

REDUCTION OF PCDD/F EMISSION BY WET SCRUBBING

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1. Introduction

Awareness of environmental effects of POP^{1,2} and evolution of regulatory requirements³, ever more stringent, have compelled a continuous advancement in air emission control and abatement technologies. Demand for operating systems, installed in the flue gas cleaning train with previous specific aims, to become efficient over *other* type of contaminants has already produced technological achievements⁴⁻⁷. The extension of control and abatement systems capability must guarantee or improve previous performances (relative to acidic gases, heavy metals, particulate matters, nitrogen oxides) and in this framework Dry or Semi-Dry techniques seem to be properly investigated, while the potential for improving the Wet options could be underestimated. Nevertheless Wet Scrubbers are widely used as pollution control equipment and generally as the preferred way for acidic emissions reduction: as a matter of fact they can reach more constant and about an order of magnitude lower outlet acid gas concentrations than alternative choices. Investigations has been therefore undertaken both on the design criteria both on the performances and chemistry of additives in Wet Scrubber (WS). The very promising, but preliminary, results hereinafter presented are considered to evaluate which separation / mass transfer mechanisms may be effective (particle separation, condensation, diffusion).

2. Material and Methods

A WS bench scale unit⁸ was installed and operated on a bypass stream of the flue gas cleaning system of the MSW Incineration Plant of Bolzano⁹- Italy. The cleaning train of this complex has, after the waste heat recovery boiler, a Fabric Filter (FF) for particulate separation, a two stage WS for acid gases and volatile metals removal and catalytic units for nitrogen oxides (SCR) and for organic compounds (CatOx) degradation. Transfer lines from the Industrial plant and all the components of the experimental unit in contact with flue gas were made of selected materials like glass, teflon or teflon lined stainless steel, chosen to overcome any interference of adsorption / release phenomena (known as memory effects¹⁰). The unit was operated (see figure 1) on the following streams: the out-stream of the Industrial WS (pos.1), the out-stream of the aforementioned WS acidic stage (pos.2), the out-stream of the FF (pos.3). Operative conditions of the experimental unit were, in this first campaign, selected to maximise wet scrubbing PCDD/F abatement efficiencies. Experimental procedure was as follows: operative conditions (temperature, gas flow rate, scrubbing water hold-up and flow rate, pH, additive concentration, and so on) were held constant for at least 100 hours to properly condition the system; afterward simultaneous samplings were started at the inlet and outlet of the unit. Sampling, by means of silanised glass probes, and analysis of PCDD/F were carried out according to EN 1948 method. All samples total dry gas volume was at least 8 Nm³. Separation and clean up procedure were based on

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chromatography. Analysis of the 17 toxic isomers were performed with HRGC-LRMS. Isomers with a concentration under the detection limit were assumed to be equal to half of the detection limit in the Toxic Equivalent Quantity calculation. Analysis of position 3 samples characterised the PCDD/F toxic isomers partition in the original stream between filtered particulate and condensable matter, in some way meaningful of vapour phase and adsorbed dioxins.

3. Results and Discussion

Experimental unit inlet streams characteristic (from position 1, 2 and 3) are summarised in table 1. Specific isomer concentrations of PCDD/F in flue gas at the three different points are shown in figure 2. There is no relevant toxicity (always in the range $0,18 \div 0,28$ ngTEQ/Nm³) or fingerprint differences among the three inlet streams. This is a further evidence that, as it is, the two stage industrial WS is not very effective in PCDD/F abatement. Further detail of the position 3 stream (see figure 3) shows that PCDD/F at the inlet of the WS are mainly in the gas phase, and only a fraction lower than 5% is associated to the particulate matter. As the average removal efficiency for PCDD/F in a WS is often reported to be of the same magnitude as the observed removal efficiency of particles from the gas¹¹, it may be inferred that traditional WS are ineffective whenever the previous particle removal system is very effective, as in the present case. A simplified approach to describe PCDD/F removal mechanisms in a WS should consider condensation, de-dusting and diffusion. As long as flue gas particles concentration is low, as in the present case (<1mg/Nm³) further particle abatements in a WS may not reduce PCDD/F TEQ more than few points %. Dioxins removal in WS is therefore mainly related to condensation / diffusion mechanisms. The former may be improved optimising scrubber design and fluid dynamics, the latter may be modified adding proper additives/sorbents. The second mechanism will be sensible to inter-phase area. Useful indications of the relative effects due to the last two mechanisms may be obtained from results in figure 4. The experimental scrubber was operated on stream from pos.1, recycling just water or a diluted (0,1% w/w) activated carbon slurry obtaining respectively PCDD/F removal ~ 30% and >98% with outlet concentration <0,02 ngTEQ/Nm³. Tests on more complex composition streams (from pos.2 and pos.3) confirm these performances. More over PCDD/F removal functionality does not reduce the acidic gas and Hg abatement capacity of the wet treatment, which can reliably reach outlet concentration of 5 and 20 mg/Nm³ respectively for HCl and SO₂ and 10 µg/Nm³ for Hg.

4. Conclusions

Wet scrubbing may be considered an effective option for PCDD/F abatements, as long as proper scrubber design and sorbent addition are applied. Tested removal efficiency exceeded 98 % with outlet loading largely below 0,05 ngTEQ/Nm³. Dioxins removal does not reduce performances in heavy metals and acid gas abatement. On the contrary advantages may be observed in Hg capture. Condensation / diffusion mechanisms both played a relevant role in the observed phenomena, but careful attention must be paid to the case specific conditions. Simultaneous PCDD/F, acidic gases, heavy metal capture may be therefore realised in the same unit. A direct comparison, on the same flue gas compositions, of the catalytic (SCR-CatOx) unit (PCDD/F outlet concentration 0,005⁹) and experimental apparatus performance (PCDD/F<0,02ngTEQ/Nm³) shows very high efficiencies for both the systems.

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6. References

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Table.1 Typical streams composition in differing sampling points

components	pos.1			pos.2			pos.3		
	(%v)	(ng/Nm3)	(mg/Nm3)	(%v)	(ng/Nm3)	(mg/Nm3)	(%v)	(ng/Nm3)	(mg/Nm3)
H2O	~20			~20			~10		
O2	~9			~10			~10		
CO			1			1			1
PCDD/F - TEQ		0,2			0,2			0,2	
Hg			0,006			0,03			0,15
Solid particles			<1			<1			<1
HCl			2			50			500
HF			<0,2			1			1
NOx			300			300			300
SOx			10			42			42
IPA		2000			2000			2000	
PCB		20			20			20	
T (°C)	62			72			200		
P(mBar)	1008			1028			1050		



