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'DE NOVO' TESTING OF DUSTS, COLLECTED IN SUCCESSIVE FIELDS OF AN ELECTROSTATIC PRECIPITATOR OF A SINTERING PLANT. (II) EFFECT OF REACTION TEMPERATURE.

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Introduction

The effect of temperature (200 to 400 °C, h) has been studied on the 'de novo' rates of formation of PCDD/F, PCBz, PCPh, and PCB from residual carbon in dust, collected in field 2 of an electrostatic precipitator cleaning the off-gas from an iron ore sintering plant. The chloroaromatics distribution and fingerprint has been analyzed at a fixed reaction time period of 30 minutes. Samples from field 1, 2, and 3 also have been tested in the same set-up, but at temperatures stepwise increased from 200 °C to maximum 800 °C. The results from these 'ballistic' experiments are compared to those of the isothermal ones. The former allow to reach higher 'de novo' formation temperatures than achievable during isothermal testing.

Materials and Methods

A sample II from ESP field 2 from a sintering plant is heated isothermally at various temperatures for 30 minutes in a stream of synthetic air, with normal composition: 20-21% oxygen in nitrogen. The original sample load of chlorinated aromatics is determined prior to the test and again after annealing at a temperature ranging from 200 to 400° C. Part of the chlorinated aromatics are volatilised and eventually condensed or adsorbed and separately analysed.

In a series of 3 'ballistic tests' the temperature every 10 minutes is increased stepwise by 50 °C and the resulting volatile chloroaromatics are analyzed; the temperature/time evolution is as follows:

Table 1: Temperature/time Relationship

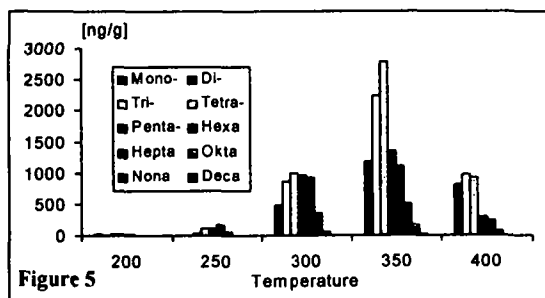
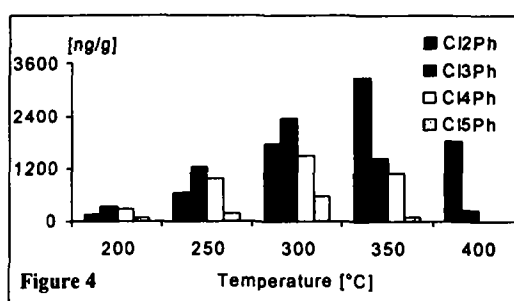
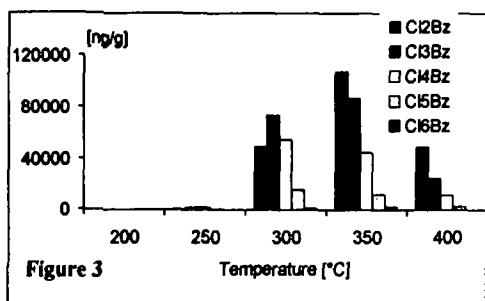
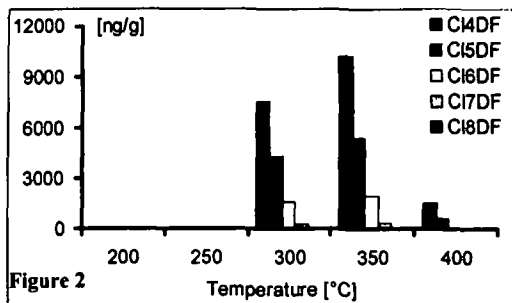
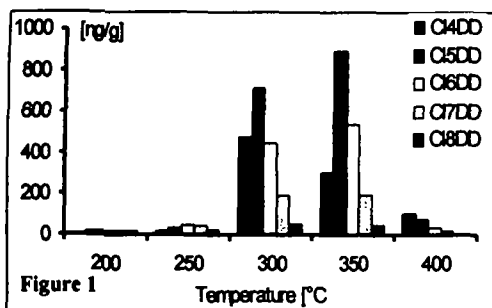
Sample	Temperature Programme
Field 3	Temperature rising from 200 to 600 °C in successive 50 °C steps; at 600 °C the test is halted, the sinterplate being clogged by volatile salts
Field 2	Temperature rising from 200 to 450 °C in 50 °C steps, every 10 minutes, followed by an isothermal soaking period at 450 °C for 70 minutes
Field 1	Temperature rising from 200 to 800 °C in successive 50 °C steps spread over 2 h

See also 'DE NOVO' TESTING OF DUSTS, COLLECTED IN SUCCESSIVE FIELDS OF AN ELECTROSTATIC PRECIPITATOR OF A SINTERING PLANT. (I) EFFECT OF REACTION TIME.

Results and Discussion: A) Isothermal experiments at 200, 250, ..., 400 °C.

The formation of chloroaromatics at 200, 250, ..., 400 °C is presented in **Figure 1** (PCDD), **2** (PCDF), **3** (PCBz), **4** (PCPh) and **5** (PCB) for a constant reaction time of 30 minutes. During annealing of the sample extensive 'de novo' activity takes place, starting at a temperature of 200 °C (Table 1). The maximum in 'de novo' activity is reached at 350 °C, except for PCPh (300 °C). The amount of chloroaromatics thus is multiplied by a factor of about 10 for PCPh, 40 for PCDD, 100 for I-TEQ, 200 for PCDF, and 700 for PCBz when compared to original load.

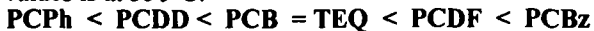
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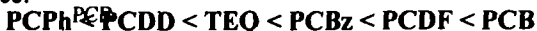
The resulting chloroaromatics are largely found in the gas phase, but PCPh adsorbs much stronger than the others, especially at low temperatures. Remarkably, the solids' load in TEQ is lower at 200 °C than for the original sample, suggesting that already at 200 °C some PCDD/F-desorption takes place, prior absorption having occurred at temperatures down to 120 °C.

Tests were reproduced in duplicate at 300 °C, in triplicate at 250 °C.

The 'de novo' multiplier is given in Table 1, showing the following sequence of the total (gas + solids) multiplier values is at 350°C:



The fraction of the chloroaromatics in the gas phase (which rises with reaction time) shows the following sequence:



which is contrary to expectations on a basis of relative volatility. This result suggests a strong chemisorption of PCPh on the particulate. Further analysis involves a consideration of the various compounds individually, since volatility rapidly declines with rising level of chlorination.

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Values (ng/g)		'de novo' multiplier							
Sample	Initial values	200°	250°	250°	250°	300°	300°	350°	400°
TEQ	3.49	1.29	90.7	2.00	2.76	95.7	126	107	10.3
PCDD	47,2	1.16	32.1	2.64	3.39	39.5	39.7	41.6	4.47
PCDF	84,8	1.80	133	2.47	3.64	149	174	210	26.2
PCBz	358	1.23	15.2	11.4	14.0	490	546	710	248
PCPh	680	1.21	4.45	5.36	4.59	13.6	9.10	8.74	3.07
PCB	102	1.00	5.29	3.61	6.52	24.7	65.8	91.5	32.7

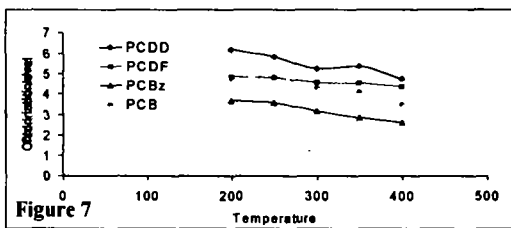
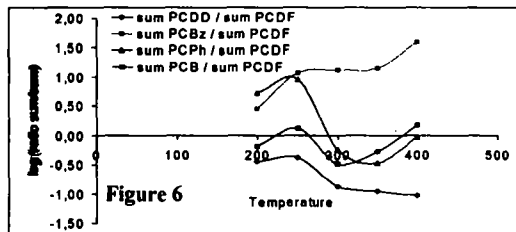
Table 1: the 'total gas + solids' multiplier

Sample	200°	250°	250°	250°	300°	300°	350°	400°
TEQ	0.74 5	2.36	1.60	1.51	18.6	24.8	4.26	0.12 8
PCDD	0.89 5	2.94	2.10	2.63	8.27	9.38	1.99	0.05 4
PCDF	0.76 7	2.37	1.57	2.22	22.3	28.3	7.35	0.24 2
PCBz	0.56 1	3.25	1.66	1.37	26.4	27.0	13.5	1.14
PCPh	1.14	2.75	2.69	3.28	3.07	3.39	0.20 4	0
PCB	0.55 7	0.78 1	1.38	6.04	2.99	3.92	2.36	0.36 8

Table 2: the 'adsorbed to solids' multiplier

The Ratio of PCDD to PCDF, PCBz to PCDF, PCPh to PCDF, and PCB to PCDF

According to the 'de novo' theory (in its simplest form) PCDD, PCDF, PCBz, PCPh, and PCB are formed by a set of parallel reactions. Hence the interest in establishing the above ratios. The latter are shown in Figure 6 as a function of temperature: it follows that PCBz predominate at high temperatures mainly, that PCPh and PCDD are related in their temperature evolution and that PCDF and PCB evolve rather similarly.



The level of chlorination

The average weight level of chlorination decreases when plotted as a function of temperature. (Note that these numerical values are biased by the absence of MCBz, MCPh, MCB, and MCDD/F through TrCDD/F). Figure 7 gives the level of chlorination as a function of temperature.

B) Results from ballistic testing

Field 3 material is the most reactive sample, followed by field 2 and 1; the sequence of rising activity coincides with rising level of heavy metals and chlorides.

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There is extensive 'de novo' formation with the following characteristics:

- 1) maximum activity typically occurs at 350 to 400 °C and/or at 400 to 450 °C; the ballistic mode of operation shifts the results towards higher temperatures;
- 2) the initial load is much higher for field 3 material than for field 2 or 1, but also the total multiplier obtained during annealing is often higher (see Table 3 for field 3 material). The multiplier of field 2 and 1 (not shown) are similar, PCBz and PCB excepted;
- 3) The level of chlorination is surprisingly constant for all chloroaromatics when plotted as a function of temperature. Chlorinating activity in Eu 13 is possibly enhanced by a high salt content, in Eu 11 by a high iron oxide content (an oxidation catalyst).
- 4) The toxicity reduction factor and the contribution of 2,3,4,7,8-PeCDF to TEQ vary erratically with temperature, without any clear trend.

Table 3: Temp. range of max. de novo activity, total amount formed and de novo multiplier

Class	TEQ	PCDD	PCDF	PCBz	PCPh	PCB
Max. rate of 'de novo' formation, at	350 - 450	400 - 450	350 - 400	300 - 350	350 - 400	350 - 400 °C
Total amount formed, ng/g	994 1-TEQ	10 200	35 300	706 000	79 300	17 100
Multiplier	346	352	419	503	29	229

Conclusions

In a series of isothermal tests (200, 250, ..., 400 °C) on an electrofilter dust sample from a sintering belt it is found that 350 °C is the temperature of highest 'denovo' activity, at least for a reaction time of 2 h. Only PCPh and - to some extent - shift this maximum towards 300 °C. Most of the chloroaromatics are in the gas phase, with PCPh showing a surprisingly strong adsorption. The results are briefly compared with those from ballistic tests, in a temperature range from 200 to 800°C, and involving samples from 3 successive fields.

Acknowledgements

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