

## ***De novo* tests on iron ore sintering dust: statistical analysis of some MINIDIP data.**

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### **Introduction**

The MINIDIP project tackled a score of dioxins-related problems arising in metallurgical industry at large and devoted especially to the iron ore-sintering plant and the Waelz process, two notorious sources of dioxins. The program was conducted in close collaboration with the industry involved and accompanied by full-scale testing; it resulted in revamping of large-scale plant and the selection of adequate abatement methods. Dr. Stieglitz and his team at the former Forschungs-Zentrum Karlsruhe (FZ-K) analysed many (mainly) filter dust samples and possibly conducted the largest number of *de novo* tests ever made, in particular on iron ore sintering samples. In this study, a survey is presented of the samples analysed and characterised, i.e. the feed mix (iron ore fines, coke, reverts, fluxing agents), about a dozen samples of belt siftings, and filter dust from fields I, II, and III of the enormous Electrostatic Precipitator (ESP) used to clean the off-gas. The *de novo* activity of feed and siftings was almost nil and attention further focused on hyperactive samples of filter dust from field ESP-II and III, even though a comprehensive comparison of fingerprints was still lacking.

In this study the original database is systematically revisited, including hitherto neglected aspects, such as dioxins' profiles of feed and grate siftings, the ballistic tests with steadily rising temperature, tests with more comprehensive dioxins' analysis ( $P = 1-8$ ) and with addition of Activated Carbon to the sample, comprehensive statistical analysis and the answers it provides to precise questions, such as these listed further under Results and Discussion. Various chloroaromatic groups occur and evolve in parallel, but their relative evolution as a function of operating conditions is systematically treated, a feature lacking in previous work. Special attention is dedicated to their relative and absolute amounts, their various implicit fingerprints (e.g., PCDD/Fs isomer groups, dirty 17, Hagenmaier fingerprint), their weight or molar average level of chlorination, and various internal ratios, such as PCDD/PCDF. After a preliminary manual data analysis statistical correlation techniques as well as Principal Component Analysis (PCA) are applied to assess the internal relations as well as the statistical significance of the numerous trends observed, as a function of time, temperature, oxygen content, and addition of suppressants. Special attention was given to the necessity of repeating experiments to assess internal variability and the validity of the conclusions. This dataset is no doubt the largest ever analysed and it is also discussed in how far it is representative for the sintering process at large, for other metallurgical processes and – at some distance – the fly ash samples from Municipal Solid Waste Incineration (MSWI) and – finally – usual types of Model Fly Ash (MFA).

### **Materials and methods**

At the times of first data analysis very little was known about the sources and origins of dioxins resulting from metallurgical sources, such as sintering of ores. Large-scale measurement campaigns were only moderately successful in pinpointing the effects of the numerous operating parameters of real industrial plant: the latter only allows moderate variation of these operating factors, because of both plant operational limitations and product quality requirements. Moreover, memory effects limit

the validity of the relationship between experimental variables and chloroaromatic outputs. Methodically varying the various operating parameters (time, temperature, oxygen, suppressants) is much simpler in small laboratory equipment. Conversely, using lab-scale tests on filter dust or model fly ash should be accompanied by effective efforts in data analysis and full plant modelling, and thus bridge the gap between expectations on the basis of lab-scale results with the full-scale outcome.

Stieglitz et al. (2003) and Buekens and Olie (2008) described the experimental procedures and investigating methods. All *de novo* tests were conducted in a small, fixed bed reactor featuring a layer of 5 g of filter dust, through which a current of moist air was led under appropriate reaction conditions, e.g. 300 °C, 21 vol. % of oxygen, 1 h reaction time. The following groups of chloroaromatic compounds were monitored both in the reactor effluent and the *de novo* test residue: chlorobenzenes (PCBz; P = 2-6), chlorophenols (PCPh; P = 2-5), polychlorinated dibenzo-p-dioxins (PCDD; P = 4-8), dibenzofurans (PCDF; P = 4-8), and biphenyls (PCB; P = 2-10). The effect of the various variables was methodically tested, i.e. temperature (200 to >500°C), time (30-240 min), oxygen (0 to 50 vol. %), and addition of four inhibitors (ammonia, triethanolamine, hydrated lime, caustic soda). Other tests were conducted using Jet-Rempi as an on-line analyser (Buekens, 2002; Thanner, 2002; Zyaykina, 2004). The evolution of chloroaromatics is linked with the low-temperature catalytic oxidation of carbon. The latter can conveniently be monitored by means of either Differential Scanning Calorimetry (DSC) (also by Differential Thermal Analysis, DTA) or Thermogravimetric Analysis.

## Results and discussion

**Temperature.** The *de novo* activity of filter dust forming chloroaromatics strongly depends on temperature. Even for the most potent filter dust activity is small, yet measurable at 200 °C and 250 °C. The results obtained at both temperatures do not coincide, however, with those at peak temperatures (300 or 350 °C) because the chloroaromatics' formation is still accompanied by other phenomena, such as chloroaromatics' desorption and dechlorination. Evolution at high temperatures still resembles that at peak temperature, as established during tests with steadily rising temperature involving filter dust from field I (200-800 °C), II (200-450 °C), and III (200-600 °C), as well as from grate siftings collected at the end of the sintering belt (200-400 °C).

**Time.** The activity of filter dust rises proportionally with time, at least at 300 and 350 °C and times between ½ and 2 h. Longer reaction times seem to lead to an asymptotic maximum value (4 h). Also other tests seem to show that only a fraction of carbon is readily available for oxidative breakdown. At low temperatures (200 and 250 °C) there is some time delay in starting the reaction.

**Oxygen.** Activity turns out to be very low for zero oxygen and is besides obscured by the occurrence of both dechlorination and desorption. There is linear rise of activity with rising oxygen content up to ca. 12 vol. %, yet this rise asymptotically continues up to 50 vol. %, though accompanied by a shift in the relative importance of the PCDD and PCDF isomer groups and gas/particle partition.

**Moisture content** in the carrier gas is an important factor, yet it was not treated systematically: the results from one dry test run were not too different from the standard moist ones.

**Activated Carbon** was added to the test sample, maintaining much more chloroaromatics in the test residue, yet did not lead to any surprising results justifying further study. Addition of **suppressants**

showed no effect for ammonia, substantial, yet incomplete suppression for triethanolamine, and deep suppression by hydrated lime and particularly NaOH.

Each single test led to a plethora of analytical data (17 2,3,7,8-PCDD/F congeners, 10 PCDD/F, 9 PCB, 5 PCBz and 4 PCPh isomer groups). Derived data were their I-TEQ and BGA toxicity equivalent, weight and molar average chlorination content, PCDD/PCDF-ratio, as well as various fingerprints, including the Hagenmaier fingerprint showing the relative importance of the various 2,3,7,8-PCDD/F congeners within their own group of isomers.

**Reproducibility and accuracy.** As a rule analytical data showed good reproducibility, typically of the order of 10 to 15 %, both internally and when confronted with the results from an external lab. Several key analyses were conducted in duplicate or even triplicate. *de novo* test

### Acknowledgement

This presentation is respectfully dedicated to the memory of the late Dr. Ludwig Stieglitz, the father of current *de novo* theory. The experimental work was mainly conducted at FZ-K, in particular by Dr. K. Hell, Dr. J. Polzer, and Dr. J. Wilhelm. Analytical work was supervised by Dr. K. Jay. The advice and encouragement of Prof. Dr. Kees Olie (Univ. of Amsterdam) is gratefully acknowledged.

The MINIDIP E.U.-project Nr. ENV4-CT97-0587, was financed by DG XII, initiated at VUB (A. Buekens) and conducted by L. Stieglitz (FZ-K), S. Marklund (Umea University), W. Esser-Schmittmann (Rheinbraun), R. Louw (Leiden University), H. Grotheer (DLR) and H. Fiedler (BfA).

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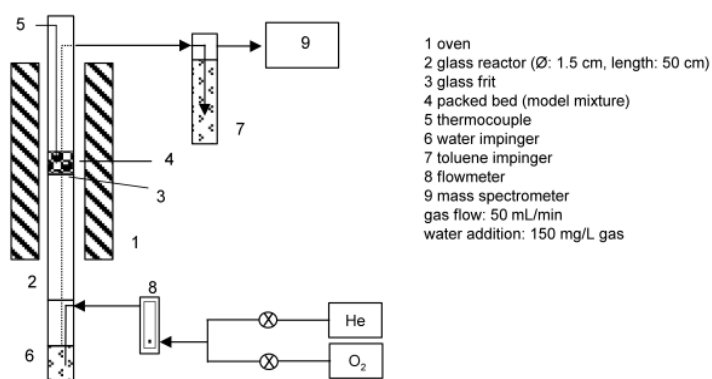


Fig. 1. The experimental set-up.

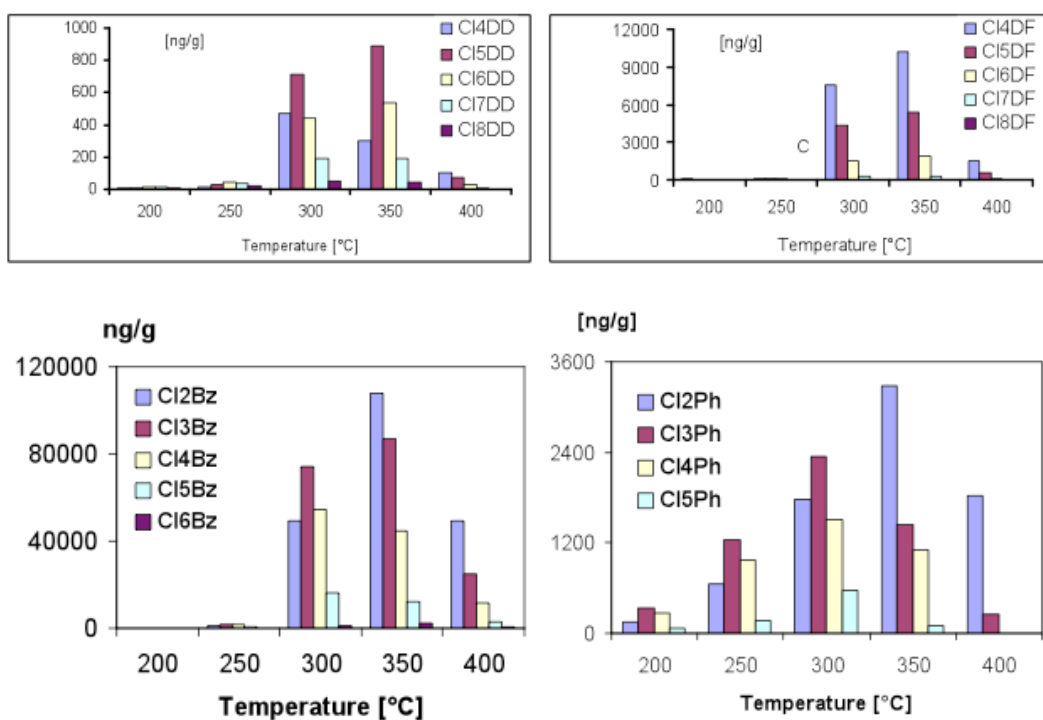


Fig. 2. The influence of temperature on PCDD/Fs, PCBz, PCPh.

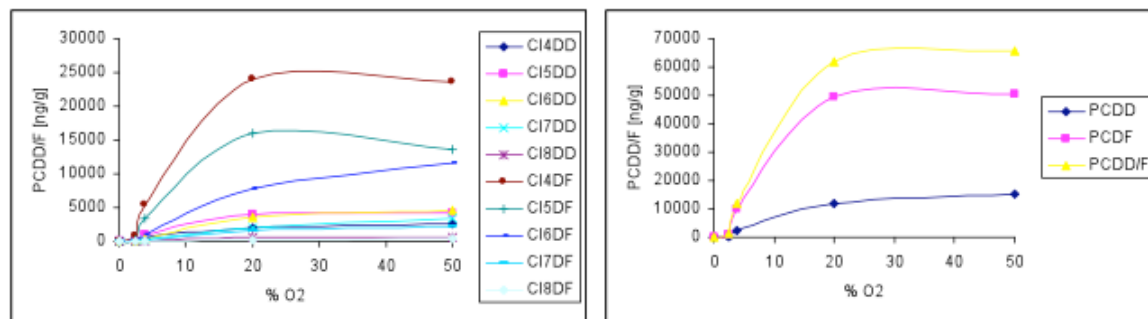


Fig. 3. The influence of oxygen on PCDD/Fs.