

# Human Exposure II – Accidental and Occupational Exposure

## ON CATALYTIC PROPERTIES OF IRON ORE AND SINTER AND ITS ROLE IN DIOXIN FORMATION AND DESTRUCTION IN IRON METALLURGY

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### Introduction

Fly ash from municipal solid waste incinerators contains considerable amounts of iron, within a range of 10-30 g/kg<sup>[1]</sup>. This relatively high content as compared to copper (around 1 g/kg) can be responsible for at least part of the catalytic formation of PCDD/F's<sup>[2]</sup>. Iron (III) nitrate and chloride (hydrates) were co-fed with aliphatic fuel or injected directly into the flame. A whole array of chloroaromatics was found in the effluent gases as well as on the fly-dust particles resulting from the combustion<sup>[2]</sup>.

As to Deacon-type reactions of several metal oxides<sup>[3]</sup>, iron exhibits properties similar to copper, but less pronounced. It was concluded though that it could also be an efficient oxychlorination catalyst.

Oxidative properties of iron (III) oxide as well as its ability to catalyze condensation reactions of chloroaromatics have been reported on<sup>[4]</sup>. It was observed that this material promotes formation of PCDD/F's only until a certain concentration, beyond which its oxidative properties take over leading to destruction of chloroaromatics. Our present work constitutes part of the EU-sponsored MINIDIP project<sup>[7]</sup>. It deals with the catalytic properties of iron sinter, the mixture of iron ore, coke (fuel) and lime (flux-agent), which is a starting material in the very large-scale pyrometallurgy of iron. It has been found that in the process of sinter production significant proportions of PCDD/F's<sup>[5]</sup> are released. Focus is on the possible formation of dibenzofurans and/or -dioxins from simple aromatics - known to be precursors to (PC)DD/F's in combustion processes – under conditions relevant for those in the real sintering.

### Sintering

This slag-like, porous material is formed in a continuous process in the sinter plant (see Figure 1). Upon ignition by gas-fueled burners (nr. 2 in the Figure) situated at the beginning of the

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belt, air is sucked through the sinter layer by means of wind legs (4). This moves the burning front down the layer while advancing towards the quench zone. At the end of the belt the sinter is quenched and collected (7). Material falling over from the belt is collected at the bottom of the wind-legs and reprocessed together with fresh mix. Resulting gas effluents upon dedusting (6) are led into a stack.

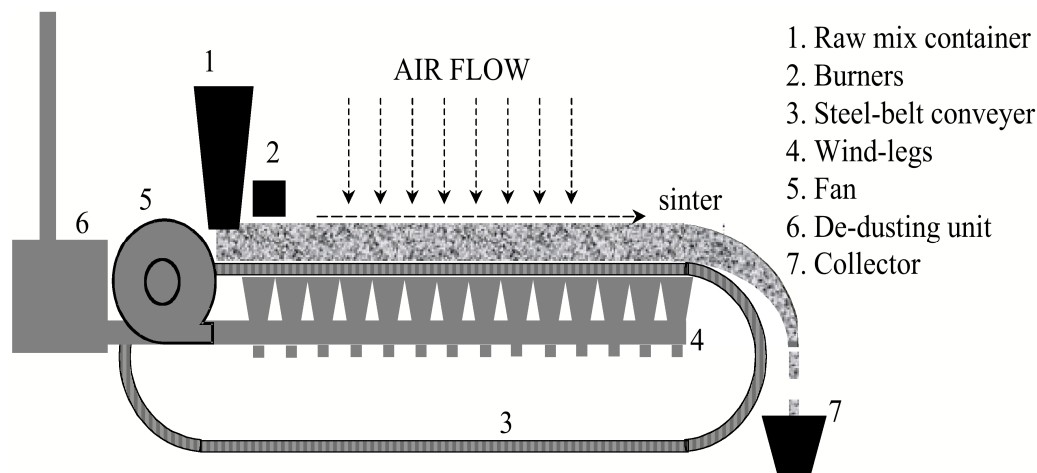


Figure 1: Schematic representation of a sinter-plant.

### Results and discussion

Experiments with a fixed bed of sieved sinter (ca. 6 g, fraction with a grain size of 2-4 mm) have been conducted in a plug-flow reactor (details on the setup will be given in the presentation). Air was used as the carrier gas. A void residence time of ca. 4 s was maintained throughout all experiments. As an introductory example, a mixture of benzene and phenol (9:1 mol/mol) has been fed with a rate of ca. 1.9 g/h. The bed was kept at 450-500°C. Benzene reacted for ca. 25% and phenol for ca. 50%. In the outflow CO and CO<sub>2</sub> were detected as predominant products. In the liquid catch oxygenated phenol derivatives (i.e. p-benzoquinone) and condensation products (diphenyl ether, *benzofuran*, and *dibenzofuran*) were present. As compared to non-catalytic runs with phenol in the feed<sup>[6]</sup> the overall conversion is much higher (one half vs. 15% at 500°C), but the yields of oxidation and condensation products were also increased. Interestingly in the run with benzene only as a feed, no such products were found.

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As the used sinter fraction was found to be almost chlorine-free (mg/kg range), in the following series, HCl was co-fed together with the substrates. Substantial amounts of chloroaromatics were found in the products, for example *dichlorophenol*. This will inevitably give rise to PCDD's.

Experiments with different feed composition and varying T, so as to get a better insight into the potentials of sinter to form and to destroy dioxins –whether from volatile precursors or via “de-novo” synthesis from the cokes, are under way and will be discussed in more detail.

### References

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