Dioxins from the Sintering Process. (III) Operating factors influencing upon 'de novo' formation of field 2 dust

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Introduction

After studying the original load of various samples and their behaviour during 'de novo' tests it is logical to study the various factors that influence upon dioxin 'de novo' formation, int.al. temperature, oxygen content of the gas. For that purpose field 2 dust was selected and the relevant operating conditions were varied systematically.

Materials and Methods

Field 2 material is only moderately charged with dioxins, but displays a strong 'de novo' formation potential. For that reason it was selected for further study :
the temperature in the 'de novo' test was varied, with temperatures of 200, 250, 300, 350, 400 °C and exposure to a synthetic moist air stream for ½ hour ;
in the process a previous 300°C test was duplicated, but using a shorter period of treatment, which allows to assess the effect of time within 'de novo' tests ;
the gas phase composition of synthetic moist air was changed to an oxygen lean atmosphere, with a composition of :

Compound	CO2	O2	H2O	N2
Vol., %	85.1	2.3	3.5	9.1
	78.3	3.7	2.6	15.4

Table 1 : operating conditions for studying the effect of oxygen on 'de novo' formation

a test was conducted with addition of ammonia to the synthetic air ; other inhibitors were also tested.

Results and Discussion : effect of temperature

The effect of the temperature is clearcut : there is some activity already as low as 200°C, but a relatively high activity is obtained throughout a wide range of temperatures for PCDD/F, PCDD, PCDF, PCBz, PCPh, PCB. Technically, the data are given in Table 2 :

Compound	PCDD	PCDF	PCBz	PCPh	PCB
Original load	47.2	84.8	358	680	175
Annealed at 200°C	54.95	152.8	439	821	643
At 250°C	1515	11280	5450	3025	1520
At 300°C	1870	12600	175500	9230	6840
At350°C	1970	17800	254300	5940	44630
At 400°C	211	2220	88900	2090	5090

Table 1 : annealing values (ng/g) for ½ h at various temperatures.

A maximum is reached at 350°C for all compound classes , except for PCPh (300°C).
The multiplication factor due to annealing, however, is unlike for the various compounds : Table 2.

Compound	PCDD	PCDF	PCBz	PCPh	PCB
Original load	100	100	100	100	100
Annealed at 200°C	116	180	123	121	367
At 250°C	3210	13302	1522	445	869
At 300°C	3962	14858	49022	1357	3909
At350°C	4174	20991	71034	874	25503
At 400°C	447	2618	24832	307	2909

Table 2 : annealing values (ng/g) for ½ h at various temperatures, normalised to the original load (= 100)

The PCDD/F, PCDD and PCDF-values can be fitted well by an empirical quadratic relationship : Figure 1.

Compounds	Relationship	R2-value
PCDD/F, total	$(PCDD/F) = -165231 + 1220.5\,t - 1.9961\,t^2$	0.945
PCDD/F, gas phase	$(PCDD/F) = -160234 + 1183.1\,t - 1.9344\,t^2$	0.9493
PCDD/F, adsorbed	$(PCDD/F) = -4997.4 + 37.447\,t - 0.0617\,t^2$	0.7566
PCDD, total	$(PCDD) = -17470 + 130.11\,t - 0.2143\,t^2$	0.9794
PCDD, gas phase	$(PCDD) = -16565 + 122.85\,t - 0.2018\,t^2$	0.974
PCDD, adsorbed	$(PCDD) = -904.28 + 7.2603\,t - 0.01125\,t^2$	0.9766
PCDF, total	$(PCDF) = -147765 + 1090.5\,t - 1.7818\,t^2$	0.94
PCDF, gas phase	$(PCDF) = -143668 + 1060.2\,t - 1.7326\,t^2$	0.9461
PCDF, adsorbed	$(PCDF) = -4096.6 + 30.212\,t - 0.0492\,t^2$	0.6508

Table 3 : correlations of PCDD/F as a function of temperature (t, °C)

Similar correlations can be established for PCBz, PCPh, PCB, but their goodness of fit is lower. Remarkably, most of the ‘de novo’ products are found in the gas phase.
For rising temperatures the (weight) average chlorination level declines, as follows from Figure 2.
In another test the various compound classes were ‘de novo’ formed ballistically, with a heating rate of 6,25 °C/minute in the interval 200-450°C, followed by 80 minutes at 450°C, to complete the usual 2h annealing period ; the following result is obtained :

Compounds	PCDD	PCDF	PCBz	PCPh	PCB
200-250 °C	2.14	2.20	< 1	< 1	1412
250-300 °C	11.68	62.18	6537	742	1116
300-350 °C	162.5	1592	93620	2213	4193
350-400 °C	570.9	5424	181700	4399	10300
400-450 °C	45.21	481.8	18580	117	4297
450 °C	40.75	605.3	13220	< 1	1962
Sum	833.18	8167.48	313657	7471	23280

Table 4 : compounds liberated during a ballistic heating test

Standardising with respect to the total amount yields the following results :

Compounds	**PCDD**	**PCDF**	**PCBz**	**PCPh**	**PCB**
200-250 °C	0.3	0.0	0.0	0.0	6.1
250-300 °C	1.4	0.8	2.1	9.9	4.8
300-350 °C	19.5	19.5	29.8	29.6	18.0
350-400 °C	68.5	66.4	57.9	58.9	44.2
400-450 °C	5.4	5.9	5.9	1.6	18.5
450 °C	4.9	7.4	4.2	0.0	8.4
Sum	100	100	100	100	100

Table 5: compounds liberated during a ballistic heating test, standardised data

Obviously 350-400°C is the most dangerous temperature range ; already at 450°C the net (i.e. formation – destruction) ‘de novo’ activity declines. The above test thus simulates the transition phase between drying and ignition. There is more similarity between compound classes than during the previous test series.
In a supplemental test the ignition will be simulated.

The oxygen concentration level of the off-gas has a marked influence upon the ‘de novo’ formation :

Compound	**Original**	**Annealed, air**	**Annealed, 2.3 %O_2**	**Annealed, 3.7 %O_2**	**Annealed NH_3**
PCDD	1.8	14197	177.7	2061	13690
PCDF	3.2	53600	1102	9178	48080
PCBz	217	329700	41680	169100	467300
PCPh	565	18802	4568	16920	26770
PCBz	101	15860	11410	11290	35400
PAH	17460	19740	10240	7652	16880

Compound	**Original**	**Annealed**	**Annealed, 2.3 %O2**	**Annealed, 3.7 %O2**	**Annealed NH_3**
PCDD	100	788722	9872	114500	760556
PCDF	100	1675000	34438	286813	1502500
PCBz	100	151935	19207	77926	215346
PCPh	100	3328	808	2995	4738
PCBz	100	15703	11297	11178	35050
PAH	100	113	59	44	97

Ammonia addition only slightly inhibits dioxin formation.

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