Revista de metalurgia

Emissions of dioxin and dibenzofuran from electric arc furnaces(•)

S.L. Figueira* and J.F.P. Gomes*

Abstract This paper describes work done in order to clarify the formation mechanism of highly toxic micropollutants, such as dioxins and dibenzofurans, from electric arc furnaces used in the production of carbon steel from scrap. The study is allowing to derive relationships between the levels of airborne micropollutants and the operational parameters of the production process so that an abatement of pollution could be achieved. By using the European standard method CEN 1948 for dioxin like compounds sampling and measurement, it was possible to determine the characteristic fingerprint of micropollutants emitted by this particular stationary source.

Keywords Dioxin. PCDD. PCDF. Iron and steel industry. Electric arc furnace.

Emisiones de dioxinas y dibenzofuranos en hornos eléctricos de arco

Resumen Este articulo contiene resultados del trabajo ejecutado para el esclarecimiento de los mecanismos de formación de los micropolutantes muy tóxicos, como dioxinas y dibenzofuranos, que son emitidos por los hornos de arco eléctrico utilizados en la producción de acero. Estos estudios han permitido relacionar las concentraciones de polutantes emitidos a la atmósfera con las condiciones operación del horno eléctrico. Utilizando el método normalizado CEN 1948 para captación y análisis de muestras de compuestos análogos a las dioxinas ha sido posible determinar el perfil característico de los micropolutantes emitidos por esta fuente.

Palabras clave Dioxinas. PCDD. PCDF. Industria del acero. Horno eléctrico.

1. INTRODUCTION

Several studies[1 y 2] have concluded that steel production is one industrial activity that has atmospheric emission sources potentially emitting micro organic pollutants to the atmosphere. This is particularly true when integrated steel production is considered as several thermal processes dealing with organic substances from fuels, iron ore and additives, as well as chlorine compounds could be involved, as described elsewhere[3].

Even non-integrated steel production, which refers mainly to steel production by electric arc furnace (EAF) from ferrous scrap, has been recognised as a potential source for emission of organic micropollutants such as dioxins (PCDDs), dibenzofurans (PCDFs), PAHs and PCBs. In particular, when the scrap results from the automobile industry, frequently includes plastics such as polyvinylchloride, this type of atmospheric emissions may be significant. In fact, dioxin like compounds result from non-complete combustion of organic matter and the source of organic compounds in EAF steel production could be oils and greases frequently contaminating scrap to be melted. Usually the formation of dioxin like compounds requires the presence of organic compounds also known as precursors such as phenols, chlorobenzenes, PCBs, chlorine, catalytic substances such as cooper or any other heavy metals and a reaction temperature between 200 and 600 °C, as shown previously[4].

Therefore, the study of the formation mechanism regarding these compounds during steel production in the EAF is quite important to define effective measures so that the emissions of dioxin like compounds could be controlled by means of its operational parameters.

(•) Trabajo recibido el día 8 de enro de 2004 y aceptado en su forma final el día 13 de mayo de 2005.

(*) Environmental Technologies Centre, ISQ – Instituto de Soldadura e Qualidade, TagusPark, Apartado 012, CTT Porto Salvo, 2780-994 Porto Salvo, Portugal(* Corresponding author Fax: 351.21.4228129 Email: jpgomes@isq.pt.

This particular study has been included in a broader project, funded by the European Commission under the Steel Research programme, regarding the reduction and definition of strategies to reduce micropollutants emission to the atmosphere. The main objective is to study the influence of scrap composition on the kinetics of PCDD/F formation, thus comprising studies on specific production EAF units to investigate the effect of scrap type and in particular, the use of large portions of automobile scrap containing significant amounts of plastics. Particular focus is also given to the influence of metal species, e.g., heavy metals, on the kinetics of formation of PCDD/Fs.

2. EAF PLANT

Experimental measurements were made on an EAF installed in a steel mill in Northern Portugal. The EAF is a DEMAG unit, built in 1976, type UHP, having a power consumption of 48 MVA and produces 77 ton of melted steel per heat, from 92 ton of inlet material. Each production cycle lasts 2 h, operating continuously in day and night shifts. The type of scrap and raw materials used is presented in table I. The EAF is shown in figure 1. Exhaust gases are collected in a hood and send through a pipe to two independent stacks, working simultaneously, the extraction flow being 135,000 Nm^3/h Each stack is equipped with different deducting systems, each consisting of a bag filter device, indicated here as "old" and "new". The flowsheet regarding the gas cleaning section is presented in figure 2. The total gas handling capacity is of 180,000 Nm^3/h. Both units work simultaneously in order to achieve a better abatement of pollutants. Unit "old" has a gas handling capacity of 80,000 Nm^3/h and a filtering area of 2,480 m^2, whereas unit "new" has a capacity of 100,000 Nm^3/h and a filtering area of 2,800 m^2.

Table I. Scrap type ranges

Tabla I. Composición media de la materia prima

Scrap type	%
Fine scrap	13.3 to 19.6
Fragmented scrap	13.2 to 16.1
Average scrap	24.9 to 31.9
Industrial scrap	27.4 to 41.9
Ferrous rejects from foundries	5 to 5.4

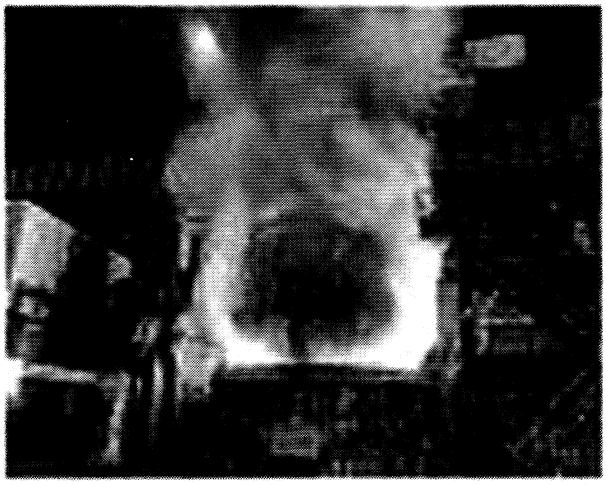


Figure 1. EAF operation, pictures taken during sampling measurements.

Figura 1. Operación del horno eléctrico.

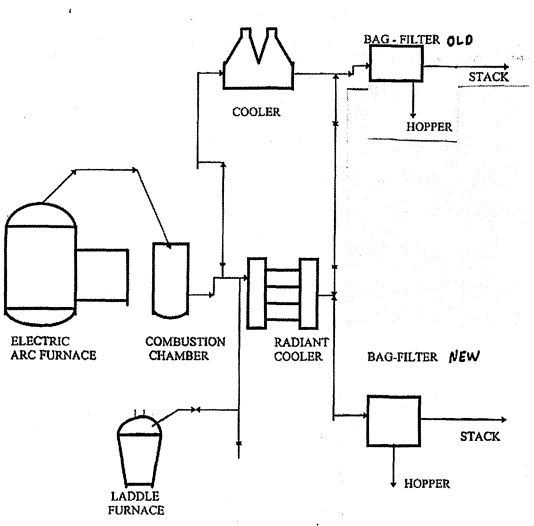


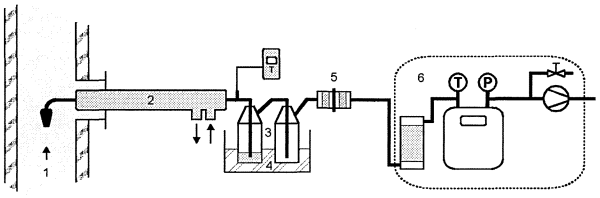
Figure 2. Flowsheet of the gas cleaning section.

Figura 2. Diagrama del equipamento de tratamiento de gases.

The nominal design outlet concentration for total suspended dust is 20 mg/Nm^3.

3. EXPERIMENTAL

Measurements were made after the deducting units both for old and new systems. A partial volume of the flue gas was extracted via a glass tube from the flue gas duct and led into the collection system, as depicted in figure 3. The glass probe was installed centrically in a water-cooled probe of titanium. The collection system consists of a condensate



1 Flue gas
2 Water-cooled sampling probe
3 Condensate flask
4 Ice bath
5 Filter cartridge (PUF plugs and plane filter)
6 Suction device

Figure 3. Sampling apparatus.

Figura 3. Aparato de muestreo.

flask, receiving the accumulating condensate and a part of the dust, and of a cartridge with two polyurethane foams, a special sorbent with proven efficiency for the separation of organic substances. The foams were installed on both sides of a plane filter with high collection efficiency. For sampling an equipment consisting of a drying tower, gas pump and gas volume meter is connected. A sampling standard (C-13-labelled 1,2,3,7,8-PCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,7,8,9-HpCDF) was added to the condensate flask before sampling. The flow of the sampled gas stream was adjusted to isokinetic conditions on the sampling nozzle. The sampling procedure is in compliance with the EU-Standard EN 1948, part 1[5], using the alternative C - water cooled probe. Emission samples were analysed according to the European Standard EN 1948 parts 2, 3,[6 y 7]. Quantitative determinations of PCDD/PCDF in various samples according to the isotope dilution method with the use of following 2,3,7,8-substituted 13C-UL internal standards.

Afterwards, extraction of the samples with appropriate solvents from the condensate, the PU-Foam, the plane filter was made. Additionally the glass sampling tube was cut into pieces and extracted too. Clean-up was done in multicolumn systems involving carbon-on-glasfibre or carbon-on-celite. HRGC/HRMS measurements with VG-AutoSpec using SP2331 and/or DB-5 capillary columns. For each substance 2 isotope masses were measured. Quantification is carried out with the use of internal/external standard mixtures. 17 congeners of PCDD/PCDF were determined, according to standard EN 1948 – Part 3 [7], as follows:

- PCDD:
  2,3,7,8-TCDD; 1,2,3,7,8-PCDD; 1,2,3,4,7,8-HxCDD; 1,2,3,7,8,9-HxCDD; 1,2,3,6,7,8-HpCDD; 1,2,3,4,6,7,8-HpCDD; 1,2,3,4,6,7,8,9-OCDD
- PCDF:
  2,3,7,8-TCDF; 1,2,3,7,8-PCDF; 2,3,4,7,8-PCDF, 1,2,3,4,7,8-HxCDF; 1,2,3,6,7,8-HxCDF; 1,2,3,7,8,9-HxCDF; 2,3,4,6,7,8-HxCDF; 1,2,3,4,6,7,8-HpCDF; 1,2,3,4,7,8,9-HpCDF; 1,2,3,4,6,7,8,9-OCDF

4. RESULTS AND DISCUSSION

The summary of obtained results is presented in table II. The values for dioxins/ furans are based on an average of six hours on the new system, resulting in an average sampled volume of 6.2 m^3; and on an average of three hours on the old system, resulting on an average sample volume of 5.9 m^3.

Within the scope of European standards there is no standardized method for the determination of the uncertainty of measurement that covers both sampling and the analytical procedure as well as the uncertainty related with the conditions of the sampling site in special. For this reason the single results are not supplied with information of uncertainty. Our experience shows that, in general, uncertainties in the range of 10 % to 20 % for the components listed in the above tables. For values near the detection limit the uncertainties are higher. Based on the measurements made, figure 3 shows the existence of individual species of dioxins and furans, in the picogram range, with a

Table II. Quantities of raw materials, products and by products during measurement tests (ton)

Tabla II. Cantidades de materia prima, produto y residuos, a lo largo de las mediciones

Test	Raw materials			Product	By-products	
	Scrap	Lime	Coke	Steel	Slag	Dust
54668	90.6	2.8	1.2	75.5	17.4	1.4
54671	82.3	2.5	1.2	72.4	13.8	1.2
54673	84.9	3.1	1.2	70.8	16.8	1.3
54682	95	2.5	1.2	83.1	14.1	0.8
54694	85.7	2.3	1.2	73.9	20.2	1.6
54696	92.5	2.3	1.2	77	18.6	1.6
54724	90.4	2.4	1.2	74.7	17.4	1.4
54728	92	2.3	1.2	76.5	18.5	1.5

prominence of 2,3,4,7,8 – PentaCDF in all measurements. In this plot, the existence of 17 searched compounds was verified. The obtained values are not homogeneous with some dispersion of the obtain results, for congeners and also for the total of the Dioxins/Furans. However, observing figures 4, 5, 6 and 7, the existence of a coherent profile is verified. This seems a very important finding within the scope of this project, as this appears to be the actual fingerprint of this particular process in what regards the emission of dioxins and dibenzofurans. In fact, it can be noted that this profile is always observed during the operation of this EAF system and is non-dependant of the gas flow rate neither of the EAF actual processing capacity. The average value obtained in these measurements is of 0.18 I-TEQ ng/m^3. However registered values are very high (in the order of the 0.83 I-TEQ ng/m^3) but very low values (approximately 0.05 I-TEQ ng/m^3) were also measured. The variations observed can possibly be explained by different production regimes, using different loads for the furnace, which were observed during sampling operations. These

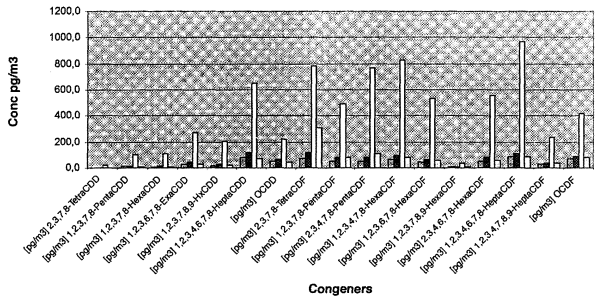


Figure 4. Diagram of 17 congeners in 8 measurements of Dioxins and Furans in the stack of the new system.

Figura 4. Diagrama de concentraciones de dioxinas y furanos medidas en el nuevo sistema.

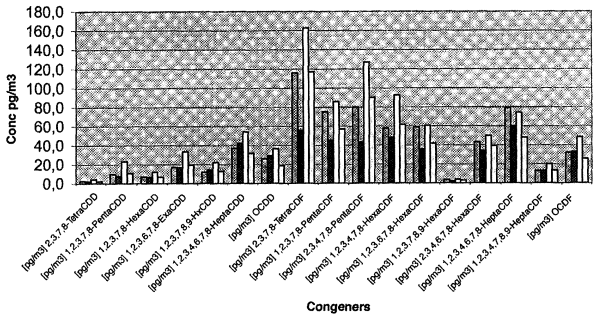


Figure 5. Diagram of 17 congeners in 8 measurements of Dioxins and Furans in the stack of the old system.

Figura 5. Diagrama de concentraciones de dioxinas y furanos medidas en el viejo sistema.

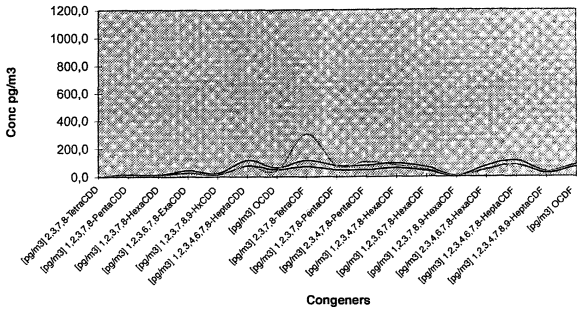


Figure 6. Profile of 17 congeners in 8 measurements of Dioxins and furans in the stack of the new system.

Figura 6. Niveles de concentraciones de dioxinas y furanos medidas en el nuevo sistema.

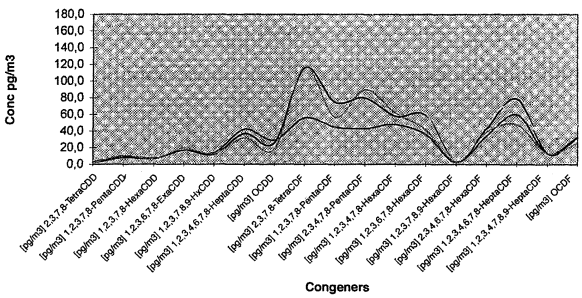


Figure 7. Profile of 17 congeners in 8 measurements of Dioxins and furans in the stack of the old system.

Figura 7. Niveles de concentraciones de dioxinas y furanos medidas en el viejo sistema.

Table III. Summary table of dioxins/furans in New and Old System

Tabla III. Emisiones de dioxinas y furanos medidas en el nuevo y viejo sistema

Concentration of the determined components, related to standard conditions (1013 hPa, 273 K), expressed as I-TEQ (pg/m^3)		
New System	**Old**	**System**
measurement 1	67	84
measurement 2	105	53
measurement 3	832	129
measurement 4	121	86
Average value	281	88

measurements are considerably long, about 6 h, and generally 4 to 6 different charges (comprising different loads) each, which contributes to the observed variability in the amount of micropollutants. Nevertheless, it can be noticed that the profile of analysed congeners seems to be nearly the same for all the sampling trials.

5. CONCLUSION

The dispersion of measured individual values, which was observed during measurements, is significant. Nevertheless, a very clear profile of dioxins and dibenzofurans does exist which can be considered as the emissions fingerprint for this process. We believe that, the fact of the new dedusting system and the old dedusting system having different flow rates, as well as different filtration areas, resulting in different particle loads, does justify the observed dispersion of values. In fact, the obtained concentrations are higher in the new system, where the majority of gas flow (55 %) and also the filtration area is bigger (53 %), an thus, a higher concentration of reactive species could be expected to exist in the new system. Also, even for the joint values the dispersion is still observed in each group, that is, for both the old and new system. As this scrap is considered to be non-contaminated and thus precursors are, *a priori*, non-existent there is a possibility of occurrence of heterogeneous reactions over particulate surface at temperatures higher than 300 °C, but as the oven temperature is higher than 1,500 °C, certain organic species are destroyed. However, we believe that the basic conditions for occurrence of De Novo synthesis (without organic precursors) do exist. This can be enhanced at temperatures higher than 250 °C and by the occurrence of metallic species acting as catalysts. However, this conclusion has to be confirmed by the determination of other organic species such as PAHs and PCBs which is to be made in the next stage of this work, as well as a detailed knowledge of chlorine and certain organic compounds in the materials fed to the furnace.

Ackwoledgments

Financial support by the European Commission, through Contract N° 7210-PR-200 is gratefully acknowledged.

REFERENCES

[1] D.R. ANDERSON AND R. FISHER, *Chemosphere* 46 (2002) 371-381.
[2] T. WANG, D.R., ANDERSON, D. THOMPSON, M. CLENCH AND R. FISHER, *Chemosphere* 51 (2003) 585-594.
[3] A.BUEKENS, L.STIEGLITZ, K., HELL, H. HUANG AND P. SEGERS, *Chemosphere* 42 (2001) 729-735.
[4] E.R. ALTWICKER, J.S. SCHONBERG, R.K.N.V.K. KONDURI AND M.S MILLIGAN, *Hazard Waste Mater.* 7 (1989) 73-87.
[5] *European Standard: CEN/EN 1948*, Part 1, 1996.
[6] *European Standard: CEN/EN 1948*, Part 2, 1996.
[7] *European Standard: CEN/EN 1948*, Part 3, 1996.