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Dioxins from thermal and metallurgical processes: recent studies for the iron and steel industry

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Abstract

In thermal metallurgical processes such as iron ore sintering and metal smelting operations, large flows of off-gases are generated. Mainly due to residue recycling in such processes, chlorine and volatile organics are always present in the feed. As a consequence of "de novo" formation, the off-gases from such processes typically contain dioxins in the range 0.3-30 ng I-TEQ/Nm³. So far there are only very few studies about the mechanisms of dioxin formation and destruction in these metallurgical processes. In an European Union (EU) research project "Minimization of dioxins in thermal industrial processes: mechanisms, monitoring and abatement (MINIDIP)", integrated iron and steel plant has been selected as one of the industrial sectors for further investigation. A large number of particulate samples (feed, belt siftings, electrofilter) were collected from the iron ore sintering installations from various steel plants and analyzed for their organochlorocompound contents. Measurable amounts of PCDD/F, PCBz, PCB were found for all samples. The various parameters influencing their de novo synthesis activity were also evaluated in laboratory experiments, and such activity was found to be moderate for samples from the ore sinter belt, but extremely high for some ESP dusts. Fine dust is active in a wide range of temperatures starting at 200°C and declining above 450°C; the optimal temperature for de novo synthesis was found to be around 350°C; some inhibitors, such as triethanolamine, may reduce de novo activity by 50 %, and lowering the O₂ concentration in the gas stream leads to a much lower amount of PCDD/F formation. On the basis of their relative mass, typical operating conditions and specific activity of the different samples, the regions in the sintering plant where de novo synthesis may take place were tentatively established. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Trace levels of dioxins and other chloroaromatics can be found in a variety of thermal and metallurgical processes such as metal scrap smelting, sintering plant from the iron and steel industry, cement kilns, power plant, etc. (Buekens et al., 1997a, 1998a). At present, there are still insufficient field measurement data to fully assess the extent of dioxin pollution caused by these industrial sources, the feed and plant operating parameters of influence and the primary measures to be taken for a reduction at the source, whereas more fundamental studies about the mechanisms of dioxin formation in these thermal metallurgical processes and the possible techniques for dioxin reduction are scarce. In the European Union (EU), a research programme has been initiated recently, namely, "Minimization of dioxins in thermal industrial processes: mechanisms, monitoring and abatement" (MINIDIP). The scope and contents of the

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programme have been reported by Buekens and Stieglitz (1997). In the first year of this research programme, iron and steel industry, more in particular the fine ores sintering process, has been selected for detailed investigation.

In an integrated iron and steel plant, one of the most important thermal operations is the sintering of raw iron ore, mostly hematite (Fe_2O_3). In the sintering process, a mixture of fine ores, coke, lime or limestone, and ironbearing residues (e.g. blast furnace flue dust, mill scale, scrap and other waste material recycled from within or outside the steel plant) is heated at high temperatures and sintered into a porous, calibrated feedstock acceptable to the blast furnace. In sintering operations, huge volumes of off-gases are generated (in the order of 1 million Nm³/h/plant). Since chlorine and volatile organic compounds are unavoidable in the feed materials, including the ores, coke and recycled iron-bearing residues, the off-gases from sintering and melting operations may contain dioxins in the range 3-10 ng I-TEQ/Nm³ according to Jager (1993) and Lahl (1993). In the MINIDIP project, one of our aims is to study the pathways of dioxin formation in these industrial processes and to develop technical control measures. Some first results will be reported in this paper.

2. Experimental method

A schematic of the sintering installations at the steel plant under our investigation is shown in Fig. 1. The heart of the process is a ca. 150 m long, 5 m wide, slowly moving, horizontal belt that supports the feed during drying, preheating, ignition, and ore sintering. The process is initiated by a gas/oil start-up burner that ignites the coke in the feed layer on top. As the feed proceeds with the belt, ambient air is aspired downwards through the charge, so that the combustion and sintering zone slowly descend through the layer until breakthrough, signalling the end of the process. The resulting sinter is then cooled and calibrated; the off spec. fractions are recycled, either as a bedding for the sintering layer (coarse), or in the feed (fine). The off-gases are generally led through a multiple-field electrostatic precipitator (ESP) for cleaning before being discharged via a stack. Typical operating parameters, temperature profile and off-gas compositions can be found in the schematic representation of Fig. 1. In most cases, the cooling takes place in separate equipment peripheral to the belt, which may be an important factor relative to total generation of dioxins. The temperature and oxygen field, the air distribution and flow patterns through the sintering belt all are complex, because of the cross-flow arrangement of feed and air, the hot sintering front, gradually moving downward through the burden, its variable porosity, temperature and composition (coke is depleted, lime converted into complex oxides, hematite is partly reduced, salts and volatile heavy metals are volatilised). In a cross and downward flow, ambient air is aspired through the burden by the large underpressure under the belt, rapidly preheated while cooling the hot sinter, then used for coke combustion in a thin seam, and the resulting hot off-gas is used to preheat, then dry the underlying feed. Then there are a series of windboxes/dividers and gas collectors with subjacent dust hoppers below the sinter belt. The details are not shown in Fig. 1 for simplicity but the temperature and velocity field as well as particle trajectories for different origins



Fig. 1. Schematic of an iron ore sintering plant.

and particle sizes have been computed by BifA within the same MINIDIP-programme.

In order to characterize the PCDD/F loads in the sinter material and to understand the possible PCDD/F formation processes, solid samples were collected from the sinter feed, a number of hoppers over the entire length of the sintering belt, as well as dusts discharged from the subsequent ESP-fields. Selected portions of these samples were extracted and analyzed for PCDD, PCDF, PCBz, PCPh and PCB. Other portions were then subjected to heat treatment using a fixed-bed flow reactor set-up at FZ Karlsruhe described previously by Stieglitz et al. (1989, 1991). Typical heat treatment conditions were at a temperature of 300°C for 2 h in flowing air. The sample from ESP field 2 was also tested at varied temperatures between 200-400°C, as well as varied gas atmospheres including (i) 3.7% O₂, 78.3% CO₂, 2.6% H₂O and 15.4% N₂ (in vol%); (ii) 2.3% O₂, 85.1% CO2, 3.5% H2O and 9.1% N2; and (iii) 0.1 M NH3 in synthetic air. Other inhibitors were tested as well. After the flow reactor experiments, the cold traps and solid sample were separately extracted and analyzed for PCDD, PCDF, PCBz, PCPh and PCB; those found in the cold traps are reported as gas-phase compounds while those found in the solid sample are reported as solid-phase compounds.

3. Results

Experimental data of organochlorocompound loads of all samples have been obtained for individual T_4 - to O₈CDD/F homologues, and the 17 "dirty" 2,3,7,8 chlorine-substituted congeners. Only representative data can be given in this paper. In Table 1, typical organochlorocompound loads in solid samples from the iron ore sintering plant are listed. All samples contain measurable amounts of PCDD, PCDF and PCB. The contents of PCDD, PCDF, PCBz, PCPh and PCB in samples from the sinter feed and ignition, sintering and cooling zone are low, but the contents of these compounds in the ESP dusts are high. In particular, the sample from ESP (field 3) contains 115 ng PCDD/F/g which is comparable with that reported for ESP ash from municipal solid waste incinerators (MSWI) (Johnke and Stelzner, 1992).

Data from annealing the samples at 300°C for 2 h in air are also compiled in Table 1. It can be seen that for samples from the sinter feed and ignition zone, the amounts of organochlorocompounds detected after annealing are approximately the same as before annealing. However, for the samples from sintering and cooling zone, slightly higher amounts of PCDD and PCDF were found after annealing. For the ESP dusts (in particular,

Table 1

Representative data of organochlorocompound loads (ng/g) in original solid samples taken at different positions of an iron ore sintering plant, and from samples annealed at 300°C for 2 h in air^a

Sample	PCDD	PCDF	PCBz	PCPh	PCB	
Sinter feed						
Original	0.5	1.4	2	bd.	52	
Annealed	0.8	2	5	bd.	75	
Ignition zone						
Original	3	4.4	27	bd.	61	
Annealed	2.2	3.3	43	bd.	68	
Sintering zone						
Original	0.2	0.3	bd.	bd.	102	
Annealed	0.7	1.8	bd.	bd.	113	
Cooling zone						
Original	1	5.4	14	8	15	
Annealed	6.6	24.4	37	2	31	
ESP field 1						
Original	0.4	1	612	97	89	
Annealed	58.8	102	4436	44	182	
ESP field 2						
Original	1.8	3.2	217	565	100	
Annealed	14 200	53 600	330 000	18 800	16 000	
ESP field 3						
Original	29	84	1405	3267	117	
Annealed	644 500	111 400	575 500	32 500	32 150	

^a bd. – below detection limits (1 ng/g); annealed – sum of gas-phase and solid-phase compounds.

Table 2 Typical PCDD/F formation rates

Sample	Formation rate (ng-PCDD/F/g min)
Sintering	0.017
Cooling	0.205
ESP field 1	1.33
ESP field 2	565
ESP field 3	6300

those from fields 2 and 3), significantly higher amounts of PCDD, PCDF, PCBz, PCPh and PCB were found; these compounds were probably formed from de novo synthesis reactions during the heat treatment similar to that in MSWI fly ash first observed by Stieglitz and Vogg (1987, 1989). From the data in Table 1, the PCDD/F formation rates have been calculated and listed in Table 2. The PCDD/F homologue profile and 2,3,7,8 chlorine-substituted congener pattern from annealing the ESP (field 3) sample are shown in Figs. 2 and 3, respectively. They belong to the so-called thermal "fingerprint" of dioxins (Buekens et al., 1998a).

Experimental data from annealing the ESP (field 2) sample at different temperatures for 0.5 h in air are

compiled in Table 3. At 200°C, de novo formation of PCDD, PCDF, PCBz, PCPh and PCB can already be observed when compared to the original loads. As the annealing temperature is increased, the amounts of these compounds rapidly increase, reaching a maximum at 300°C for PCPh, and at 350°C for PCDD, PCDF, PCBz and PCB.

Results of testing the ESP (field 2) dust at varied gas atmospheres are shown in Fig. 4. It can be seen that decreasing the gaseous O₂ concentration led to a dramatic reduction in PCDD/F formation; apparently, gaseous O₂ initiated the de novo synthesis of organochlorocompound, in agreement with prior observations for MSWI fly ash (Stieglitz and Vogg, 1987, 1991). Finally, ammonia addition was tested for possible inhibiting effects on PCDD/F formation but the results so far were not encouraging (Fig. 4).

4. Discussion

There are very few prior studies about the mechanisms of dioxin formation in thermal metallurgical processes. One speculates, in analogy to MSWI, that



Fig. 2. PCDD/F homologues from annealing ESP (field 3) sample at 300°C for 2 h in air.



Fig. 3. The 2,3,7,8 chlorine-substituted congeners from annealing ESP (field 3) sample at 300°C for 2 h in air.

Table 3

Organochlorocompound formation	(ng/g) from ESP	(field 2) sample when	the sample was a	nnealed at different	temperatures for	: 0.5 h
in air ^a						

	Original	200°C	250°C	300°C	350°C	400°C
PCDD						
Solid phase		42.2	138.6	390	94	2.6
Gas phase		12.7	1376.2	1475	1972	208.6
Sum	47.2	54.9	1514.8	1865	1966	211.2
PCDF						
Solid phase		65.1	200.8	1888	623	20.5
Gas phase		87.7	11 080	10 702	17 196	2200
Sum	84.7	152.8	11 281	12 590	17 819	2220.5
DCD-						
FCB2 Solid phase		201	1163	9466	4830	400
Gas phase		238	4283	166 043	249 471	88 498
Sum	358	439	5446	175 509	254 301	88 907
Sum	550	-59	5440	175 505	254 501	00 907
PCPh						
Solid phase		778	1871	2085	139	bd.
Gas phase		43	1154	7143	5803	2087
Sum	680	821	3025	9228	5942	2087
РСВ						
Solid phase		73	128	409	374	148
Gas phase		570	1388	6430	44 255	4944
Sum	175	643	1516	6839	44 629	5092

^a Solid phase - found in the solid sample; gas phase - found in cold traps. bd. - below detection limits.



Fig. 4. Influence of gas atmospheres on PCDD/F formation (annealing time: 2 h).

dioxins can be formed by homogeneous, gas-phase reactions, and by heterogeneous gas-solid reactions (condensation of aromatic precursors and de novo synthesis). Our study results given above indicate that de novo synthesis of PCDD/F is a plausible possibility for iron ore sintering plants. Temperatures from 250°C to 400°C are most suitable for de novo synthesis to occur. In the sintering process, such temperatures are reached (1) while preheating the feed after its drying is completed, (2) while cooling the sinter, after passage of the ignition and sintering front through the layer, and (3) during the cooling of the sinter, discharged from the belt. It is notable that dioxins, generated in step (2) still have to pass through an incandescent layer, so that destruction is at least partial. The measured PCDD/F formation rates for samples from the feed, the sintering and the cooling, however, are very low (see Table 2). Based on a travelling time of the sintering material in the

appropriate temperature zone of 20 min and followed by cooling for 10 min (*), one may estimate the amount of PCDD/F formation as follows:

$$\begin{array}{l} 0.017 \; (ng\text{-}PCDD/F/g \; \min) \times 20 \; (min) \times 300 \; (t/h) \\ + \; 0.205 \; (ng\text{-}PCDD/F/g \; \min) \times 10 \; (min) \\ \times \; 300 \; (t/h) = \; 0.102 \; (g\text{-}PCDD/F/h) \\ + \; 0.615 \; (g\text{-}PCDD/F/h) = \; 0.717 \; (g\text{-}PCDD/F/h). \end{array}$$

According to the phase distribution of PCDD/Fs shown in Table 3, one part of these PCDD/Fs from de novo synthesis will remain in the solid phase and be discharged with the sintered material, and the other part will desorb to the gas phase and be carried by off-gas flow either for the part already sintered or report to the off-gas stream, for the part below ignition zone where some of the PCDD/Fs may be destroyed by the high temperature.

Extremely high de novo synthesis activities have been found for the finer ESP dusts (see Table 1). But the temperature at ESP is only 110–140°C and below the temperature range of de novo synthesis. On the other hand, the off-gas leaves the sintering belt at temperatures exceeding 400°C at breakthrough to 50–80°C in the feeding and drying zone of the belt; hence passages and ducts leading the off-gas from the sintering belt to the ESP may have suitable zones for de novo synthesis to occur. Assuming a dust loading of 0.5 g/Nm³, a residence time of 10 s, a gas flow rate of 500 000 Nm³/h, and using the measured PCDD/F formation rate of ESP (field 2) dust, one may estimate the amount of PCDD/F formation as follows:

565 (ng-PCDD/F/g min) × 0.5 (g/Nm³) × 10 (s) × 500 000Nm³/h = 0.0235 (g-PCDD/F/h).

Interestingly, this estimated amount of PCDD/F formation in the gas passages after the sintering belt is one to two orders of magnitude lower than that of in-bed formation. Considering, however, the various uncertainties relating to the variability in feed composition, in temperature/time relationship on the belt, residence time and activity of particulate entrained with the off-gas, the fact that PCDD/F from top of the bed formation may subsequently be destroyed in the high-temperature ignition zone, and the possibility that highly active material deposits in hot zones of the collector duct, it is clear that further study and modelling is necessary to elucidate sources, their relative importance and measures to reduce them. Expressed in concentration units, the above estimated amount of PCDD/F formation is equivalent to 1.48 µg/Nm³ or about 30 ng I-TEQ/Nm³, which compares reasonably well with actual measurements of the off-gas dioxin emissions $(3-15 \text{ ng I-TEQ}/\text{Nm}^3)$ in this plant.

It is most intriguing that de novo synthesis occurs not only on MSWI fly ash as is well known, but also on other particulate matters generated by thermal processes, e.g., particulate samples collected at a copper smelter (Buekens et al., 1998a) and the iron ore sintering plant reported in the present paper. Basically, de novo synthesis is the oxidative breakdown and transformation of macromolecular carbon structures to aromatic compounds (Stieglitz et al., 1991, 1995; Huang and Buekens, 1995, 1996). Residual, unburnt carbon from combustion sources such as char, soot and carbon in fly ash is often based on graphitic structures; their low-temperature oxidative degradation can lead to a whole range of aromatic compounds including PCDD/F. Furthermore, in most circumstances, the amount of chlorine present is much higher than the amount of PCDD/F generated, so chlorine is in oversupply; thus annealing of solid carbon structures can lead simultaneously to all T₄- to O₈CDD/ F homologues and the "dirty" 2,3,7,8 chlorine-substituted congeners (Figs. 2 and 3). The distribution of PCDD/Fs is probably controlled by thermodynamic and in the second place, catalytic factors, giving rise to the thermal "fingerprint" of dioxins.

The results of testing de novo synthesis under varied gas atmospheres in Fig. 4 have shown that PCDD/F formation by de novo synthesis may be reduced by lowering the O₂ level. For the iron ore sintering process, this may be achieved by recirculating off-gas and increasing the depth of the burden; also, more attention to the management of iron-bearing recycled streams and the use of active inhibitors potentially are effective ways for dioxin reduction. Other technical measures are injection of activated carbon and use of fabric filtration (endof-pipe control), rapid cooling in the high-temperature regions of the gas passages, and use of possible dioxin formation inhibitors (Buekens and Huang, 1998b). Modifications of the design of the sintering belt to enhance combustion efficiency and lower hydrocarbon and dust emissions may also be useful (Gebert et al., 1995).

5. Summary

Laboratory study on a number of solid samples collected from an iron ore sintering plant has shown considerable but distinct activity in the de novo synthesis of organochlorocompounds. The de novo synthesis may take place during sintering and cooling, as well as in the off-gas passages and collector ducts to the ESP. The amounts of PCDD/F and other chloroaromatics formed from de novo synthesis have been estimated on the basis of PCDD/F formation rates measured in laboratory, and these estimations appear to be in good agreement with plant measurements of the PCDD/F emission levels. The typical "fingerprint" of PCDD/F, characterised by PCDD < PCDF and a declining importance OCDF < HpCDF < HxCDF < PeCDF < TCDF is well reproduced by the annealing testing of the solid samples. Similar results are being gathered for other metallurgical processes. Therefore, de novo synthesis is a plausible pathway of PCDD/F generation in industrial metallurgical processes.

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