INVESTIGATION OF DIOXIN FORMATION MECHANISMS UNDER SINTERING CONDITIONS BY USE OF PILOT POT

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Introduction

Sinter plants are operated by the majority of European ironmakers as a primary feed for modern high productivity blast furnace operation. Furthermore, sinter plants play an important role in recycling revert materials generated within the iron and steel works (i.e. mill scale, iron-bearing dust and sludge). However this waste management practice introduces further several organic compounds into the process, which may be responsible, in combination with traces of chlorine in the feed materials, for the generation of small quantities of chlorinated hydrocarbons.

Furthermore, in the iron and steel industry, the sintering process has been identified as a significant source of dioxin emissions, which are ranging typically from 0.5 to 5 ng I-TEQ/Nm^3. As regulations on dioxin emissions in the air are tightened, careful emission monitoring and reduction of PCDD/F (PolyChlorinated DibenzoDioxins and Furans) are essential. Existing end-of-pipe techniques are very expensive for sintering plants because of the large quantities of waste gases to be treated (from 300,000 to 1,250,000 Nm^3/h). Therefore, it is important to investigate the factors controlling the emissions of PCDD/F at source in order to develop effective, low-cost and more flexible countermeasures.

The present paper is devoted to the development of dioxin measurements on sintering pot and to the investigation of mechanisms of dioxin genesis under sintering conditions.

Methods and materials

The preparation of the BF charge consists in sintering fine particles together into porous clinker referred to as sinter. The sintering raw materials (fines ores, fluxes, solid fuels, revert materials…) are blended completely and are dampened to form micropellets. The mixture to be sintered is loaded on continuous travelling grate (layer from 400 to 600 mm deep). At the start of the grate, a canopy of gas burners ignites the coke breeze of the mixture. A powerful fan draws air through the entire length of the sinter bed into distribution chambers underneath the grate referred as wind boxes (Figure 1). All the fumes from the wind boxes are collected and treated before evacuation at the main sintering stack.

As the sinter mixture proceeds along the grate, the combustion front (1300-1480 °C) is drawn downwards through the mixture (Figure 2). The solid fuel (coke breeze and/or anthracite) is fully combusted before reaching the end of the grate and the last one or two wind boxes are used to begin the cooling process. Then sinter falls off the end of the cake. It is crashed and screened.

The IRSID pilot pot (section: 40 x 40 cm^2) is a batch reactor that simulates the behaviour of one part of the grate above, with only one wind box. In the context of environmental studies, the sintering pot has many advantages. It allows to follow continuously a lot of pollutants (CO, CO_2, O_2, SO_2, NO, CH_4 and total VOCs (Volatile Organic Compounds), dust) and then to investigate their formation mechanism. Contrary to industrial conditions, operating parameters and raw materials are well known and controlled, and then the effect of each parameter can be precisely determined.

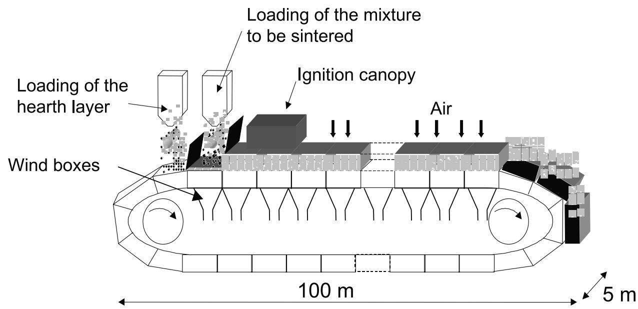

Figure 1. Layout of a sinter plant.

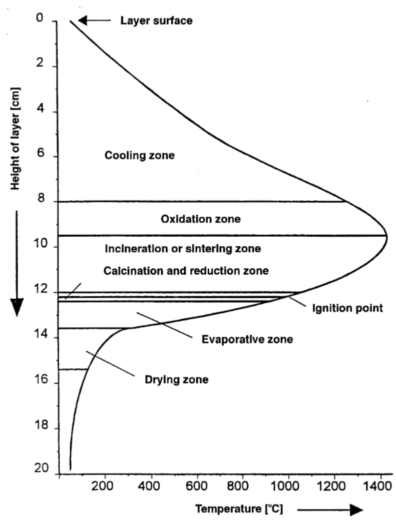

Figure 2. Sintering reactions[1].

First measurements of dioxin were carried on sintering pot to evaluate the feasibility of such measurements. Indeed, the pilot pot is a batch reactor, so that temperature, off-gas flows and fumes composition change drastically during cooking and sampling duration is quite short (circa 30 min. for 4 h. on strand). Because dioxin is emitted in tiny amounts, sintering pot size and rigorous preparation of sinter feed are the major key points to obtain emissions higher than detection limits and good reproducibility.

Thus for the trials presented in this paper, loaded mix is ca. 190 kg and specific return fines preparation procedures have been adopted. Table 1 summarises the operating conditions during VOCs and dioxin investigations.

Table 1. Operating conditions for trials presented in this paper (ts for ton of sinter)

%/mineral mix		Sintering parameters	
Iron ores	81.85		
Limestone	13.9	Moisture (%/dry mix)	7.5
Lime	1.35	Total bed depth (mm)	600
Olivine	2.9	Hearth layer (mm)	45
Solid fuel	4.8	Suction (mm water)	1,700
Return fines	35.2	Return fines level (kg/ts)	380

The objectives of the trials carried out can be thus classified:

– evaluation of sintering pot potentialities for PCDD/F measurements: feasibility, reproducibility
– dioxin balances for complete and interrupted (1/3 and 2/3) sintering experiments in order to investigation dioxin formation mechanisms under sintering conditions.

Results and discussion

PCDD/F (the 17 target congeners from the Toxicological Equivalent from NATO) have been measured for different mixes sintered on sinter pot: a reference one and three ones with adding by-products to this reference mix (i.e. mill scale, large chlorine input, and both revert materials).

Dioxin measurements on the pilot pot can be made in spite of short sampling times and evolving conditions during sintering:
– concentrations obtained during these trials are ranging from ca. 0.5 to 3.7 ng I-TEQ/Nm^3 at 15.4 % O_2, dioxin emission levels and fingerprints are in good agreement between pot and strands;
– measurements carried out in the same conditions are reproducible in the time and the differentiation on pilot pot has been shown by increasing chlorine (+ 190 g/ts) and organic matter inputs which drive to greatly increase dioxin emissions;
– measured level for the reference mix is 10 times higher than the detection limit, which offers the possibility to investigate abatement solutions.

In order to progress in the understanding of dioxin formation mechanisms during sintering process, mass balances have been carried out for complete and interrupted sintering experiments (35 and 79 % exactly).

During complete sintering, fumes are the major output of PCDD/Fs and PCDF dominate (85 % of total non weighted PCDD/F). During quench experiments, PCDD/F condense in raw zone and especially just after the flame front and they are only evacuated from the bed by the burnthrough. The emission profile along the sinter strand (main exhaust in the last windboxes) as shown by several siderurgists[2,3] is also obtained.

Fingerprints evolve during sintering process: mix feed contains mainly PCDD (with 70 % of OCDD) and fumes mainly furans (85 % of PCDF). The transition mix feed/raw zones/sinter/RF/fumes seems to be progressive.

PCDD/F balances for complete sintering reveal a different behaviour between PCDD and PCDF (both those used for the I-TEQ but also for each homologues):

– total PCDD output is equal to the input, OCDD output with smaller than the input, whereas the other PCDDs increase slightly, which can be explained by dechlorination,

– PCDFs are formed during sintering in a large and rather progressive way (except OCDF which increased not so much (3 times against 10 times for the other PCDF).

This conclusion has to be pointed out because it indicates that large part of dioxin formation occurs continuously in bed during sintering operation. PCDD/F formed in this way condense on cooler burden beneath and are volatilised when temperature raises at the end of cooking.

These interrupted sintering experiments and the impact of raw materials leading to high dioxin emissions (> 3 ng I-TEQ/Nm^3 at 15.4 % O_2) allow to show that formation in wind boxes seems to contribute only as a secondary way on dioxin exhausts. Dioxin formation should be prevented therefore along the whole bed and not only in the last layer before the exit of the flame zone. These results put in evidence the impact of the sinter feed composition on PCDD/Fs reduction at source.

These experiments established clearly the potentialities of the IRSID sinter pot for investigations in terms of reproducibility and differentiation. The environmental benefits of this work have been seen to be very significant in improving the understanding of dioxin formation and in studying the impact of some raw materials or sintering conditions on PCDD/F emissions.

Pilot pot is relevant to carry out tests for prospection and then optimisation because it is to be well equipped to allow a global approach (multi-pollutants and taking account both metallurgical and environmental results). Moreover, as operating conditions and raw materials are well known and well controlled, the effect of each parameter can be precisely determined.

In order to reduce further PCDD/F emissions at source, other studies are undertaken on pilot pot to evaluate the impact of raw materials (mill scale, ESP dust, solid fuels, iron ores…) and process conditions.

References

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