

## EFFECT OF SINTER MIX COMPOSITION UPON THE FORMATION OF PCDD/FS IN IRON ORE SINTERING

Raymond Fisher<sup>1</sup>, David R. Anderson<sup>1</sup>, David T. Wilson<sup>1</sup>, Derek Hemfrey<sup>2</sup> and Trevor A. T. Fray<sup>3</sup>

<sup>1</sup> Corus R, D & T, Swinden Technology Centre, Rotherham, S60 3AR, United Kingdom

<sup>2</sup> Corus Strip Products UK, Port Talbot, SA13 2NG, United Kingdom

<sup>3</sup> Corus Construction and Industrial, Scunthorpe, DN16 1BP, United Kingdom

### 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 the five UK sinter plants 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 slightly above the achievable release limit of 1 ng I-TEQ/Nm<sup>3</sup> specified by the UK Environment Agency for new plant. Although emission concentrations are close to the achievable release limit, Corus UK has undertaken fundamental studies to investigate the effects of sinter mix composition on the formation of PCDD/Fs.<sup>3,4</sup> The sintering process is operated under tight process control and it is therefore not possible to examine the influence of wide changes in raw mix composition on production plants. However, 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 considers the effects of fuel type and chloride content of the raw mixture on the formation of PCDD/Fs, which formed part of a multi-partner multi-national project that was part-financed by the European Coal and Steel Community.

### 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.

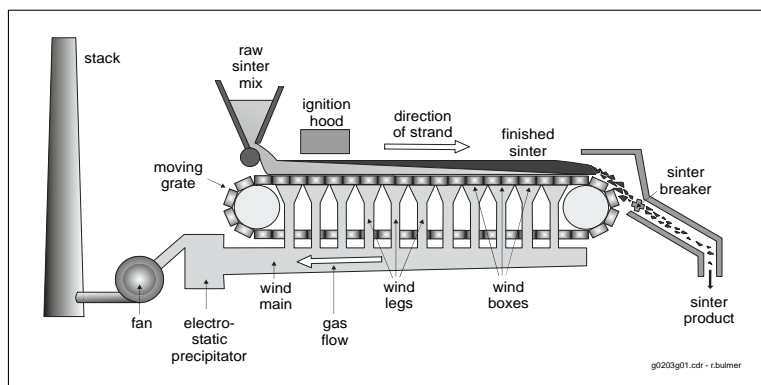


Figure 1 Schematic of a typical sinter plant

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**

### The experimental sinter box apparatus

The sinter box used in these 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.

### 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 or mixtures of coke breeze and anthracite were employed as fuels at an overall addition rate of 3.3% by weight. The chloride content of the mixture was varied by adding either potassium chloride or revert materials such as blast furnace flue dust or sinter electrostatic precipitator dust to the mixture at the blending stage.

### Sampling and analysis

Emission samples were obtained from the waste gas duct using a standard US EPA Method 23 sampling train and the resulting samples were analysed for PCDD/Fs using a UKAS-accredited method based on US EPA Method 23. High resolution gas chromatography – high resolution mass spectrometry (HRGC-HRMS) was employed for analysis with use of a Hewlett Packard 5890 GC, equipped with a DB5-MS column (60 m x 0.25 mm; 0.25 µm film thickness), coupled to a Micromass Autospec Ultima high resolution mass spectrometer.

The soluble chloride contents of the raw sinter mixtures were determined by potentiometric titration with silver nitrate using a silver electrode (ABB Instrumentation Ltd Model 45 02) for end-point detection.

## Results and Discussion

### Effect of fuel composition

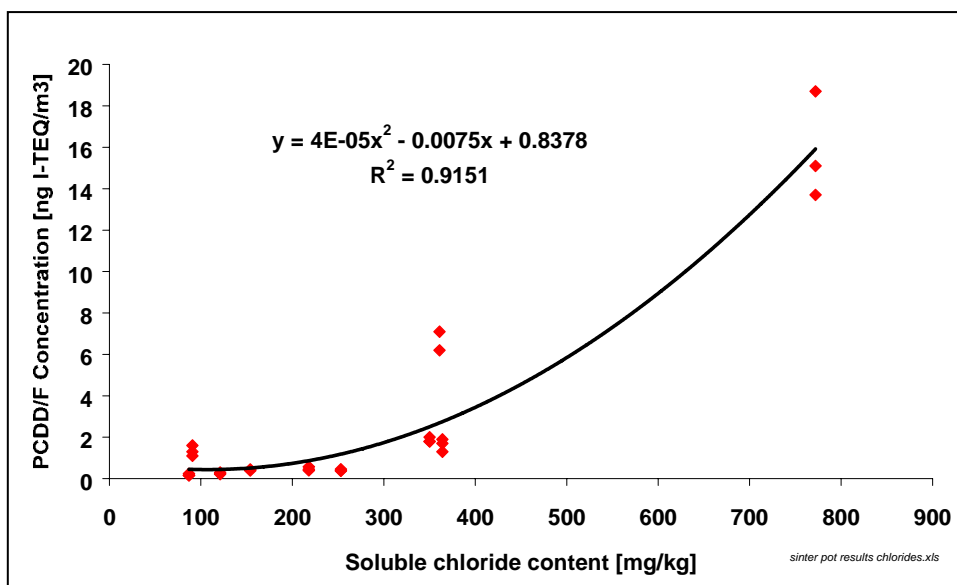
Metallurgical grade coke breeze is generally recognised as being the best fuel for the iron ore sintering process. On an integrated iron and steelworks the main source of coke breeze is the undersize fraction from the screening of blast furnace coke. However, when internal coke breeze supplies are limited it is necessary to seek other sources of coke breeze, or to use alternative fuels such as anthracite. In the EU, the IPPC Best Available Techniques Reference Document on the Production of Iron and Steel<sup>5</sup> discourages the use of anthracite as a fuel in the sintering process on the grounds that it can lead to increased emissions of organic compounds owing to its volatile content. Generally, where anthracite is employed in sinter plants it is used to replace up to 60% of coke breeze. The results of sinter box tests with 25 and 60% replacement of coke breeze with a low volatile anthracite are presented in Table 1 and show that the use of this product did not have any significant influence on the emissions of PCDD/Fs.

Fuel	PCDD/F concentration ng I-TEQ/Nm <sup>3</sup>
Coke breeze	0.18
Coke breeze/25% anthracite	0.25
Coke breeze/60% anthracite	0.17

**Table 1** Effect of anthracite addition additions on emission of PCDD/Fs in the sintering process

### Effect of chloride

The influence of raw mix chloride content on PCDD/F 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.



**Figure 2** Effect of soluble chloride content of raw mix on emission of PCDD/Fs

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 raw mix soluble chloride content exceeds 350 mg/kg. However, Corus UK's sinter plants generally operate with chloride contents in the range 150 to 250 mg/kg, which lie in a region of the curve where variations in chloride content have only 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.

### Conclusions

In the sintering of iron ore replacement of up to 60% of the coke breeze fuel with low volatile anthracite has no significant effect on PCDD/F emissions.

The chloride content of the raw sinter mix has a marked influence on emissions of PCDD/Fs at concentrations above 350 mg/kg. However, Corus UK sinter plants operate with less than 250 mg/kg of chloride in the raw mix and within this range variations in chloride content have a relatively small effect on PCDD/F formation.

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