

Dioxins from the Sintering Process. (I) Particle Characterisation and SEM/wet analysis of Samples.

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Introduction

The sintering process is an essential step in an integrated iron & steel plant, since it converts ore fines as well as ferrous reverts from all over the steel plant into a porous, calibrated feedstock acceptable in the blast furnace. The feed of the process consists of a moist agglomerate of (mainly) haematite (Fe_2O_3) ores, cokes and lime or limestone, apart from recycled fractions. The heart of the process is a 50-100 m long, 3-5m wide, slowly moving, horizontal belt that supports the feed during drying, heating, coke ignition, ore sintering and cooling. The process is initiated by means of a start-up burner that ignites the feed layer on top. As the feed proceeds with the belt ambient air is aspirated downwards through the charge, so that the combustion and sintering zone slowly descend, until breakthrough signalling the end of the process. The resulting sinter then is cooled, discharged, broken and calibrated before its use in the blast furnace. Fines are recycled in the charge, together with dust removed from the off-gas from this and other plant.

The process off-gas is first collected in separate chambers, situated below the belt, then led to dust collection by large collectors. Over about half of the belt the off-gas leaves the belt only slightly above ambient (ca. 50°C), after heat exchange with the cold, moist feed layer. When carbon ignites, temperature quickly and almost linearly rises to attain a temperature of about 400°C (measured below the belt). By both sifting and entrainment particulate from the bed is conveyed by the flow of air; such siftings settle in a series of hoppers situated at the bottom of the gas collectors, from which they were sampled in this study. The temperature profile, gas velocity profile and particulate trajectories have been computed by another MINIDIP partner, BifA.

Sintering thus generates a huge flow of off-gas, composed of the combustion products from the active, burning layer, and of volatiles and moisture from the cokes, ores and other feed streams. The off-gas typically contains 15 % O_2 , 5% CO_2 , 15 g CO/Nm^3 , and (in mg/Nm^3): 300 dust, 300 SO_2 , 350 NO_x , 0-10 HCl , 0-5 HF , a trace of Cl_2 (iron oxide is an oxidation catalyst!) and, most importantly, 3-15 ng I-TEQ dioxins/ Nm^3 , but higher and lower values have also been recorded. This paper relates to some efforts devoted to the elucidation of the dioxin forming processes, that probably depend on the following factors: the carbon, chlorine, catalytic metals (Cu, Zn, Pb, ...) content of ore and recycle feed streams, the temperature/time relationship during drying, heating, sintering and cooling and in the off-gas ducts & collector, the off-gas composition, ... Assuming a temperature domain of $250\text{-}400^\circ\text{C}$ for dioxin formation, in analogy to MSW-incineration, the dust collector operates at too low a temperature (ca. 120°C) for dioxin generation. In order to explain dioxin formation two pathways can be proposed: 1) the precursor route, which proceeds over the condensation of 2 precursor (polychlorophenols, PCPh, or polychlorobenzenes, PCBz) molecules and 2) the 'de novo' carbon gasification route.

The detailed mechanism of dioxin formation on the sintering belt remains unknown. The necessary ingredients all are present in the feed, more in particular:

chlorine is introduced under the form of KCl and NaCl in the ores and under miscellaneous forms in recycle streams,

carbon is fed under the form of cokes and can be generated in situ by charring of oil and other organics from recycle streams,

catalytic metals are available in the ores ; moreover it is plausible that the bulk of the charge (Fe₂O₃ and Fe₃O₄) also exerts catalytic activity,

oxygen is derived from the stream of air, passing through the charge.

The cokes available in the charge thus is chlorinated and oxidised catalytically, at 250 to 500°C, i.e. prior to its ignition, generating a wide array of chlorinated aromatics, such as PCBz, PCPh, PCDD, PCDF, PCB, ... It is still somewhat unclear where and when formation takes place, in the bulk of the layer, or from fine, entrained particles. A plausible sequence is : 1) no formation as long as the charge is wet and cold, 2) once dry the charge is rapidly heated by a cross-flow of hot gas, containing volatile metal chlorides, that condense, supplying both the necessary chlorides (KCl, NaCl) and the catalytic metals (Pb, Zn, Cu, ...), required for 'de novo' synthesis to take place, 3) as the temperature rises further dioxins present are either volatilised and report to the off-gas or destroyed, 4) during and after ignition (> 550°C) only destruction is plausible, 5) during cooling further 'de novo' formation seems unlikely, since carbon has largely been depleted and chlorides and heavy metals volatilised. However, we found surprisingly high 'de novo' active in materials sampled from the finished sinter being cooled.

Materials and Methods

In order to investigate the extent and mode of dioxin formation the following procedure was selected :

samples were taken of sinterbed feed material, of grate siftings under the whole length of the sinterbelt, and of the dust collected in various fields of an electrostatic precipitator,

the samples were characterised with respect to particle size by sieving and dry Laser methods (fines) and by wet/SEM- chemical and microscopic analysis,

the original PCDD, PCDF, PCBz, PCPh, PCB, PAH-load of the particles was established, as well as AOX- and EOX, TC, TOC and TIC-values,

after a standard 'de novo' test the same classes of compounds were again determined, both in the adsorbed and the volatilised state. Also specific tests were conducted to assess the influence int.al. of temperature, oxygen, HCl, carbon, inhibitors, ...

statistical relations were established for the various parameters and fingerprints were analysed.

Results and Discussion

All samples analysed contained measurable amounts of PCDD, PCDF, PCB, and PAH, whereas PCBz and PCPh were only found in part of the samples, all at a ng/g level. Surprisingly little variation was found between feed, various sections of the sintering belt (including the last section) and dust collected in the first E-filter fields ; only the last field is much higher in dioxins. Also, little difference appeared between fines (< 63µ) and coarser fractions, which was contrary to expectations.

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average 5 samples from the ignition zone : 3.34 +/- 1.85 ng PCDD/F/g

average 3 samples from the last section : 4.06 +/- 1.59 ng PCDD/F/g

average 9 samples from feed, ignition and last section : 3.43 +/-1.79 ng PCDD/F/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 – 102 (feed 52)	89- 777
PAH	140 – 12100 (feed 668)	2625- 26800

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

It is remarkable that the PCDD/F and thus the TEQ-load barely vary, whatever position on the sintering belt the siftings are collected at, and whatever their particle size fraction. The former is in contrast with literature statements, that there is a definite peak in dioxin generation, coinciding with the high temperature zone (ca. 400°C), corresponding to ignition breakthrough (Pütz, Gudenau, 1996), as far as the belt siftings are typical for its load.

The 'precursors' PCBz and PCPh also are hardly affected by sample position or size fraction : PCBz rise about one order of magnitude above the feed value, whereas PCPh remains undetected until the last section. Generally, however, in MSW-incineration much higher precursor values are found. PCB-values remain remarkably constant. PAH-values vary erratically from sample to sample.

FRACTION	Feed	Dust Field 1	Dust Field 2	Dust Field 3
Fe	59	46	32	17
CaO	4.5	5	4	2
C	1.6	4.7	3.8	2.9
K ₂ O	0.02	6	8	12
Na ₂ O	0.01	1	4	8
Pb	n.d.	0.7	2.5	4.2
Zn	0.01	0.05	0.2	0.3
Cu	n.d.	0.05	0.2	0.3
Cl	n.d.	5	15	25

Table 2 : indicative values (wt.%) with respect to sinterbelt feed and E-filter dust composition.

A definitely higher load of precursors is found on the E-filter dust samples. In the first field the latter consist mainly of ore and lime particles, but in the second and especially third field chloride salts and heavy metals are becoming increasingly important (Table 2). The question thus arises : are dioxins mainly formed from the very large mass on the sintering belt (typically 500-1000 Mg/h), or are they due to the entrained particles, as in MSW-incineration ? When it comes to mass

ratio, or to residence time, the former are definitely overweight. On the other hand the reactivity of the particulate could be much higher. For that reason 'de novo' tests were conducted on the aforementioned fractions and discussed under II.

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