

Dioxins from the Sintering Process. (IV) Characterisation, analysis and 'de novo' testing of sintering belt siftings. Influence of temperature, hydrogen chloride and activated carbon addition.

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Introduction

In a previous contribution the effect of various operating conditions upon the 'de novo' dioxin formation potential was studied. This contribution similarly deals with that of sintering belt material, more precisely grate siftings collected from hoppers situated along the sintering belt and from cooling the sinter

Materials and Methods

For the *de novo* experiments with sinter belt material, 5g of the individual samples were filled in a horizontal quartz reactor and subjected to heat treatment. The composition of gas phase was chosen analogous to air (20%O₂/70%N₂/10%H₂O and addition of 1000ppm HCl in the respective runs) with a flow rate of 200ml/min. For the experiments with the addition of activated carbon (AC), the samples were mixed with 2% fine grind Activated Carbon (WAKO Pure Chemical Industries, Ltd., Japan).

Details about clean up and analysis methods used for the experiments with sinter belt samples are reported elsewhere [1,2].

Results and Discussion

PCDD/F formation potential of the sinter belt material

To test the material sampled on the sinter belt with respect to PCDD/F concentration and *de novo* formation potential, we chose a sample of siftings from the early stage of the sinter belt process (unreacted material = sample A) and compared it to a sample from the finished sinter (fully reacted Sample X).

The PCDD/F concentration in sample A was about 7.5ng PCDD/F, 0.14ng-TEQ/g, almost identical to the value established at FZK (7.34ng). Sample X, 0.18ng PCDD/F and 0.007ng-TEQ/g (tab.1), for reasons unknown, was much lower than previously established FZK-values, of 4, 6.45, and 1.73 ng PCDD/F/g. The isomer pattern and the homologue distribution in the samples were comparable to those found in fly ashes from waste incineration.

During heat treatment (1h) in the presence of air, sample A did not show significant *de novo* formation (tab.1), the PCDD/F amount and TEQ value after 1h heat treatment at 300°C did not change significantly (-12 %). When increasing the temperature to 335 and 370°C (1h) we found already a significant destruction of PCDD/F (at 370°C 70% of starting PCDD/F were destroyed). Sample X showed a very low initial load but significant *de novo* potential in the heat treatment (tab.1). However the PCDD/F amount was still less compared to sample A.

Therefore the PCDD/F concentration and the *de novo* formation potential of these sinter belt samples is two to three orders of magnitude lower compared to fly ashes from MSW-incineration.

To test the limiting factor in the PCDD/F *de novo* formation potential of the sinter belt samples, we also investigated the influence of gas phase HCl and the effect of the addition of activated carbon (an excellent carbon source for PCDD/F formation [3]) on the sinter belt sample A. When the gas phase contained HCl (1000ppm/300°C/1h), which is 1-2 orders of magnitude more than the HCl (or, more exactly chlorides) present in the off-gas (after dust collection) the PCDD/F amount (15.5 ng/g) and the TEQ value (0.3ng/g) only doubled. With the addition of activated carbon (2wt%/300°C/1h) we found again a marked increase in PCDD/F amount (24ng/g) and of the TEQ (0.44ng/g). When subjecting the activated carbon spiked sample to the heat treatment at 300°C in the presence of HCl we observed a further increase (tab1.). However, the most impressive increase of PCDD/F we observed when performing the same experiment at 370°C (1h). The resulting PCDD/F amount (160ng/g) and TEQ value (5ng/g) in this experiment is already comparable to PCDD/F amounts found in fly ashes.

Therefore two limiting parameters of these sinter belt samples are the "quality" of the present carbon and the Cl-source. In another paper oxygen was also identified as an essential factor. In the first assessment of correlation of plant parameters in respect to total PCDD/F formation, the most significant parameter was indeed the HCl concentration. However with a factor of ($r=0,3$) also this correlation was only weak.

The total carbon found in sinter plant samples range widely . In our estimation the quality of the carbon may also play a significant role on the PCDD/F amount formed and therefore needs further detailed investigations. In the course of DSC-study of the various samples it was often noticed that there are 2 temperature domains of carbon oxidation. Similar, but non-identical results can be inferred from the weight losses established for electrofilter dust samples, from field 1, 2, and 3, using thermogravimetric analysis.

The PCDD/F concentration on the belt material has to be judged in respect to the amount actually found in off gas from the sinter plant. The mass balance recalculation of 3-15ng-TEQ/Nm³ correspond to 0.12-0.6 ng/g sinter material. Therefore the actually found 0.14ng-TEQ in sample A and the 0.007-0.04ng-TEQ in sample X can be regarded as significant in respect to the final PCDD/F concentration in the off-gas.

sample	T (°C)	HCl ppm	activated carbon (wt%)	PCDD (ng/g)	PCDF (ng/g)	TEQ (ng/g)
A (crude)				2.5	5	0.14
A	300			2.2	4.2	0.14
A	335			1.7	3	0.10
A	370			1.2	2.3	0.08
A	300	1000		6.5	9	0.3
A	300		2	13	11	0.44
A	300	1000	2	28	23	0.68
A	370	1000	2	52	115	5.0
X (crude)				0.047	0.184	0.007
X	300			0.3	0.86	0.03
X	370			0.3	1.78	0.042

Table 1: PCDD/PCDF amount and TEQ value of sinter belt material resulting from the *de novo* experiments during 1h heat treatment (20%O₂, 70%N₂, 10%H₂O, 200ml/min flow)

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The above data are analysed on a basis of fingerprint:

Expt.	level Average chlorination PCDD	level Average chlorination PCDF	Toxicity equivalence factor	Ratio of PCDD to PCDF
Before ann.	6.61	5.52	65.5	0.46
300°C , 1h	6.39	7.76	53.6	0.57
335°C , 1h	6.04	7.14	43.4	0.62
370°C , 1h	5.90	7.13	48.6	0.56
300°C 1h/HCl	6.00	5.14	52.2	0.72
370°C 1h/HCl	6.52	5.71	41.2	1.22
300°C 1h/HCl AC	5.63	5.60	54.7	1.12
300°C 1h/HCl AC	6.70	6.34	75.7	1.22
370°C 1h/HCl AC	5.21	4.94	33.4	0.46
Expt.	level Average chlorination PCDD	level Average chlorination PCDF	Toxicity equivalence factor	Ratio of PCDD to PCDF
Before ann.	6.89	5.70	54.0	0.48
300°C 1	6.58	5.03	45.8	0.57
370°C 1	5.72	4.91	57.7	0.17
370°C 1	6.64	6.43	72.2	0.42

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