

EFFECTS OF FABRIC FILTER AND ACTIVATED CARBON ON PCDD/F CONGENERS DISTRIBUTION IN FLUE GAS OF A SECONDARY CASTING ALUMINIUM PLANT

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Introduction

In flue gas from most combustion processes, polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are usually found in vapour phase as well as bound to particulate matter (PM) solid phase. The particle-bound PCDD/F emissions at stack are largely controlled by particulate air pollution control devices (APCD). The PCDD/F in vapour phase may escape from these devices and their emission could be controlled by powered activated carbon injection. As the partitioning has severe implications on PCDD/F emission at stack, information on the partition in flue gas is very important in selecting and designing PCDD/F control devices. In a previous paper¹, we reported the main results obtained in a study on a secondary casting aluminium plant with the specific aim to investigate the formation and release of PCDD/F. Following this, here we report the partitioning and the removal efficiency of the 2,3,7,8 substituted congeners of PCDD/F both from vapour and solid phases in flue gas at the fabric filter (FF) inlet and the outlet (stack emission).

Materials and methods

The plant

The investigated plant is a secondary aluminium casting plant situated in an Italian valley 40 km north east of Brescia, which represents about 30% of the Italian secondary aluminium production. Secondary aluminium is made from recycled scrap from all over Europe, collected from aluminium processing companies, and metal items that have reached the end of their life cycle. The production consist of aluminium bars (60%) and aluminium in a molten state (40%), delivered in specially designed transport "ladles" that pour the metal straight into the furnaces ready for final forging. This is an undoubted advantage in term of saving in melting time and energy consumption.

The flue gas treatment line of the plant is equipped with post combustor (PC), quenching chamber (QC), activated carbon injection, reactor to increase the fly ash diameter and FF.

Sample collection and analysis

The flue gas was sampled upstream and downstream the FF under isokinetic conditions, following the filter-cooler method UNI EN 1948–1/99 and 2006 updates. The minimum overall time of sampling was that required for a complete working schedule of one of the two furnaces. A previous study² indicated that the partitioning of vapour phase PCDD/F decreased with the increase of filter loading during the flue gas sampling. Hence, during each sampling the fiber filter was replaced with the frequency needed to minimize the pressure drop effect and the adsorption of PCDD/F onto particulate.

PCDD/F in solid phase and in condensate from vapour phase were separately analysed to obtain information about their distribution in the two phases. The analyses of 2,3,7,8 substituted PCDD/F were performed following the methods UNI EN 1948–2,3/99 and 2006 updates for extraction and purification and the method UNICHIM n. 825 for quantification. PCDD/F analysis of sample extracts was conducted with HRGC/HRMS. A high resolution gas chromatograph VARIAN CP/3800 and an high resolution mass spectrometer triple quadrupole MSD VARIAN 1200-ALS VARIAN CP8400 equipped with capillary column DB5-MS and CP-SIL88 were used.

PM was quantified with a manual gravimetric method (UNI EN13284-1/03).

Results and discussion

Table 1 represents the experimental runs (#) together with sampling date and sampling point identification, the flue gas temperature, the PM concentration in flue gas and the PCDD/F mass flow (nmol/h) in vapour and solid phases. Data elaboration is carried out at 2,3,7,8 PCDD/F congeners level. Results are presented in terms of Equivalent Toxicity (ng I-TEQ/Nm³) or mass flow in flue gas (nmol/h), to eliminate flow rate inconstant influence and to evaluate real PCDD/F increase and decrease.

The PCDD/F distribution between vapour and solid phases depends on properties of each congener and it is strongly affected by PM concentration as well as particle size distribution and properties³. Vapour-solid PCDD/F outcomes included experimental as well as theoretical aspects. The former are related to the flue gas temperature changes along the cleaning system and during sampling, the knowledge of congeners physico-chemical properties and the artefacts that could arise from conventional sampling technique. The latter include the use of equilibrium thermodynamics in systems that are in non equilibrium states, the strength of the interactions between each congener and PM matrix (physisorption and/or chemisorption), the adsorption-desorption mechanisms in flow systems and the related activation energies, the fractional surface coverage and the mobility of adsorbed species. Moreover, the study of PCDD/F partition between vapour and solid phases involves aggregated data measured on very complex matrices. Moreover, at present time, technologies for real time PCDD/F sampling both in vapour and solid phases are not available on the market. Thus, the only way to gain knowledge on this important problem seems to be the sampling under controlled filter loading conditions.

Following this, the PCDD/F partitioning between vapour and solid phases was studied upstream and downstream the FF (Figure 1) using the function FI³ calculated with the equation:

$$(FI)_i = \log [(C_v/C_s)_i]$$

where C_v and C_s are the vapour and solid phases mass flow (nmol/h) of the i -th PCDD/F congener. A positive or negative FI value indicates that the i -th PCDD/F congener is mainly present in vapour or in solid phases.

At the FF inlet (Figure 1), FI is less than zero for all congeners but not for 2,3,7,8 TCDD and 2,3,7,8 TCDF e.g., the penta to octa congeners are mainly present in the solid phase. At the FF outlet, all the congeners are mainly present in vapour phase ($FI > 0$) and FI decreases as chlorination percentage increases. Thus, the FF retains particle-bound PCDD/F but not vapour phase PCDD/F.

The PCDD/F removal efficiencies ($RE = 100 * (\text{Inlet} - \text{Outlet})/\text{Inlet}$) were separately calculated for each congener in vapour and solid phases. The solid phase removal efficiencies are independent from temperature and almost 100% for each congener. The vapour phase PCDD/F removal efficiencies are lower than in the solid phase and they are related to temperature and molecular weight. Figure 2 reports the vapour phase removal efficiency in runs #A, #B and #C performed at different temperatures: inlet temperatures decrease from 128° to 101° to 95°C and outlet temperatures decrease from 103° to 85° to 89°C. In run #A, the efficiencies are negative for all the congeners. In run #B, positive removal (40% – 65%) is observed for all the congeners except OCDD and OCDF. In run #C, the removal efficiencies are positive (48% - 98%) and regularly increase with the chlorination level of PCDD/F congeners. Thus, removal efficiencies in vapour phase increase when flue gas temperature decreases and it seems that flue gas inlet temperatures lower than 100°C are needed to obtain a stabilization of removal efficiencies.

Figure 3 shows the comparison between vapour phase percentage distribution of each congener at FF inlet in runs #A, #B, and #C (separately calculated for PCDD and PCDF). Low chlorinated PCDD/F congeners percentage decreases with the temperature decreasing (the only exception is 2,3,7,8 TCDD) whereas that of high chlorinated congeners increases, the trend inversion is observed for 1,2,3,4,6,7,8 HpCDD or 1,2,3,6,7,8 HxCDF. Taking into account that low chlorinated congener RE at 95°C inlet temperature aren't greater than 60% whereas those of high chlorinated congener reach 98%, the low chlorinated congeners predominate in the vapour phase downstream the FF i.e., at stack emission.

The overall result of temperature lowering at FF inlet is a very good removal efficiency which, as expected, increase with increasing of molecular weight together with an important decrease of congeners mass flow. However, equivalent toxicity value at stack is still significant due to the contribution of low chlorinated congeners.

With the aim to reduce the equivalent toxicity emission at stack, the effect of the activated carbon injection to PCDD/F partitioning between vapour and solid phases was studied in run #D. To separate the activated carbon effect from the temperature ones, the inlet and outlet temperatures in run #D were higher than 100°C and similar

to those in #A. In run #A, 28 % of the overall PCDD/F mass flow is found in vapour phase at the FF inlet whereas a decrease to 0.1% is observed when activated carbon is injected (#D). Figure 4 shows PCDD/F congeners distribution in vapour phase at FF inlet in the two runs: for PCDD, a reduction of each congener and a great increase of OCDD percentage is observed as a consequence of the activated carbon injection whereas the distribution variation in PCDF doesn't follow a clear trend. Table 2 shows the contributions to the equivalent toxicity in runs #A and #D. No significant variation is observed in solid phase. On the contrary, the PCDD/F vapour phase contribution to the equivalent toxicity decreases from 42% in #A to 0,1% in #D. Hence, despite an increase of PCDD/F mass flow in vapour phase between FF inlet and outlet (run #D), the total equivalent toxicity is 0.1 ng I-TEQ/Nm³.

Results indicate that the particle-bound PCDD/F removal efficiencies in the fabric filter are independent from flue gas inlet temperature and are almost 100% for each congener. The vapour phase PCDD/F removal efficiencies are lower than the values for solid phase and they are related to temperature and molecular weight. In particular, removal efficiencies of vapour phase PCDD/F increase when flue gas temperature decreases and, at lowest temperature, increase when molecular weight increases. It seems that flue gas inlet temperatures less than 100°C are needed to ensure partitioning to the solid phase. The injection of activated carbon reduces the PCDD/F mass flow percentage in the vapour phase at the fabric filter inlet from 28% to 0.1%. The corresponding Equivalent Toxicity at the point of emission is reduced from 8.30 to 0.1 ng I-TEQ/Nm³.

References:

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2. Ryan S., Touati A., Wikstrom E. and Gullet B. *Organohalogen Compounds* 2003; 63: 45.
3. Kai Hsien, Chi and Moo Been, *Chang Environ. Sci. Technol.* 2005; 39: 8023.

Table 1: Experimental runs, with sampling date, sampling point identification and parameters analyzed

#	Sampling Date	Sampling Point	T (°C)	PM (mg/Nm ³)	PCDD/F solid phase (nmol/h)	PCDD/F vapour phase (nmol/h)
A	03.06.06	FF inlet	128	4990	26133	10150
		FF outlet	103	0.2	68	13922
B	05.08.06	FF inlet	101	3400	25508	5093
		FF outlet	85	0.2	35	2877
C	09.21.06	FF inlet	95	3200	129041	50247
		FF outlet	89	0.2	150	9146
D ^a	10.15.07	FF inlet	137	2533	16884	22
		FF outlet	117	2.1	105	142

^a With powered activated carbon injection

Table 2: Equivalent toxicity partitioning between vapour and solid phases in runs #A and #D

#	Sampling Point	PCDD/F solid phase (ng I-TEQ/Nm ³)	PCDD/F vapour phase (ng I-TEQ/Nm ³)
A	FF inlet	11.43	8.27
	FF outlet	0.020	8.30
D ^a	FF inlet	12.87	0.009
	FF outlet	0.031	0.069

^a With powered activated carbon injection

Figure 1: Function FI values in vapour phase at FF inlet and outlet in runs # A, B, and C

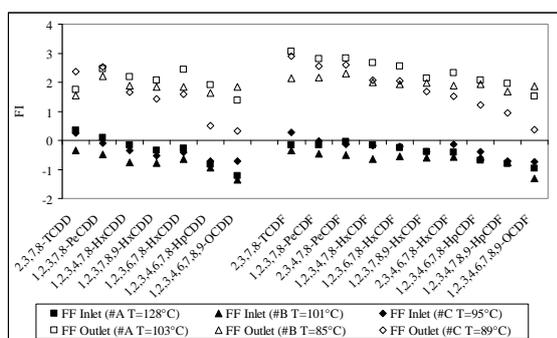


Figure 2: PCDD/F FF RE in vapour phase in runs # A, B, and C

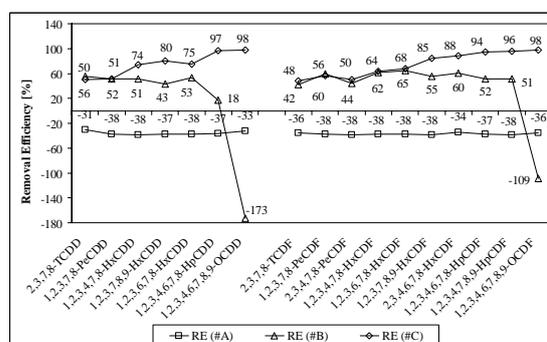


Figure 3: PCDD/F congener distribution in vapour phase at FF inlet in runs # A, B, and C

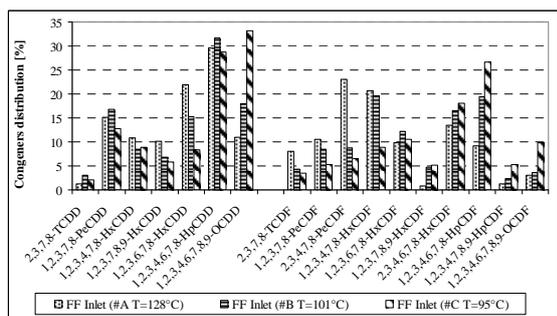


Figure 4: PCDD/F congener distribution in vapour phase at FF inlet in runs #A and #D

