

FORMATION AND SUPPRESSION OF PCDD/Fs IN IRON ORE SINTERING

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Introduction

The emission of PCDD/Fs from the integrated iron and steelmaking process has been investigated by Corus UK (formerly British Steel plc) since 1995. Preliminary studies¹ established an emissions inventory which showed that iron ore sintering is the only noteworthy source in this process route. Further research^{2,3} showed that emissions from the main waste gas stacks of the five UK sinter plants were in the concentration range 0.28 to 4.4 ng I-TEQ/Nm³ from 94 measurements. The overall mean was 1.21 ng I-TEQ/Nm³ which is slightly above the achievable release limit of 1 ng I-TEQ/Nm³ specified by the UK Environment Agency for new plant. An environmental survey⁴ around a 4 Mt/annum iron ore sintering plant in the UK showed that there was minimal impact. The highest soil concentration was 24.6 ng I-TEQ/kg which is towards the lower end of the range for UK urban soils 4.9 to 87.3 ng I-TEQ/kg as reported by the UK Environment Agency⁵. Although emission concentrations are close to the achievable release limit, Corus UK has undertaken studies into the formation and suppression of PCDD/Fs to investigate means to further reduce emissions. These studies are discussed here with results from recent trials.

Iron Ore Sintering in the Integrated Iron and Steelmaking Process

The production of steel by this route involves a series of closely-linked processes whereby iron is extracted from iron ores in the blast furnace and converted to steel in the basic oxygen steelmaking (BOS) furnace. Iron ore is prepared as a feed suitable for the blast furnace using the sintering process, an agglomeration process, in which blends of iron ore fines, fluxes, fuel in the form of coke, and some recycled materials such as dusts and grits from other processes, are fused together to produce a clinker-like material. The well-mixed blend is laid upon a slowly-moving continuous grate (sinter strand) as a bed, typically 40 - 60 cm deep and 4 - 5 m wide.

DIOXIN REDUCTION

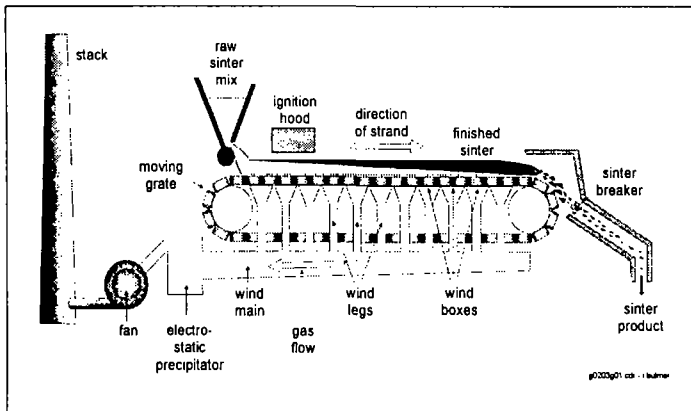


Figure 1 Schematic of a typical sinter plant

The bed is ignited under an ignition hood and the resulting combustion zone is slowly drawn down through the bed by a strong flow of air produced by powerful fans. The heat generated causes partial fusion of the iron ores and flux resulting in the formation of large pieces of sinter product. After leaving the strand, the sinter product is cooled, screened and transferred to the blast furnace. The waste gases exit the bottom of the bed and are drawn through windboxes situated beneath the strand, then via a series of windlegs into the waste gas main. The waste gases are de-dusted in an electrostatic precipitator (ESP), pass through the fan and are emitted to atmosphere via the main stack.

Experimental

Plant Trials

In various trials, emission samples were collected from several places of the waste gas system of the sinter plant; from the stack, wind main before and after the ESP, and from alternative windlegs underneath the sinter stand. Samples of solid materials were also taken; raw sinter mix, finished sinter product and dust from the ESP. In the suppressant trial, urea was added in the form of prills to the raw mix. This trial used different addition rates with one rate per day: 0, 40, 80, 100 and 140 kg/hour, concluding with a further 0 kg/hour condition. Emission sampling for PCDD/Fs was undertaken each day in the waste gas main after the ESP.

Sampling and analysis

Emission samples were obtained using a standard US EPA Method 23 sampling train. Analysis was undertaken using UKAS-accredited methods based on US EPA Method 23 for stack emission samples and US EPA M1613B for the analysis of solids and dusts. Gas chromatography – high resolution mass spectrometry was employed using a Hewlett Packard 5890 fitted with a DB5-MS column (60 m x 0.25 μm) coupled to a Micromass Autospec Ultima mass spectrometer.

ORGANOHALOGEN COMPOUNDS

DIOXIN REDUCTION

Results and Discussion

The PCDD/F concentrations of solid materials for two sinter blends are listed in Table 1.

Sample	PCDD/F Concentration (ng I-TEQ/kg)	
Raw sinter mix	0.12	0.46
ESP dust	75	186
Finished sinter product	<0.01	0.01

Table 1 PCDD/F concentrations in solid samples

The concentrations for raw mix were very low and are insufficient to account for PCDD/F emissions in the sinter plant waste gas, suggesting that PCDD/Fs are formed within the process. The PCDD/F concentrations in the waste gas stream before the ESP and after the ESP were 1.8 and 1.6 ng I-TEQ/Nm³, respectively. This indicates that PCDD/Fs are not formed in this region, which is to be expected given that the temperature of 160 °C in the ESP is below the range 250 – 450 °C generally considered to be favourable for PCDD/F formation⁶, and that an ESP, although effective at removing dust particles, is ineffective at collecting PCDD/Fs. Results for windleg measurements are depicted in Figure 2, together with values for temperature and moisture.

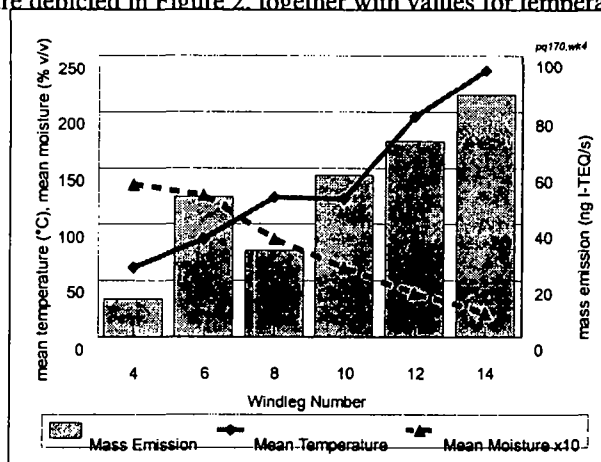


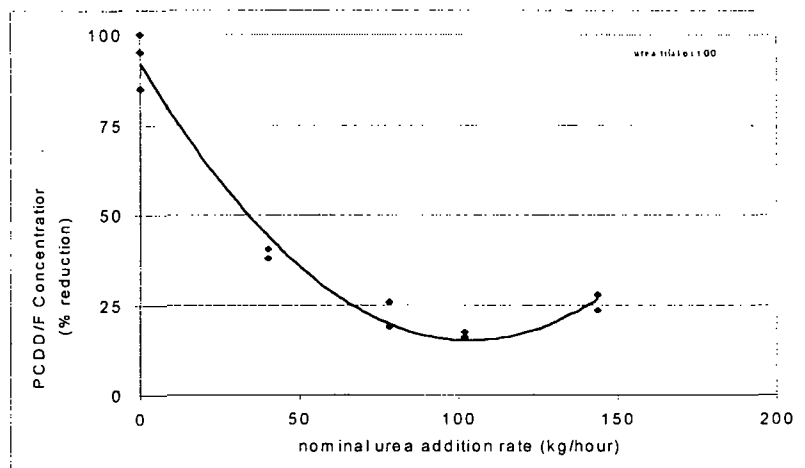
Figure 2 Variation in PCDD/F mass emission, waste gas temperature and moisture in windlegs along a sinter strand.

Figure 2 shows that the mass emission of PCDD/Fs is greater where the waste gas temperature is higher. This could suggest that PCDD/Fs are formed in the windboxes between the strand and the windleg, or are formed within the sinter bed. However, the temperatures in the windlegs are only in the range 60 to 220 °C, below the 250 to 450 °C considered most likely for formation⁶, and the residence time is in the region of milliseconds, so it is thought most unlikely that PCDD/Fs are formed in the windboxes. It is much more likely that PCDD/Fs are formed within the sinter bed

DIOXIN REDUCTION

itself, ahead of the flame front where temperatures rise up to 1100 °C but zones of 250 to 450 °C also exist. It is thought that formation occurs from either precursor molecules such as PCBs, or from *de novo* synthesis, or a combination of both mechanisms. PCDD/Fs are then mobilised by the heat from the flame front and are carried by the air flow to be trapped by condensation on cooler burden at lower parts of the bed. As the flame front moves downwards, the trapped PCDD/Fs are revolatilised and are swept downwards until there is no cold material left, and then into the windlegs. Further support for this theory arises from preliminary suppression studies⁷ where ammonia gas was injected into windboxes 12 and 14 where PCDD/F emission concentrations are greatest. This injection had little or no effect upon PCDD/F concentrations, suggesting that PCDD/Fs had already been formed in the bed, preventing ammonia from suppressing formation.

Suppression trials^{7,8} have been successful when urea was added to the raw sinter mix prior to the strand, with up to 50% reduction in PCDD/F emissions. Results for continuing suppression trials are reported here in Figure 3 for another UK sinter plant. These indicate that formation and emission of PCDD/Fs can be suppressed by over 50 % with only small addition rates of urea, confirming the earlier results. Higher addition rates did not provide total suppression. Analysis of ESP dusts taken during the trial showed that dust PCDD/F concentrations were also reduced, from 140 ng I-TEQ/kg with no urea addition, to between 80 to 120 ng I-TEQ/kg with addition. This confirms that PCDD/F formation is suppressed, and the reduction in emission concentrations was not just through better collection of PCDD/Fs by the ESP. Urea addition appears to offer cost-effective PCDD/F suppression and trials are continuing to confirm the long-term viability of the



technique.

Figure 3 Plot of reduction in PCDD/F emission concentration against the nominal urea addition rate. The PCDD/F concentration was measured in the main waste gas main after the ESP.

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