DIOXINS EMISSIONS FROM HOT BLAST CUPOLAS

Dr. DUQUET B[1], – FIANI E[2]

[1] Centre Technique des Industries de la fonderie, 44 avenue de la Division Leclerc, 92318 Sèvres Cedex France ; [2] ADEME: Agence de l'Environnement et de la Maîtrise de l'Energie, 2 square La Fayette BP 90406, 49004 Angers Cedex 01 France.

Introduction

The foundry, considered as a whole, emits very few dioxins, as demonstrated by the values reported in the foundry BREF[1]. Nevertheless, certain foundries, according to the configuration of the fume treatment circuit are liable to emit more than 0.1 ng i-TEQ/Nm^3 [2]. An understanding of the mechanisms operating in the formation of dioxins in such melting plant is necessary in order to reduce their possible release, because the chemical reactions involved are complex.
CTIF has performed a study, jointly funded by the French Agency for the Environment and Energy Management ADEME, in order to attempt to elucidate the mechanisms which in certain cases contribute to the formation of dioxins in cupolas.[3]

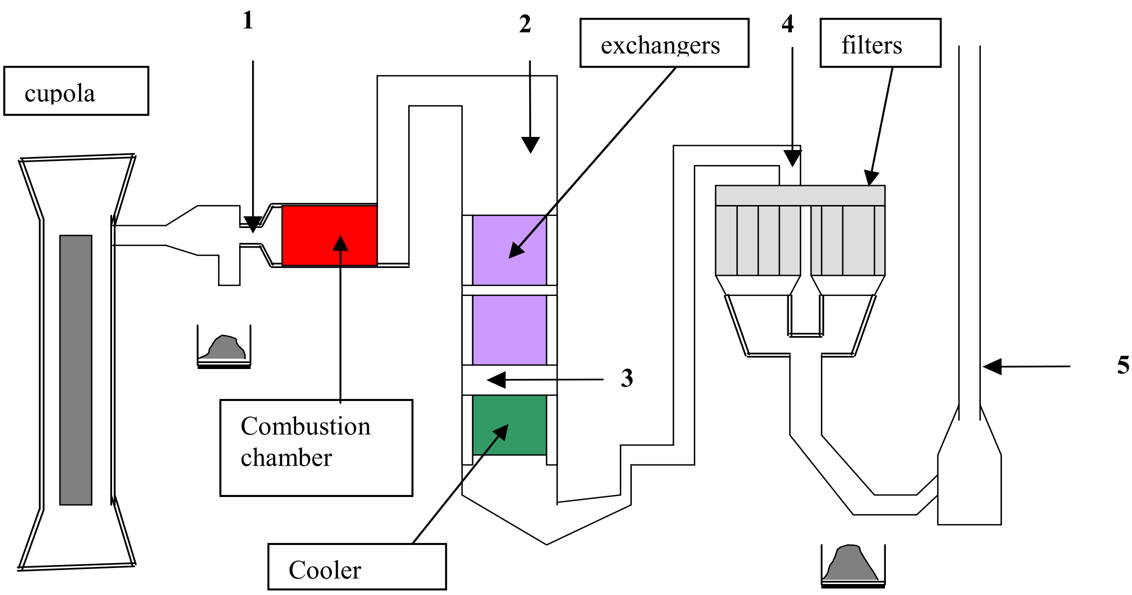
Cupolas are counter-flow furnaces used for melting a mixture of cast iron and/or steel in order to produce cast iron [4]. The charges enter at the top. As they descend, their temperature rises in contact with the combustion gases until they attain the melting point. In cupolas, the ingredients required which could contribute to the formation of dioxins are coke, which contains chlorine, and scrap iron, which may possibly contain hydrocarbons assimilated to precursors. In order to conduct this study, a hot blast cupola was used.

Materials and Methods

Cupola characteristics

The samples were taken at 5 points along the fume circuit according to the configuration of the cupola. The measurements at points 1, 2, 3, 4 and 5 were taken simultaneously in order to avoid any differences due to operation of the cupola. Dioxin precursors were evaluated at point 3. The measurements were taken with and without injection of oxygen via the tuyeres.

Schematic representation of the sampling points



For the measurements without oxygen injection, the cupola was operating at a capacity of 23.5 t/h. The blast rate, calculated during the sampling period, attained 17,063 m^3/hour. The rates of CO, CO_2, O_2 and dusts were measured at various points in the fume treatment circuit. Between the cupola and the combustion chamber (point 1), the rate of CO was high (13.5%) and the dusts were concentrated in the fumes. This indicates the presence of unburnt gases. The fumes, the CO and part of the dusts were burned in the combustion chamber. At the stack, the rate of CO was down to 3.5 mg/Nm^3 sec and the rate of dusts was low (5.6 mg/Nm^3 sec).

Results and Discussion

Operation without oxygen injection

The gases at the output from the hot blast cupola (point 1) contain dioxins and the PCDDs represent by far the largest proportion (70.3% of the total). At point 1, the conditions (low oxygen content : 8.2%, high concentration of CO :13.5%) are therefore favourable to the presence of unburnt gases and to the formation of the most chlorinated PCDDs. At point 2, the dioxins content fell to 0.043 ng iTEQ/Nm^3 which is a 95% reduction compared with point 1. The combustion chamber therefore effectively destroys the dioxins. Upstream of the dusts extractor (point 4), the dioxin content increases to attain 0.710 ng i-TEQ/Nm^3. The portion of the circuit : downstream of the combustion chamber – dusts extractor therefore encourages the formation of PCDD and PCDF. These compounds are formed by the *de novo* process. After dusts extraction, the concentration of dioxins at the stack (point 5) was down to 0.563 ng i-TEQ N/m^3.

Results of the PCDD and PDCF measurements in the fume treatment circuit, with and without oxygen injection

Expression of the results	**Upstream of the combustion chamber (point 1)**		**Downstream of the combustion chamber (point 2)**		**Upstream of the dusts extractor (point 4)**		**Stack (point 5)**	
Without oxygen injection	PCDD	PCDF	PCDD	PCDF	PCDD	PCDF	PCDD	PCDF
ng i-TEQ/Nm^3	0.615	0.260	0.007	0.036	0.336	0.374	0.193	0.370
Total PCDD+PCDF ng i-TEQ/Nm^3	0.875		0.043		0.710		0.563	
With oxygen injection	PCDD	PCDF	PCDD	PCDF	PCDD	PCDF	PCDD	PCDF
ng i-TEQ/Nm^3	0.223	0.184	/	/	0.069	0.105	0.079	0.159
Total PCDD+PCDF ng i-TEQ/Nm^3	0.407		/		0.174		0.239	

Operation with oxygen injection

The composition of the metallic charges and the coke were identical during the two sampling periods. During the measurements with injection of O_2, the cupola was operated at a capacity of 22.3 t/h. The blast rate was 15,040 m^3/h and the rate of oxygen injection, relative to the blast rate, amounted to about 5%. The dusts content was 8,992 mg/Nm^3 with oxygen i.e. a reduction of some 40% at point 1 and 0.8 mg/Nm^3 at the stack i.e. a reduction of some 86% compared with operation without oxygen. At the stack, the dioxin emissions with oxygen injection were 57% and the reduction concerns both the PCDDs (59%) and the PCDFs (53%).

In the dusts in the cyclone, 70% of the dioxins are PCDDs and only 30% are furans. The cyclone located just at the output from the cupola contains “raw” molecules only slightly converted, from the raw materials, in particular from the coke. In the dusts in the combustion chamber, the concentration of dioxins was significantly increased to 0.0066 ng i-TEQ/g. In the dusts in the filter, the concentration increased to attain 0.144 ng i-TEQ/g.

Search for PCDD/PCDF in the dusts

Samples	Cyclone		Combustion chamber		Dusts extractor	
Compounds	PCDD	PCDF	PCDD	PCDF	PCDD	PCDF
ng i-TEQ/g	0.0013	0.0006	0.0039	0.0027	0.0818	0.0628
% of the total PCCD/PCDF	70	30	60	40	57	43
Total PCDD/PCDF ng i-TEQ/g	0.0019		0.0066		0.1446	

The flux of dioxins, calculated on the basis of the measurements taken at the stack and in the dusts then related to a tonne of liquid metal, was used to determine the proportion of dioxins released from the stack and that which was absorbed by the dusts. For a tonne of liquid metal produced, this hot blast cupola generates 1.45 mg i-TEQ of dioxins of which 99.94% are trapped by the dusts and 0.06% are released by the stack.

Identification of the dioxin precursors

Gas samples were taken in order to check for the possible presence of precursors, but only when the cupola was operating without oxygen injection.
Certain molecules, which could lead to the formation of PCDD and PCDF by the *de novo* process, were sought at point 3, between the heat exchanger and the cooler.

Search for precursors at point 3

Substance	Concentration mg/m^3	Substance	Concentration mg/m^3
phosgene	< 0.159	chloro-ethylene*	< 1.648
acetaldehyde	< 0.017	penta-chloro-phenol	< 0.206
butyraldehyde	0.170	chloroform	< 0.164
formaldehyde	0.111	1-2 dichloroethane	< 0.164
furfuraldehyde	0.170	dichloro-methane	1.902
isoveraldehyde	< 0.170	carbon tetrachloride	< 0.164
α pinene	0.168	1-1-1 tri-chloro-ethane	< 0.164
β pinene	< 0.168	tri-chloro-ethylene	< 0.164
C8 – C10 hydrocarbons	< 0.161	tetra-chloro-ethylene	< 0.164
C10 – C12 hydrocarbons	0.535	alpha HCH	< 1.632
C12 – C16 hydrocarbons	< 0.161	beta HCH	< 1.632
C16 – C20 hydrocarbons	< 0.161	delta HCH	2.121
C20 – C30 hydrocarbons	< 0.161	gamma HCH	< 1.632
C30 – C40 hydrocarbons	< 0.161	hexa-chloro-benzene	< 0.816
carene	< 0.168	1-2-3 tri-chloro-benzene	< 0.164
methyl-ethyl-ketone	0.321	1-2-4 tri-chloro-benzene	< 0.164
methyl-isobutyl-ketone	< 0.161	1-3-5 tri-chloro-benzene	< 0.164

At point 3, aldehydes, and alkenes, methyl-ethyl-ketone and hydrocarbons with 10 and 12 carbon atoms were found.
Other chlorinated organic compounds were sought at the heat exchanger output (point 3), which is a zone which would appear to be favourable to the formation of PCDD and PCDF as the fumes cool down.
The results identified only dichloro-methane and delta hexa-chloro-cyclo-hexane. They also showed the absence of direct precursors (penta-chloro-phenol, chloro-benzene etc.) downstream of the combustion chamber.

The mechanisms responsible for the formation of dioxins are complex. At the cupola output, the carbon-based dusts are ideal supports for the formation of PCDD/PCDF in view of the composition of the charges, in particular coke which releases the ingredients indispensable to the synthesis of dioxins. The results confirm that the carbon-based dusts play a major role in the synthesis of dioxins in the cupola, and favour the formation of PCDD/PCDF, especially the most highly chlorinated congeners. During the formation process of PCDD/PCDF, the precursor molecules pass through the gaseous phase to an absorbed phase by condensing on the particles in the presence of chlorine. This reaction is catalysed by a metallic ion at the surface of the dusts.

The physical parameters involved in these reactions are essentially temperature, the time spent by the gases in the cooling zone and the composition of the gases (CO, CO_2 and dusts). In hot blast cupolas, more than 95% of the dioxins are destroyed in the combustion chamber. The synthesis of PCDD/PCDF by the *de novo* process occurs downstream of the combustion chamber, in the heat exchangers and the cooler, due to the presence of residual organic molecules. This zone, located between the combustion chamber and the dusts extractor therefore constitutes the critical zone for the reformation of dioxins. The latter react together by addition and condensation reactions to form aromatic cycles and heterocycles. The dioxins are to a large extent adsorbed by the dusts which are subsequently collected by the dusts extractor.

One of the solutions for reducing the release of dioxins at the stack of cupolas is to use oxygen injection. This ensures better combustion of the carbon-based particles and reduces the total amount of combustive (air + oxygen), and apparently therefore the quantity of fumes and the entrainment of associated dusts. However, it is also important to restrict the reformation of dioxins by the *de novo* process downstream of the combustion chamber. One promising approach is the addition of inhibitors which complex the catalysts and form compounds other than dioxins which considerably reduces the rate of dioxin emissions from the stack. This is one of the techniques which is intended to be implemented in the coming months, in the context of the European DIOFUR project.

Acknowledgements

CTIF thanks ADEME for its financial contribution and the two castings for their participation to this project.

References

1. EUROPEAN COMMISSION. *Reference Document on Best Available Techniques in the Smitheries and Foundry Industry*, 2004; 365 p. http://eippcb.jrc.es.

2. DUQUET B. Dioxins emission from cupola. Intern. *Conf. on cupolas*. Trier, March 18 – 19, 2004.

3. DUQUET B. Emissions de dioxines par les cubilots. *Fonderie Fondeur d'Aujourd'hui,* 2006; 252; 31-43.

4. GODINOT P., PICHOURON J., STEPHAN J. *ADEME report on cupolas*, 1998.