertically in an oven. Dust (5 g) from the electrostatic precipitator (ESP) of two metallurgical plants (an ISP and a ZRP) was placed on a glass frit in the middle of the glass tube and flushed with a gas stream of 20 % oxygen in helium (50 mL/min). The volatile organic compounds were collected in a toluene impinger. The extract of the dust and the solution of the toluene impinger were cleaned-up separately.

The experiments with ISP-dust were conducted with and without addition of basic compounds at 300 °C for 2 hours. Tested were triethanolamine (TEA; 0.2, 0.5, 1 and 5 %), $Ca(OH)_2$ (2 and 5 %), NaOH (2 and 5 %), urea (1 %) and ammonia (200 ppm). The experiments with the dust from the ZRP were performed with $Ca(OH)_2$ (2 and 5 %) at 350 °C and 2 hours. TEA, $Ca(OH)_2$, NaOH and urea were mixed with the dust material prior to the experiments and ammonia was added as aqueous ammonia to the gas phase (150 mg 0.1 n NH_3(aq)/mL, gas flow: 50 mL/min).

Methods: The PCPh, PCBz, PCB and PCDD/F were quantified by ^{13}C-internal standards. The PCPh, PCBz and PCB were analyzed by HRGC/LRMS with a 60 m DB-5 column and the PCDD/F by HRGC/HRMS (HP5890 - Fisons Autospec) with a 60 m DB-Dioxin column.

Results and Discussion

Inhibition of PCDD/F formation on dust samples of an iron ire sinter plant (ISP)

The characteristics and reactivity of the dust from the 3 successive fields (denoted here as I, II, and III) in an electrofilter of an ISP have been discussed elsewhere[5]. Addition of ammonia (200 ppm) into the gas phase did not influence the PCDD/F formation (**Figure 1**).The PCDD/F concentration was reduced between 30 and 56 % by addition of TEA (mechanically mixed with the dust), with a sizeable reduction occurring already for 0.2 % of TEA, while 1 % TEA yielded the best results. Even stronger inhibition rates were obtained with $Ca(OH)_2$ addition, since 2 % $Ca(OH)_2$ reduced the PCDD/F de novo formation by 63 % and spiking the dust material with 5 % $Ca(OH)_2$ reduced it by 93 %. Addition of NaOH yielded even better results. For explaining the inhibition of the PCDD/F formation several mechanisms have been advanced, e.g. transformation of the catalytic active copper chlorides into copper amine complexes or basic copper chloride, which do not support the PCDD/F formation. Furthermore, the basic compounds might react with intermediately formed HCl and withdraw it from further chlorinating steps of the carbon or precursors. $Ca(OH)_2$ proved also to be a good inhibitor on dust material of the last ESP-field (ESP-III): the PCDD/F formation decreased here by 96 % (**Figure 1**) by addition of 2 %$Ca(OH)_2$.

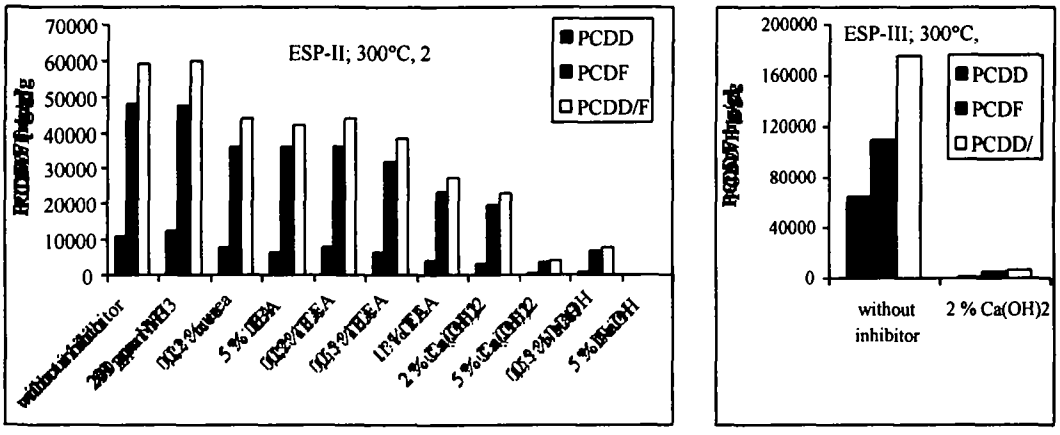


Figure 1: PCDD/F concentration [ng/g] after thermal treatment of dust material of the ESP – II and III of an iron ore sinter plant with and without addition of a basic compounds at 300 °C and 2 hrs.

The various inhibitors tested not only reduce dioxins, but also related chloroaromatics; **Figure 2** shows the data obtained for TEQ, PCB, PCDD, PCDD/F, PCDF, that show a parallel evolution when applying different doses of TEA, and of PCBz and PCPh. Especially the latter deviated in reduction yields. From the results on TEQ, PCDD, and PCDF it follows that the internal distribution of 'dirty 17' within the PCDD/F is also affected by TEA-addition (see part II of this paper).

The question can now be raised whether the addition of basic substances really reduces PCDD/F formation, or merely shifts their distribution towards the lower (< 4) chlorinated species. For this reason the full range of MCDD/F through OCDD/F was considered, with results given in **Figure 3**.

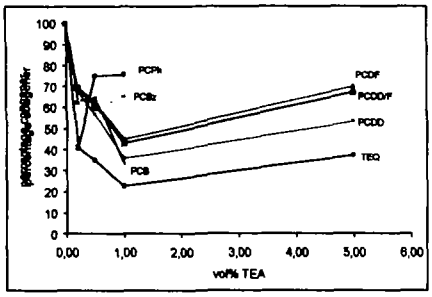
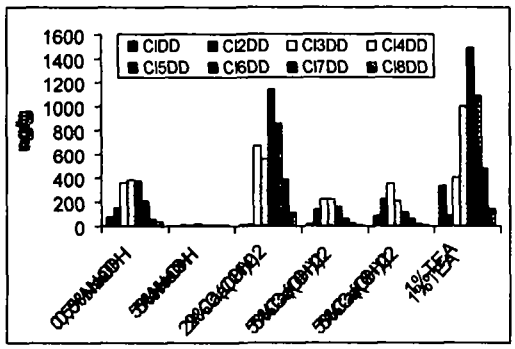


Figure 2: Percentage reduction of the 'de novo' yield of TEQ, PCB, PCDD, PCDD/F, PCDF, PCBz and PCPh, upon applying different doses of TEA during a standard test, i.e. annealing at 300 °C for 2 hrs.



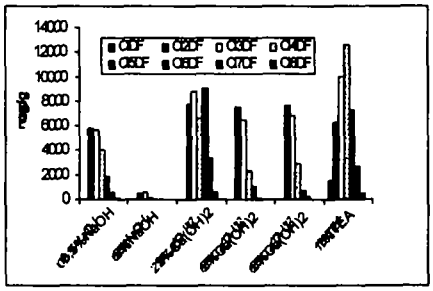


Figure 3: Addition of basic substances, full range of MCDD/F through OCDD/F

Inhibition of PCDD/F formation on dust samples of a zinc recycling plant

MINIDIP successfully adressed the problem of dioxin emissions from Waelz plant (using a two stage lignite coke adsorber). Inhibition was also found an efficient means of dioxin reduction:

	original	without inhibitor, test at 350°C, 2h	Idem, after adding 2 wt. % Ca(OH)2
PCDD	23	2000	23
PCDF	8	1820	183
PCDD/F	31	3820	206

Table 1:PCDD/F concentration [ng/g] after thermal treatment of dust collected from the quench cooler of a Waelz plant with and without addition of $Ca(OH)_2$ (at 350 °C and 2 h)

Conclusions

In a series of standard 'de novo' tests a number of basic inhibitors were tested, more in particular ammonia (without effect), triethanolamine (TEA) at 0.2, 0.5, 1, and 5 wt.% addition, 2 and 5 wt. % of Ca (OH)2 and 0.5 and 5 wt. % of NaOH. TEA was an effective inhibitor of PCDD/F-formation, but the mineral basic substances performed even better, resulting in an almost complete suppression of 'de novo' activity for 5 % of NaOH.

The results with lime were confirmed using dust from a second metallurgical process (Waelz unit for recycling of zinc from dust arising in the iron & steel industry).

Acknowledgements

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