

## 'DE NOVO' TESTING OF DUSTS, COLLECTED IN SUCCESSIVE FIELDS OF AN ELECTROSTATIC PRECIPITATOR OF A SINTERING PLANT. (I) EFFECT OF REACTION TIME.

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### Introduction

Polychlorinated dibenzodioxins and -furans (PCDD/F) are formed by condensation of precursors and also by 'de novo' synthesis. The latter refers to a low temperature (200 to 500 °C), catalytic gasification of residual carbon in particulate of various origins<sup>1,3</sup>. Gasification may be limited by reaction time: when the particulate is cooling down while being carried along by the flue gas and eventually captured in a dust collector, reaction time in the temperature domain of high activity typically is only 5 to 30 seconds and inadequate for a complete gasification of residual carbon. In case the particulate settles from the flue gas the reaction time may rise to hours, before the particle leaves the plant, e.g. upon rapping the boiler, cleaning of baghouses, discharging of dust hoppers, etc. In that case gasification may still be incomplete, but only in case it is catalytically, temperature, chlorine or oxygen limited. A variety of other chlorinated aromatic compounds, e.g. polychlorinated benzenes (PCBz), phenols (PCPh), or biphenyls (PCB) are also formed. Purpose of this research is to mimic essential features of the dioxin generating processes by simulation at a laboratory scale; such a 'de novo' dioxin generating treatment involves the exposure of dust to a stream of moist air under dioxin generating conditions (e.g. 300 °C, 2 h of exposure of electrostatic precipitator dust from plants such as municipal solid waste incinerators (MSWI), iron ore sintering plants (ISP) etc<sup>2,4,5,6</sup>. Such tests allow to evaluate the influence of reaction time and temperature, oxygen and moisture content of the flue gas, addition or elimination of inhibitors, catalysts, or reactants. This test is vital in the study of dioxin formation conditions, since it is virtually impossible to study the mechanism and rates of chloroaromatics formation at a real scale industrial plant, because a) the various operating variables can only be varied within a narrow domain and b) 'memory effects' caused by deposits or absorption into synthetic construction materials smoothen out the dioxin output, whatever the operating conditions tested. One of the characteristic features of the MINIDIP-Programme was to test particulates of various origins, e.g. feed material from the iron sintering plant, belt siftings arising in the baking and cooling of iron ore, and dust from the 3 successive fields of an electrostatic filter. In this paper new experimental data are presented, relating the effect of reaction time on the rate of 'de novo' formation, as observed under carefully reproducible laboratory conditions. Compared to the 'de novo' synthesis from dust particles separated in a Municipal Solid Waste (MSW) incinerator it can be stated that:

1. the materials on or falling through the sintering belt are rather inactive in their PCDD/F-generation rates, only the particulates collected in the successive fields of an E-filter are active, very active, or even hyperactive materials<sup>1</sup>. Still, it is believed that the material on the belt is the major source of dioxins, given the disproportionately large amount of material on the belt (200 to 1000 Mg/h), compared to that collected by the filter (80 to 400 kg/h), and the much longer residence time on the belt (30 to 50 minutes) than in the flue gas (15 to 25 seconds);
2. the PCDD/F-content is strongly retained upon the MSW-incinerator fly-ash, whereas most powders from metallurgical processes are only poorly adsorptive, so that the chloroaromatics produced report to the gas phase, whereas those in MSWI mainly remain adsorbed on the fly-ash,
3. the original dust reflects the history of the average particle sample, including the formation of chloroaromatics in the active temperature window and their further adsorption during the cooling of the particle.

## Materials and Methods

**Materials:** The 'de novo' dioxin and other chloroaromatics generating experiments were conducted in a tubular glass reactor (1.5 cm diameter x 50 cm length) mounted vertically in an oven. Dust (5 g) e.g. from the second field of the electrostatic precipitator (ESP) of an ISP was placed on a glass frit in the middle of the glass tube and contacted for a variable time period (of 1, 2, or 4 hours) and temperature (200, 250, ... to 400 °C) with a gas stream of 20 % oxygen in helium (50 mL/min). The volatile chloroorganics were collected in a toluene impinger. The extract of the dust and the solution of the toluene impinger were cleaned-up and analyzed separately.

**Methods:** The PCPh, PCBz, PCB and PCDD/F were quantified by <sup>13</sup>C-internal standards. The PCPh, PCBz and PCB were analyzed by HRGC/LRMS with a 60 m DB-5 column and the PCDD/F by HRGC/HRMS (HP5890 - Fisons Autospec) with a 60 m DB-Dioxin column.

## Results and Discussion

When using a 'de novo' test to study PCDD/F formation on dust samples it has been found that the following reaction conditions often lead to a maximal output of dioxins: 300 °C, 2 h. In this work the effect of time (and also temperature and of basic inhibitors) has been studied methodically.

**Tests at 300°C:** Tests are conducted for reaction times, ranging from 30 to 240 minutes, with tests of 30 and 60 minutes in duplicate, that at 120 minutes in triplicate. The variability in the data is surprisingly low. Apparently, using 5 grams of material suffices to provide reproducible results.

**Figure 1** shows the evolution of the total amounts (adsorbed + volatilized) of PCDD, PCDF and PCDD/F as a function of time, rising linearly with time, then tending towards a limiting value;

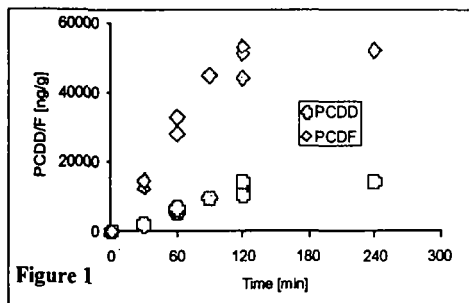


Figure 1

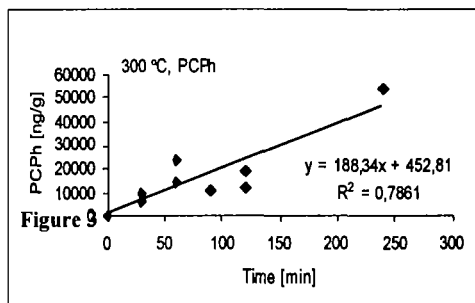


Figure 3

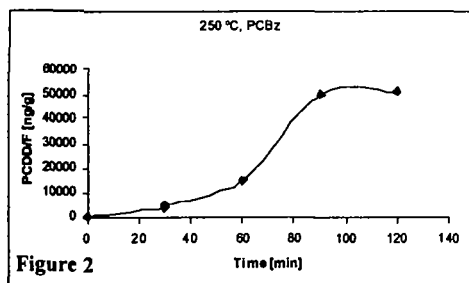


Figure 2

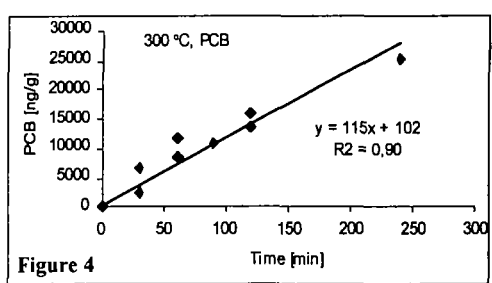


Figure 4

**Figure 2, 3 and 4** present a similar picture for PCBz, PCPh and PCB. The data spread is higher and the level of the limiting values is much better defined for PCBz than for PCPh or PCB. All data were statistically evaluated.

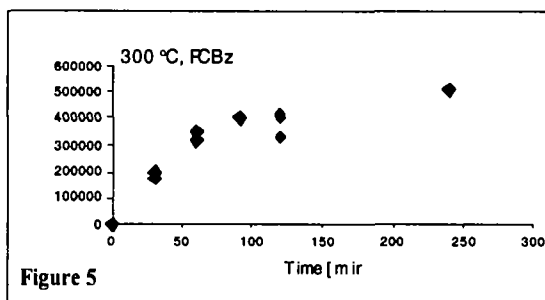


Figure 5 gives the picture from PCBz at 250°C, no direct correlation is found between the different points.

Tests at 250 °C: The linear dependence of the 300 °C is no longer to be found and a quadratic rise represents the data much better for reaction times up to 90 or 120 minutes, this is presented at Figure 6.

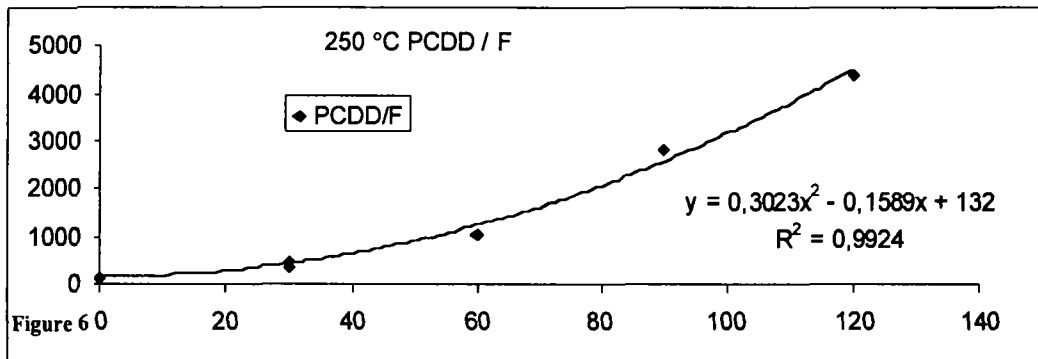
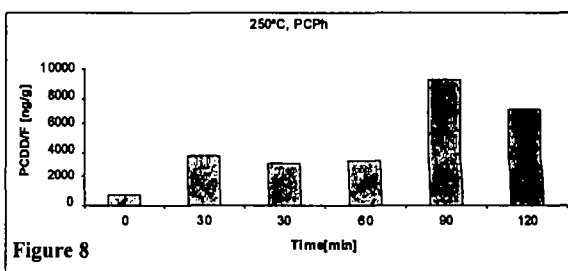
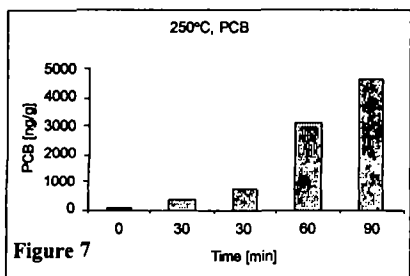


Figure 7 and 8 present a similar picture for PCB and PCPh. No correlation is presented because linearity is nowhere established.



It is difficult to explain this behavior by means of either heat or mass transfer restrictions relating to carbon gasification, since the latter should be much more pronounced at 300 than at 250 °C. The only remaining hypothesis is a kinetic/mechanistic one. An initial latency period could be due to

1. a slow chemisorption of, say precursors or oxygen,
2. a reaction involving consecutive steps, eg a slow reaction of carbon with chlorides, or another step preliminary to the reaction proper. A slow desorption of chloroaromatics is a less plausible explanation since the chemisorbed products, in principle, are extracted during sample preparation.

### Conclusions

A 'de novo' testing method was used to study the formation of various chloroaromatics as a function of reaction time by a slow gasification at 300 °C of carbon in dust, collected in field 2 of the electrofilter cleaning off-gas from an iron ore sintering plant. There is strong 'de novo' formation, with the amount of chloroaromatics linearly increasing with time in the first 1 to 2 hours, to level off afterwards, and an increasing share of chloroaromatics found in the gas phase. When the same test is conducted at 250 °C, there is a period of latency, resulting in a quadratic increase of chloroaromatics with time. This phenomenon is probably to be explained by a set of consecutive physico-chemical steps or reactions.

### Acknowledgements

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### References

1. Dickson, L.C., Lenoir, D., Hutzinger, O., 1992. Quantitative Comparison of de Novo and Precursor Formation of Polychlorinated Dibenzo-p-dioxins under Simulated Municipal Solid Waste Incinerator Postcombustion Conditions. *Environ. Sci. Technol.* 26 (9), 1822-1828.
2. Stieglitz, L., Vogg, H., 1987. On Formation Conditions of PCDD/F in Fly Ash from Municipal Waste Incinerators, *Chemosphere* 16 (8-9), 1917-1922.
3. Stieglitz, L., 1998. Selected Topics on the De Novo Synthesis of PCDD/PCDF on Fly Ash. *Environmental Engineering Science* 15 (1), 5-8.
4. Vogg, H., Stieglitz, L., 1986. Thermal Behavior of PCDD/F in Fly Ash from Municipal Incinerators. *Chemosphere* 15 (9-12), 1373-1378.
5. Buekens A., Rivet F., Huang, H., Stieglitz, L., 1999. Experimental Study of 'de novo' Formation illustrated by various case-studies. *Organohalogen Compounds* 41, 55-58.
6. Stieglitz, L., Polzer, J., Hell, K., Weber, R., Buekens, A., Rivet F., 1999. Dioxins from the Sintering Process. (II) Samples and their propensity to form Dioxins, as derived by a 'de novo' laboratory test. *Organohalogen Compounds* 41, 113-115.