Dioxins from the Sintering Process. (V) Characterisation, analysis and 'de novo' testing of Samples. Statistical correlations

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Introduction

With the purpose of identifying the factors that influence upon dioxin formation the effect was studied of temperature, of time, of oxygen, hydrogen chloride, activated carbon addition, ammonia inhibitor addition. The most important results are :
PCDD/F-formation as low as 200°C, with a clear maximum formation rate occurring between 250 and 350°C ;
Similar results are obtained for the other compound classes, but with slight shifts in their favourite temperature domain :
PCB show a sharp maximum at 350°C,
PCBz have a maximum at 350°C, but high activity at 300°C,
PCDF have a maximum at 350°C, but high activity at 300 and 250°C,
PCDD have a maximum at 350°C, but similar activity at 300 and 250°C,
PCPh have a maximum at 300°C, but activity in the same temperature domain as the others,
This suggest analogous rather than identical modes of formation ;
The 'de novo' formation follows approximatively a first order law in oxygen ;
The addition of HCl and activated carbon enhances (de novo' formation, but not to a dramatic extent ;
Ammonia is only a weak inhibitor, if effective at all ;

In order to study the reason for such differences statistical as well as analytical and instrumental methods were applied.

Materials and Methods

For the various samples organic halogen AOX and extractable organic halogen EOX were established, as well as total carbon TC, total organic carbon TOC, total inorganic carbon TIC ; moreover Differential Scanning Calorimetry was used for determining temperature effects while heating the samples.

Results and Discussion

The available AOX and EOX-values fall broadly in 2 groups :1) the feed and the grate siftings, and 2) fly-ash samples :

Sample	AOX before annealing	AOX after annealing	EOX volatiles	PCDD/F before annealing
Feed	40.9	31.9	11	1.95
Sintering belt				
ignition	18.9	21.6	8.7	7.34
baking, ½	n.d.	n.d.	n.d.	n.d.
baking, ¾	69.4/65.1	52.4/62.2	12.7/46.3	2.89/3.96
cooling	54.8/39.4/22.6	42.9/35.6/28.9	17.1/ 7 /8.8	4.01/6.45/1.73
Electrofilter dust				
field 1	122.5	86.9	5.9	1.355
field 2	746.9	500.8	611.2	5.025
field 3	957/1897	779/699.4	203/1725	113.4

Table 1: Values for AOX (prior to and after annealing), EOX(volatile fraction), and PCDD/F (before annealing).

Correlations were established between a) AOX-values and PCDD/F before annealing, b) AOX-values and PCDD/F after annealing and c) EOX-values and volatile PCDD/F with the following results :

	AOX	EOX	TOC	TC	TIC
Sum PCDD/F	0.3273	0.9933	-0.2226	-0.2896	-0.4064

Table 2: results of correlation

One problem with this correlation is that the dust samples are chemically much different from the others, especially samples field 3 and 2. The correlation PCDD/F is basically determined by the field 3 data, most others are well grouped. The 2 values for field 3 samples are from samples taken on different dates, probably with other composition, and most distinct in their original load and 'de novo' potential.

Similarly, it follows from the previous Table that there is poor and negative correlation between TC, TOC, TIC-values and PCDD/F. Total, inorganic and organic carbon also yield information on

the extent of burn-off during sintering and the composition of the entrained dust. Values for carbon (TC, TOC, TIC) are given in Table 3.

Parameter	TC,before	TC,after	TOC,bef.	TOC,after	TIC, bef.	TIC,after
Feed	3.28	2.94	n.d.	n.d.	n.d.	n.d.
Ignition	1.68	2.6	1.57	2.47	0.11	0.13
Baking1/2	n.d.					
Baking, ¾	1.47/2.15	1.13/1.61	1.09/1.74	0.85/1.16	0.38/0.41	0.28/0.45
Cooling	1.52/1.27/1.03	1.57/1.20/0.93	0.81/0.82/0.33	0.77/0.80/0.42	0.71/0.45/0.70	0.80/0.40/0.51
Field 1	4.23	3.14	3.7	2.77	0.53	0.37
Field 2	3.38	2.34	3.15	2.03	0.23	0.31
Field 3	1.47/2.53	1.13/0.62	-/2.51	-/0.6	-/0.02	-/0.02

Table 3 :TC, TOC, TIC-values prior to and after annealing

The carbon removal by annealing is limited and not so reproducible.

Finally, it seems interesting to verify the quality of correlations between PCDD, PCDF, PCBz, PCPh, PCB and PAH. This leads to the following results:

Correlation of PCDD/F with	Polychlorobenzenes PCBz	Polychlorophenols PCPh	Polychlorobiphenyls PCB
Correlation Parameter, R2	0.682	0.6325	0.6075

Table 4: correlation parameter R2 between compound classes

Also PAH are correlated with PCDD/F, but the R2-value is only 0.3466.

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