

## EFFECT OF CHLORIDE ON THE FORMATION OF PCDD/Fs AND WHO-12 PCBs IN IRON ORE SINTERING

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### Introduction

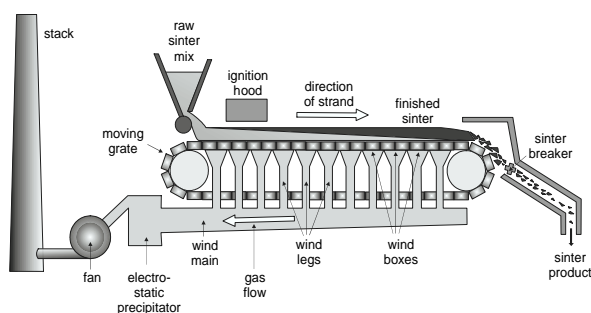
The emission of PCDD/Fs from the integrated iron and steelmaking process has been investigated by Corus UK (formerly British Steel plc) since 1995. Preliminary studies<sup>1</sup> established an emissions inventory that showed that iron ore sintering is the only noteworthy source in this process route. Further research<sup>2</sup> showed that emissions from the main waste gas stacks of five UK sinter plants that were operated in the 1990s and early part of this century were in the concentration range 0.28 to 4.4 ng I-TEQ/Nm<sup>3</sup> from 94 measurements. The overall mean was 1.21 ng I-TEQ/Nm<sup>3</sup> which is below the existing release limit of 2 ng I-TEQ/Nm<sup>3</sup> set by the UK Environment Agency for UK sinter plants but above the achievable release limit of 0.1 to 0.5 ng I-TEQ/Nm<sup>3</sup> specified in the European Reference Document on best available techniques in the Iron and Steel Industry.<sup>3</sup> Although emission concentrations meet the current interim release limit, Corus UK has undertaken fundamental studies to develop process-integrated techniques for reducing emissions of PCDD/Fs, with particular focus on the effects of sinter mix composition on the formation of PCDD/Fs.<sup>4,5</sup> More recently, studies have been carried out to investigate the formation of dioxin-like PCBs in iron and steelmaking processes. The sintering of iron ore is an essential stage in the so-called integrated steelmaking process and its main purpose is to prepare fine ores for use in the blast furnace. The sintering process is operated under tight control and it is therefore not possible to examine the influence of wide changes in raw mix composition on production plants. However, it has been demonstrated<sup>6</sup> that such studies can be performed using an experimental sinter box that simulates the sintering process and allows process conditions to be varied over a wider range than is possible on production plants. The work presented here is concerned with studies on the effects of chloride content of the raw mixture on the formation of both PCDD/Fs and WHO-12 PCBs.

### Iron Ore Sintering in the Integrated Iron and Steelmaking Process

The production of steel by the integrated steelmaking 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.

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.



**Figure 1 : Schematic of a typical sinter**

## Experimental

### The experimental sinter box apparatus

The sinter box used in the experiments is essentially a small pilot plant that permits a sample charge of ~ 80 kg of raw sinter mixture, containing blended ores, fluxes and fuel, to be sintered in batch firings. The sample volume is cylindrical in shape and has a cross-sectional area of ~ 0.1 m<sup>2</sup> and a bed depth of ~ 500 mm. The sinter mixture is packed around the edges with a high grade iron ore to reduce heat losses by minimising air flow at the edges. The mixture is ignited using a propane gas burner located above the bed and, once the fuel particles at the surface have been ignited, the burner is extinguished and the flame front is propagated by drawing air through the bed with a fan. Typically each firing takes ~ 30 mins and three or four test firings were run on each test mixture in a single day.

### Raw mix preparation

On each day of operation sufficient mixture was prepared for four test firings by mixing the raw materials in a drum mixer/pelletiser together with the requisite amount of water to achieve a blend moisture content of ~ 7% by weight. The resulting micropellets were loaded into the sinter box and fired as described above.

Sinter mixture composition

All of the test firings were made using a base mixture that contained five high-grade iron ores in the same relative proportions and the blend composition was adjusted by the addition of limestone and olivine to achieve a lime:silica ratio of 1.60 in the product sinter. Coke breeze was employed as fuel at an overall addition rate of 3.3% by weight. The chloride contents of the raw sinter mixture were varied by adding appropriate amounts of potassium chloride to the mixture at the blending stage. A series of six experiments was carried out wherein potassium chloride was added to the raw sinter mixture in order to vary the chloride content of the raw mixture in the range 0 to 797 mg chloride/kg of raw mix.

Sampling method

Emission samples were collected by use of a UKAS-accredited method (ISO17025) based on US EPA Method 23. The sampling train, a Graseby Andersen Manual Stack sampling train (Graseby Andersen, Bedfordshire, UK), was composed of a heated glass-lined sampling probe and filter equipped with a glass fibre filter element and a water-cooled XAD-2 sorbent trap. Samples were collected isokinetically through a heated glass-lined sampling probe, particulate were collected on a glass fibre filter contained in a heated filter box whilst vapour phase PCDD/Fs and PCBs were trapped on XAD-2 resin contained in a water-cooled trap. XAD-2 sampling kits were previously spiked with PCDD/F and PCB sampling standards (EDF-4054 / EC-4978, Cambridge Isotope Laboratories, LGC Promochem, UK). The analytical samples consisted of the filter, XAD-2 resin, and solvent washings from the glassware of the sampling train.

Analytical procedure

The operation of the laboratory for PCDD/Fs and PCBs analysis has been described in more detail elsewhere<sup>7</sup> Samples were analysed using UKAS-accredited (ISO17025) methods for PCDD/Fs and WHO-12 PCBs. Briefly, samples were spiked prior to extraction with the <sup>13</sup>C<sub>12</sub> internal standard solutions of the methods US EPA 23 and 1668A (EDF-4053 / EC-4977, Cambridge Isotope Laboratories, LGC Promochem, UK). Samples were extracted with toluene by accelerated solvent extraction (150°C, 2000 psi) using a Dionex ASE 200. Multi-layered silica chromatography columns were used for the initial clean-up of total extracts, Florisil chromatography was used to separate PCDD/Fs from PCBs, then basic alumina chromatography was performed to remove large amounts of saturated hydrocarbons from the PCB fractions<sup>8</sup>. Prior to analysis, recovery standards were added to the final PCDD/F and PCB fractions (EDF-4055 and EC-4979, Cambridge Isotope Laboratories, LGC Promochem, UK). Analyses for PCDD/Fs and PCBs were conducted by high resolution gas chromatography - high resolution mass spectrometry (HRGC-HRMS) using a Hewlett-Packard 6890 gas chromatograph fitted with a 60 m x 0.25 mm x 0.25 µm DB5-MS capillary column and coupled to a Micromass Autospec Ultima high resolution mass spectrometer. The MS was operated at 10,000 resolution in the positive ion mode at 34 eV energy with perfluorokerosene as the mass range calibrant.

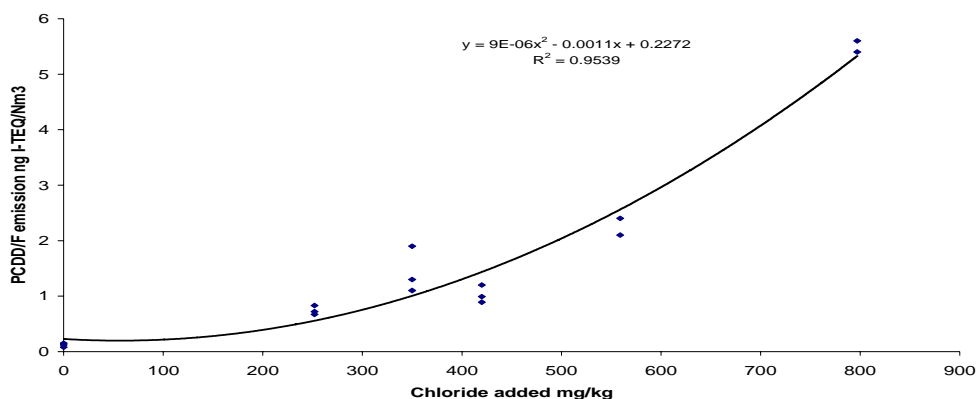
## Results and Discussion

### Effect of chloride on emissions of PCDD/Fs

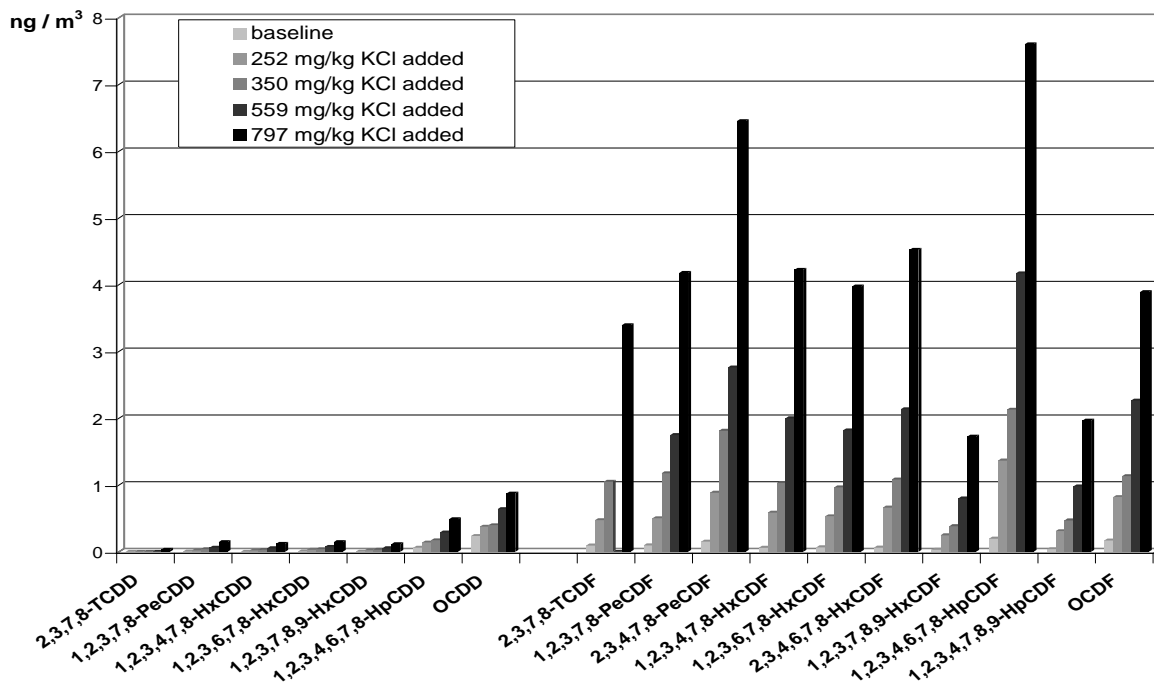
The influence of raw mix chloride content on PCDD/F I-TEQ emission concentration is shown in Fig 2 from which it may be seen that the data may be fitted to a second-order polynomial equation.

As may be seen the emission of PCDD/Fs rises sharply as the raw mix chloride content increases and there is a marked effect when the added chloride content exceeds 250 mg/kg. However, Corus UK's sinter plants generally operate with total chloride contents in the range 150 to 250 mg/kg, which clearly lie in the region of the curve where variations in chloride content have a relatively small influence on PCDD/F formation. These findings help to explain why it has not been possible to detect any correlation between chloride content of the feed material and PCDD/F emissions from production plants.

It has been found from earlier work that the congener profile of sinter plant emissions is very consistent from one plant to another and is dominated by PCDFs, which typically account for more than 85% of the I-TEQ. As may be seen in Fig. 3, the congener profile is not affected by the chloride content of the raw sinter mix and the concentration of each of the 17 2,3,7,8-chlorinated congeners increases in roughly the same proportion as the chloride content increases.



**Fig. 2** Effect of adding chloride (as potassium chloride) to sinter mix on emissions of PCDD/Fs



**Fig. 3. Emissions of 2,3,7,8-PCDD/Fs with the addition of various amounts of chloride (as potassium chloride)**

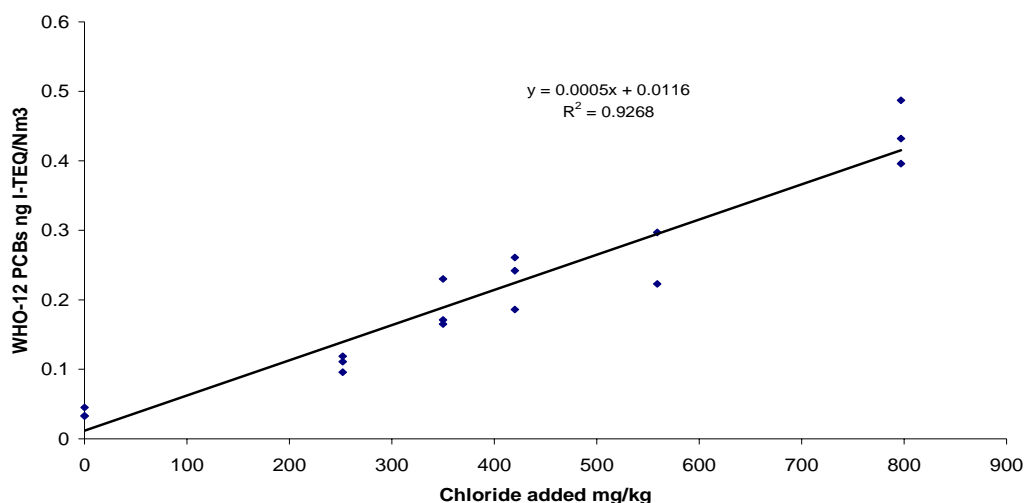
The congeners present in highest concentrations in sinter plant emissions are 1,2,3,4,7,8-HxCDF and 1,2,3,4,7,8,9-HpCDF, but invariably it is found that the main contributor to the I-TEQ of the emission is 2,3,4,7,8-PeCDF, which typically accounts for 55 to 60% of the I-TEQ.

#### Effect of chloride on emissions of WHO-12 PCBs

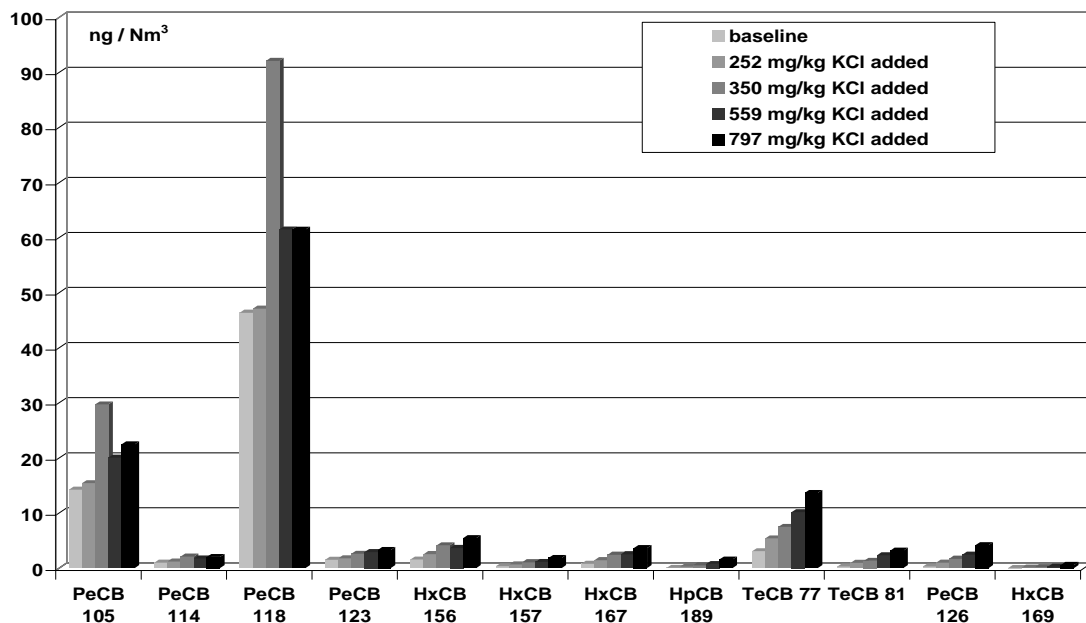
The effect of chloride on the emissions of WHO-12 PCBs is presented in Fig. 4 from which it is seen that there is a strong linear correlation between the WHO-12 I-TEQ concentration and the added chloride concentration. The WHO-12 I-TEQ was invariably lower than that of the PCDD/F I-TEQ concentration and the WHO-12 I-TEQ : PCDD/F I-TEQ ratio was in the range 0.07 to 0.418.

The congener profiles (in terms of congener concentrations) at different chloride addition levels are presented in Fig. 5. As may be seen, there is a general increase in the concentration of each congener as the amount of added chloride increases with the exception of PCBs #105 and #118, where the highest concentrations occurred at 350 mg/kg of added chloride. The discontinuity observed in this instance is difficult to explain, although it may simply be due to an atypical event. As is evident from Fig. 4, PCBs #105 and #118 were the most abundant congeners

present in sintering emissions and these together account for more than 80% of the total concentration of WHO-12 PCBs. However, PCB #126, which contributes typically 1 to 2% of the total concentration of WHO-12 PCBs, is the only noteworthy contributor to the total I-TEQ and accounts for 90 to 95% of the WHO-12 PCB I-TEQ. As a result the WHO-12 I-TEQ concentration for iron ore sintering emissions is essentially that due to PCB #126. This may be attributed to the relatively high TEF (0.1) of PCB # 126 in comparison to other WHO-12 PCBs.



**Fig. 4** Effect of adding chloride (as potassium chloride) to sinter mix on the emission of WHO-12 PCBs



**Fig. 5. Emissions of WHO-12 PCBs with the addition of various amounts of chloride (as potassium chloride)**

#### Correlation between emissions of PCDD/Fs and WHO-12 PCBs

The strong correlations between emissions of PCDD/Fs and WHO-12 PCBs and the added chloride content suggests that a common mechanism is involved in the formation of these species. Indeed, Scholz et al.<sup>9</sup> showed that PCBs could be formed by the de novo synthesis and subsequently act as precursors to the formation of PCDFs.

#### **Conclusions**

In the sintering of iron ores the chloride content of the raw sinter mixture mix has a significant effect on the emissions of both PCDD/Fs and WHO-12 PCBs. For conventional sinter plants that are used for preparation of iron ores for the blast furnace the chloride contents of the raw sinter mixture are generally below 250 mg/kg and are as low as can be reasonably achieved given the inherent chloride contents of iron ores which are typically in the range 50 to 100 mg/kg. At such chloride concentrations the total PCDD/F and WHO-12 PCB I-TEQ emissions may be expected to be below 1.5 ng I-TEQ/Nm<sup>3</sup>.

#### **Acknowledgements**

The authors thank Mr W.H. Brignall and Dr R. Alderdice for their support for this project, and are grateful to Ms S.M. Goodman, Mr J.T. Abbott, Mr N. Schofield and Mr M. Winnell for their varied contributions to work presented here, and to Dr P.D.E. Brooks for helpful comments with the manuscript.

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