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INHIBITION OF PCDD/F 'DE NOVO' FORMATION BY ADDITION OF BASIC COMPOUNDS TO DUST FROM METALLURGICAL PLANTS: EXPERIMENTAL RESULTS AND DISCUSSION OF INHIBITION MECHANISMS.

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Introduction

Polychlorinated dibenzodioxins and -furans (PCDD/F) together with a variety of other chlorinated aromatic compounds are formed 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 atmosphere¹⁰ or by addition of basic compounds e.g. triethanolamine^{7,9}, or of sulfur dioxide⁸ 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

The experimental and analytical procedures were described elsewhere, in contributions discussing the effect of reaction time and temperature on the 'de novo' formation of chloroaromatics.

The experiments with ISP-field II 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 NH₃(aq)/mL, gas flow: 50 mL/min).

Results and Discussion

Inhibition of PCDD/F formation on dust samples of an iron ore sinter plant (ISP): results.

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 elsewhere⁵. 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.

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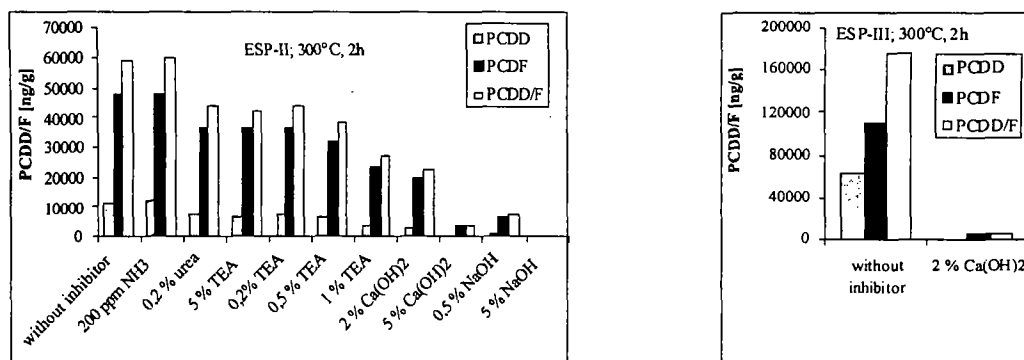
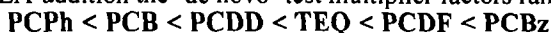


Figure 1: PCDD/F concentration [ng/g] after thermal treatment of dust material of the ESP – II and III of an iron ore sinter plant with and without addition of a basic compounds at 300 °C and 2 hrs.

The various inhibitors tested not only reduce dioxins, but also related chloroaromatics; **Figure 2** shows a parallel evolution for TEQ, PCB, PCDD, PCDD/F, PCDF when applying different doses of TEA, and of PCBz and PCPh. Especially the latter deviates 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. 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**. It follows that inhibition is often also accompanied by a lower level of chlorination.

Discussion: The sample from field 2 is very active during a 'de novo' test, the original TEQ-values being multiplied by a factor of ca. 600 for gas + solids, or a better defined 14.2 for the solids alone. Addition of TEA to the air stream progressively decreases the solids' load, whereas the total (gas + solids) shows a minimum value when 1.0 vol. % of TEA is added. Similar results are obtained for PCDD, PCDF, PCBz, PCPh, PCB, although some differences also appear, most notably for PCPh in the presence of strong bases; moreover the gas phase fraction strongly decreases by a 0.2 % addition of TEA, less so at higher addition volumes. For the standard test, as well as after TEA-addition the 'de novo' test multiplier factors rank as follows:



The original sample **homolog profile** is comparable to that of MSW-incineration, with maximum concentrations of HpCDD for PCDD, of PeCDF for the PCDF. Annealing (no TEA-added) has a marked dechlorinating effect, leading to maxima of PeCDD for the PCDD, and of TCDF for the PCDF; addition of TEA somewhat further enhances dechlorination. The **PCDD/PCDF-ratio** decreases with rising TEA-addition and is lower for the gas phase than for adsorbed to solid values, because of the lower PCDD-volatility. According to the 'de novo' theory (in its simplest form) **PCDD, PCDF, PCBz, PCPh and PCB** are formed by parallel reactions.

From this data it follows that the inhibition by TEA and by mineral bases affects the different chloroaromatics differently.

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Hence the interest for their relative value in the inhibited systems:

| Ratio | PCDD/PCDF | PCBz/PCDF | PCPh/PCDF | PCB/PCDF |
|-----------------------------------|------------------|---------------|----------------|-----------------|
| Original sample | 0.557 | 4.22 | 8.02 | 1.20 |
| After Annealing for 2 h at 300 °C | 0.232 | 9.08 | 0.424 | 0.296 |
| Id., with 2 % Ca(OH) ₂ | 0.154 | 11.2 | 0.506 | 0.210 |
| Id., with 5 % Ca(OH) ₂ | 0.114 +/- 0.0195 | 30.6 +/- 4.52 | 1.73 +/- 0.256 | 0.739 +/- 0.342 |
| Id., with 0.5 % NaOH pulverized | 0.157 | 23,0 | 0,973 | 0.563 |
| Id., with 5 % NaOH pulverized | 0.206 | 35,2 | 2.38 | 0.928 |
| Id., with 5 % NaOH solution | 0.254 | 7.40 | 1.84 | 2.195 |
| Id., with 0.2 % TEA-addition | 0.221 | 7.23 | 0.136 | 0.321 |
| Id., with 0.5 % TEA-addition | 0.206 | 7.77 | 0.281 | 0.347 |
| Id., with 1 % TEA-addition | 0.181 | 11.7 | 0.391 | 0.309 |
| Id., with 5 % TEA-addition | 0.173 | 5.24 | 0.051 | 0.056 |

Table 1: The Ratio of PCDD to PCDF, PCBz to PCDF, PCPh to PCDF, and PCB to PCDF; original sample, and after thermal treatment with and without addition of inhibitors; all values at 300 °C and 2 h.

The level of chlorination

TEA does not significantly affect the average level of chlorination: PCDF remains unchanged, PCDD and PCPh show only a small decline, and PCBz seems to be even higher chlorinated upon TEA addition.

The toxicity reduction factor allows to assess in how far I-TEQ is representative for PCDD/F. A usual value in MSW-incineration is 50 to 60, corresponding to fairly high levels in chlorination of PCDD/F. The values of the ISP tend to be lower, mainly reflecting lower levels of chlorination.

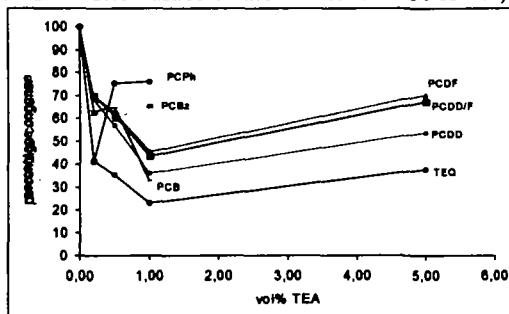


Figure 2: Percentage reduction of the 'de novo' yield of TEQ, PCB, PCDD, PCDD/F, PCDF, PCBz and PCPh, upon applying different doses of TEA compared to those obtained during a standard test, i.e. annealing at 300 °C for 2 hrs.

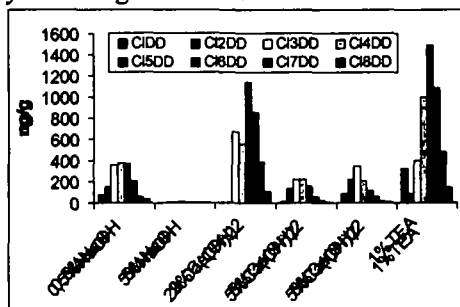


Figure 3: Addition of basic substances, full range of MCDD through OCDD

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

MINIDIP successfully addressed the problem of dioxin emissions from Waelz plant (using a two stage lignite coke adsorber).

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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 2: 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 5wt.% 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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