

# DIOXIN PREVENTION & REDUCTION

## ABATEMENT OF DIOXIN EMISSIONS IN ELECTRIC ARC FURNACE EXHAUST FLUE GAS

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### Introduction

Steel is more and more produced in electric arc furnaces (EAFs) using scrap as a raw material; comaterials associated with scrap (mineral ones such as copper and tin, organic ones such as paint, plastics, rubber, oil...) lead to undesirable gaseous emissions, such as PCDD/F (PolyChlorinated Dioxins and Furans).

The French Environment Regulatory Administration publishes monitored value of PCDD/Fs emissions from MWI and Industry. The French Steel Industry is thus credited with 150 g TEQ/year, a figure down from 500 g given in earlier publications, from estimations obtained without experimental data. The EAFs themselves emit 36 g TEQ/year, with individual fluxes ranging from 0.1 to 13 ng-TEQ/Nm<sup>3</sup>. As regulations on dioxin emissions at the stack are tightened, careful monitoring and development of effective, low-cost and more flexible countermeasures are essential.

At EAF stack, Volatile Organic Compounds (VOCs) emissions are directly related to organics input, so that it is essential to use clean scrap and keep scrap clean on a sustainable basis. Nevertheless, concerning PCDD/F emissions, the correlation between input and output is not so clear-cut as far as trace elements are concerned, because formation from inorganic elements are possible and because condensation and adsorption can cut off emission peaks under very specific conditions.

Two strategies have been evaluated to tackle the problem of controlling PCDD/F emissions. The first one consists of trapping PCDD/F by condensation. The second one is to practise optimized post-combustion in terms of abatement efficiency, operating residence time and temperature.

### Methods and materials

An electric arc furnace is a batch reactor. Scrap is usually loaded into baskets together with fluxes for the slag formation. During the initial period of smelting, the applied power by the electrodes is kept low to prevent damage to the furnace walls and roof from radiation whilst allowing the electrodes to bore into the scrap. Once the arcs have become shielded by the surrounding scrap the power is increased to achieve melting. Oxygen lances and/or oxy-fuel burners are more and more used to assist in the early stages of melting (for increasing productivity). Furthermore oxygen may be brought to the liquid steel by specific nozzles in the bottom or side wall of the EAF for metallurgical reasons<sup>1</sup>.

Most of the existing plants extract the primary off gases of the EAF roof (referred as the 4<sup>th</sup> hole in the case of 3 electrodes). The treatment of fumes is performed in post-combustion chambers (designed to burn CO into CO<sub>2</sub> and H<sub>2</sub> into H<sub>2</sub>O and thus avoid explosions inside the dry dust-collecting system), heat exchangers followed by bag filters.

In this article, two approaches have been followed:

– calculation of PCDD/F condensation curves in order to assess condensation as an abatement technique,

# DIOXIN PREVENTION & REDUCTION

– and experiments at the laboratory scale in order to achieve a proper post-combustion for low residence time and temperature.

The experiments were performed in a quartz Continuous Jet Stirred Reactor already used in previous investigations<sup>2</sup>. This reactor includes an annular preheating; the stirring of the gas-phase volume is achieved by means of four turbulent jets flowing out of the nozzles of a cross-shaped injector located at the center of the reactor. A good mixing is obtained for residence times ranging from around 0.3 to 3 s.

The dibenzofuran (DBF) was chosen as a model molecule, because it is not toxic, has the same structure and is more stable than all PCDD/Fs. The DBF oxidation has been studied at around 900 °C, at atmospheric pressure, and high dilution in helium: 0.12 % of DBF; the equivalence ratio was 0.7 to 7 for oxygen, and the residence time ranged from 0.3 to 1 second<sup>2</sup>.

## Results and discussion

### *Use of condensation to reduce dioxin emissions at the stack*

An important behavior of dioxins and furans has not been discussed yet, although it plays an important role in trapping the PCDD/F molecules in the dust in the bag filter. Indeed, measurements of PCDD/Fs concentration carried out on dust exhibit values of 598 pg-TEQ/g<sub>dust</sub> within a range of 30 to 2630. Some better understanding of this deposition is necessary with the expectation of using this knowledge to propose better abatement solutions than those which are currently available.

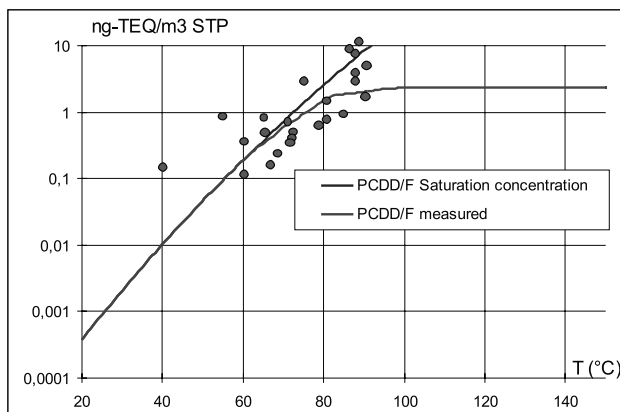
PCDD/Fs have low boiling and melting points and high saturated vapor pressures below the melting point. The 17 congeners taken into account in the calculation of the TEQ (Toxicological Equivalent) concentration have thus a boiling point in the 438-537 °C range and a melting point in the 196-305 °C range<sup>3</sup>. We have used these thermodynamical data to calculate the saturated vapor pressure and the saturation concentration of each congener as a function of temperature in the 25-200 °C range, using an Antoine's law formulation. Adding up the results as a linear combination of the various congeners with their weights in the TEQ calculation leads to the TEQ saturation concentration, obtained with the assumption that each congener is freely available. From a practical standpoint this assumption is unrealistic and the actual amount of each congener initially present in the fume has to be taken into account. Using actual data from measurements carried out on an EAF, we calculated the curves for each congener and those for the TEQ (Figure 1).

The first congener to condense is the octachlorodioxin, followed by the heptachlorodioxin until the tetra-chlorodioxin in that order. Condensation only starts in the 125-60 °C range. Once it has started, the concentration decreases very rapidly, i.e. an order of magnitude (one power of 10) for 15 °C. Figure 1 summarizes the results in terms of TEQ for the case of the actual EAF emissions taken as an example. Also plotted on the graph are literature data published by Werner et al.<sup>4,5</sup>. They correlate very satisfactorily with the calculation, given the uncertainty of the dioxin concentration measurement and the fluctuations of the temperatures in the dust cakes. We can thus consider that our interpretation, i.e. that deposition of PCDD/Fs in dust is entirely driven by physical condensation, is confirmed.

The dependence of emissions on temperature has already been described by several authors<sup>5,6,7</sup> but this is the first time that the very simple physical phenomenon of condensation is quantitatively demonstrated to be at the very root of the observations.

Practically speaking, this has a number of very important consequences. First, EAF dust is the major concentrator of PCDD/Fs, accumulating as much as 80-95 % of the emissions and actually filtering them out of the smokestack fumes above the saturation level. Such a non-linear effect is one major reason why there is little or no correlation between smokestack emission and cleanliness of the charge. Whether this brings the smokestack levels of PCDD/Fs low enough to meet the environment regulations depends on the level of temperature in the dust. This temperature is usually chosen for

# DIOXIN PREVENTION & REDUCTION



**Figure 1.** Comparison of the TEQ saturation curve we calculated and experimental data from 4,5

technological reasons related to the nature of the material that the bag-filters are made of, normally well above the condensation temperature range discussed before. It is possible, practically, to bring the temperature down to the required levels by mixing primary exhaust air with secondary exhaust air, as the example of Arbed has shown<sup>5</sup>.

## *Optimized post-combustion of fumes*

Post-combustion efficiency is usually described in terms of the *3T-rule*, which specifies residence Time (> 2-6 sec), Temperature (> 700-1200 °C) and Turbulence (“high”) necessary to achieve a proper post-combustion.

The oxidation of dibenzofuran (DBF) was studied using the perfect mixer already mentioned, as well as that of the decomposition products that it generated, as a function of temperature (from 800 to 950°C), of residence time (from 0.3 to 1 s) and of oxygen input (from 0.2 to 2.1 %).

Figure 2 shows a typical result at 900 °C and for a residence time of 324 ms ( $x^{\circ}\text{DBF} = 0.12\%$ ). As oxygen input increases, the various species originating from DBF dissociation increase to a maximum before they approach zero at 2.1 % of oxygen, which is slightly above the stoichiometry for oxidation of DBF (1.69 %). Under excess of oxygen and with good mixing, it is possible to obtain a total consumption of DBF but also a complete destruction of all the intermediate products under rather moderate conditions (900 °C, 0.3 s).

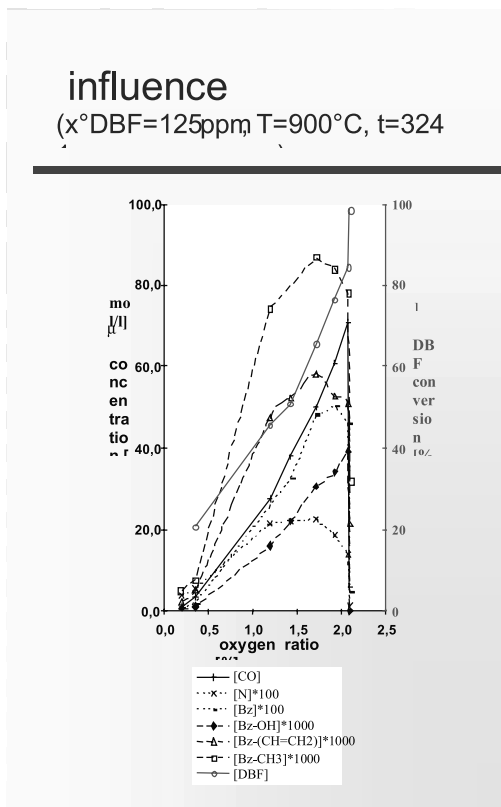
The transposition of the perfect post-combustion concept to an actual PC chamber would be based on the following principles:

- temperature always above 900 °C, space time > 0.5 second, oxygen in excess (richness > 0.8)
- introduction of fumes and air by swirl burners to obtain an excellent mixing;
- continuous flame obtained by supplementary natural gas burners when CO emissions are low;
- hot refractory walls (they are cooled by water-jacket in conventional chambers) which would avoid cold spots and a boundary layer in which harmful species or potential dioxins precursors would not be destroyed.

This would lead to more efficient units, but also of smaller volume, thanks to space times of approximately 0.5 second and temperatures close to 900 °C. These new solutions have to be tried at the pilot scale (electric arc furnace capacity of 6 tons).

Two ways are opened to tackle the problem of dioxin emissions at EAF stack: condensation by precise control of bag filter temperature and use of optimized post-combustion.

# DIOXIN PREVENTION & REDUCTION



**Figure 2.** DBF and products concentration and conversion ratio of DBF vs.  $\text{O}_2$  input)

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