Dioxins from the Sintering Process. (II) Samples and their propensity to form Dioxins, as derived by a 'de novo' laboratory test.

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Introduction

In a first contribution attention was paid to the PCDD, PCDF, PCBz, PCPh, PCB and PAH-load of samples, consisting of the sinterbelt feedmix, siftings gathered from various hoppers along the collector duct under the belt and later size classified, and fly-ash samples from successive E-filter fields. It was found that the dioxin load was surprisingly constant among the samples, the dust from the last E-filter field excepted. In this paper the same samples are 'de novo' tested, i.e. exposed for 2 hours at 300°C to a moist air stream, then the new charge is established for all the above compounds, as well as their amounts volatilised during the test. The purpose of the test is to compare the activity of the samples, i.e. the extent of additional formation and/or destruction under standardised conditions, selected to obtain maximal dioxin formation.

Materials and methods

One feed sample, grate siftings from 4 different positions along the sintering belt, corresponding to off-gas temperatures measured below the belt at ambient (ignition zone), 140 +/- 20 °C (middle of the temperature rise), 320 °C (3/4 of finishing), and 315°C (cooling). The following conditions were tested : 2h, 300°C, 50 ml/min. of synthetic air, with 150 mg moisture/l. Two other samples were tested for 1h, 300°C, 200 ml/min., with 10 vol.% moisture.

Results and Discussion

The PCDD/F values in the original samples are 2 to 3 orders of magnitude lower than for MSW-incineration (except for the field 3 dust) and also the precursor values seem quite low. After annealing, however, there is marked change for some samples : PCDD/F are multiplied by 100 for dust samples, 10 during cooling and not at all during roasting. Dramatic effects occur similarly for the other compounds, but not always similarly for all samples or sample groups :

Compounds	Range siftings (feed), ng/g	Range in E-filter dust, ng/g
PCDD/F	0.45 – 7.34 (feed 1.95)	1.36 – 2240
PCBz	<1 – 31 (feed 2)	217 – 9600
PCPh	<1 – 16 (feed < 1)	97- 3270
PCB	12 – 90 (feed 52)	89- 777
PAH	140 – 12100 (feed 668)	2625- 26800

Table 1 : Range of values of the original load of the sinterbelt siftings (and the feed) and the E-filter dust. The low values are from field 1 and 2, the high from field 3.

Compounds	Range siftings (feed), ng/g	Range in E-filter dust, ng/g
PCDD/F : baking cooling	1.69 – 6.07 (feed 2.9) 4.96 -30.9	160 – 176,000
PCBz : baking cooling	<1 – 134 (feed 5) 37- 2810	4440 – 575,000

PCPh : baking cooling	<1 - 4 (feed < 1) 2 - 3	44- 32,500
PCB : baking cooling	68 – 155 (feed 81) 26 - 81	182- 32,200
PAH : baking cooling	140 – 12100 (feed 119) 25 - 305	565- 255,000

Table 2 : Range of values of the total (i.e. adsorbed + volatilised) 'de novo' load of the sinterbelt siftings (feed) and the E-filter dust after a standardised test. The low values are from field 1 and 2, the high from field 3.

Compounds	Range siftings (feed), ng/g	Range in E-filter dust, ng/g
PCDD/F : baking cooling	0.84 – 3.18 (feed 2.09) 1.33 – 7.84	1.96 – 5240
PCBz : baking cooling section	<1 – 112 (feed 5) 6 - 11	158 – 4790
PCPh : baking section cooling	<1 - 4 (feed < 1) 2 - 3	15 - 711
PCB : baking cooling	20 – 155 (feed 48) 12 - 67	88 - 1004
PAH : baking cooling	<1 – 2260 (feed 119) 16 - 274	320- 2480

Table 3 : Range of values of the adsorbed 'de novo' load of the sinterbelt siftings (feed) and the E-filter dust. The low values are from field 1 / 2, the high from field 3.

Comparison of Tables 1, 2 and 3 shows the following :
the values in Table 2 for PCDD/F still compare with those in Table 1 and show even lower spread than the original charge; in other words, the dioxin load of different samples becomes even more similar after annealing for 2hours at 300°C ;
surprisingly the test yields 3-5 times higher dioxin loads for cooling samples than for the baking ones, despite a process linked lower content of carbon and (volatile) chlorides and heavy metals ;
annealing increases the load of PCBz, especially at the end of the sinterbelt ;
PCPh remain very low aand become even lower after annealing ;
PCB increase slightly during baking;
PAH decrease by annealing ;
Dust from field 3 assumes high values after annealing ; apparently it shows an appropriate composition and structure for dioxin, PCBz, PCPh and PCB generation ;
From Table 3 it follows that, for the dust exhibiting these high annealing values, only little remains adsorbed and the bulk of the products reports to the gas phase.
It can be concluded that annealing the various sinterbelt samples and the feed leads to sizeable 'de novo' formation for PCBz, especially when cooling ; dioxins (PCDD/F) show little 'de novo' formation for materials being sintered, but more so for the ones taken during cooling ; the reverse picture holds for PCB, with an increase during sintering and unchanged values during cooling; PCPh do not seem to play an important role at all, whereas PAH are destroyed by annealing.
Attention was paid to the (weight) average level of chlorination; the values obtained are summarised in the next Table 4:

Compound	PCDD	PCDF	PCBz	PCPh
Feed	5.98	4.74	2	n.d.

Ignition	6.42	5.24	3.33	n.d.
Baking 1/2	6.15/5.81	5.50/5.68	n.d.	n.d.
Baking 3/4	6.40/6.35	5.19/5.33	3.18/3.06	n.d.
End	6.62/5.40/ 5.39	4.84/4.58/4.64	3.06/2.43/2	4.38/4.13/n.d.

Table 4. average (weight) chlorination level of various compounds, in order of increasing particle size, where more than 1 value is given.

Since the general fingerprint is a 'thermal' one this indicates that 'de novo' formation by carbon gasification is more important than from precursors, such as PCPh. On the other hand, PCBz seems to be a good surrogate for dioxins.

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