# Destruction of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Fabric Filters


## Recent Experiences with a Catalytic Filter System

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# ABSTRACT

Sustained catalytic destruction and removal of dioxins/furans from the environment has been demonstrated at municipal waste incinerators (MWI) in Europe. This paper details the full-scale field experiences of a catalytic filtration system that both destroys dioxins/furans and removes particulate to levels significantly lower than the regulatory limit.

The dioxin destruction performance of three MWI's is detailed. The long-term destruction performance of a catalyst filtration system in Belgium will be described. The system has consistently reduced effluent concentrations of dioxins/furans to significantly less than 0.1 ng I-TEQ/Nm³ of flue gas for over three years. Additionally, the case study of a MWI in Harelbeke, Belgium will describe the use of the catalytic filtration system to overcome the limitations of other dioxin/furan control technologies. Finally, the application of this catalyst filtration system to the French MWI, Thonôn-les-Bains, will be described.


# INTRODUCTION

### Description of Catalytic Filter System

The catalytic filter system employed is the REMEDIA™ D/F Catalytic Filter System. This system is an evolution of two proven technologies: catalysis and surface filtration. The system consists of an ePTFE membrane and a catalytic felt substrate. The membrane, which is a GORE-TEX® membrane, captures submicron particulate, including heavy metals, without allowing particles to penetrate or pass through the catalytic felt substrate. Gaseous PCDD/Fs, however, pass through the membrane and into the catalytic felt substrate. This substrate is a needlepunched felt made from ePTFE fibers containing a proven dioxin-destroying catalyst. The catalytic felt destroys gaseous PCDD/F by means of a catalytic reaction. PCDD/F molecules diffuse on the catalyst surface and react to form trace amounts of $CO_2$, $H_2O$, and HCl. The catalysis and surface filtration principles are illustrated in Figure 1.

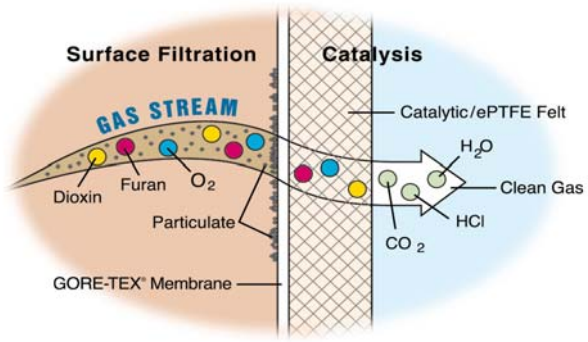


**Figure 1.** Cross-sectional view of the catalytic filter. The membrane removes particulate while the catalytic felt destroys gaseous PCDD/F.

## THE MUNICIPAL WASTE INCINERATOR, CITY OF THONÔN-LES-BAINS, FRANCE

The UIOM (Usine d'incinération des Ordures Ménagères) Thonôn-les-Bains processes municipal waste from the region of Chablais, France, which includes 30 communities such as Thonôn, Evian, Morzine and Avoriaz. It is owned by STOC (Syndicat de Traitement des Ordures Ménagères du Chablais), and is operated by RONAVAL of the group CGEA ONYX.

### Plant Description

The plant started up in 1988. The incinerator line consists of an ITISA Volund grate furnace with a design capacity of 36,500 tons of municipal waste per year, and a boiler that produces 14 t/h of steam. The steam is supplied to adjacent industries. The flue gas is cleaned by a 2- field ESP followed by a

dry absorption system (BICAR® injection) and fabric filter. The plant configuration is shown in Figure 2.

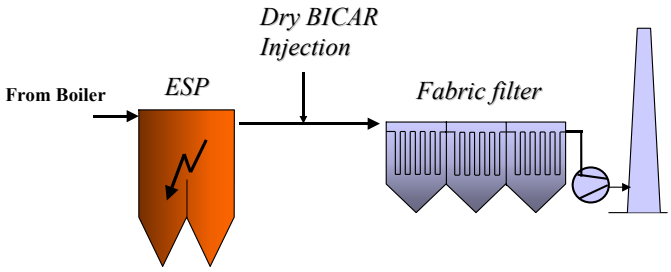


**Figure 2.** Plant Configuration for the UIOM Thonôn-les-Bains.

### Regulatory Status

The new Directive 2000/76/EC of the European Parliament (December 4, 2000) on the Incineration of Waste must be implemented by January 1, 2003 for new plants, and by January 1, 2006 for existing plants. The limit for PCDD/F is 0.1 ng I-TEQ/$Nm^3$ @ 11% $O_2$. The local authorities decided to install measures for the control of PCDD/F by end of the year 2000 to ensure compliance at the earliest possible date.

### Alternatives Considered

The fabric filter is operated at 200°C in order to minimize corrosion of the air pollution control (APC) system and to reduce the stack plume.

The initial proposal was to install an injection system for powdered activated carbon (PAC). This was seen as a proven and widely used technology to control PCDD/F. Because of the high temperature range of the fabric filter, there were concerns that hot spots in the hoppers and in the dust conveying and storage system could lead to ignition of the carbon. Alternatives that would be compatible with the operating conditions were evaluated. These included non-flammable additives and a catalytic reactor. The non-flammable additives were not proven technology to control PCDD/F at temperatures above 200°C, and the catalytic reactor would have exceeded the projected budget. For these reasons, the catalytic filter material was selected.

The REMEDIA™ D/F Catalytic Filter System was installed into the fabric filter in August 2000.

### Emission Measurements

Beginning in July 2000, several Dioxin measurements were performed at the stack in compliance with EN 1948, the European standard for the sampling and analysis of PCDD/F. The results of these measurements are shown in Figure 3. Before the installation of the catalytic filters, the stack PCDD/F concentration was 1.9 [ng I-TEQ/$Nm^3$]. After installation of the catalytic filters, stack measurements were conducted in October and November 2000, and again in January 2001. The January 2001 measurement campaign was supported and partly financed by ADEME[1]. The results indicate a significant reduction in the PCDD/F emissions with the REMEDIA filter system.

[1] ADEME: ***A**gence **d**e l'**E**nvironnement et de la **M**aîtrise de l'**É**nergie*, French Environment and Energy Management Agency

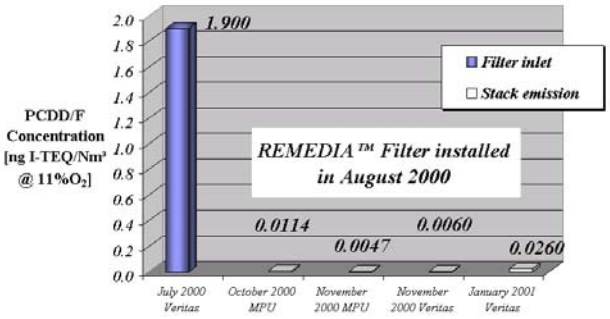


**Figure 3.** UIOM Thonôn-les-Bains, PCDD/F Measurements. All measurements performed at the stack. Measurements performed by MPU, Berlin, Germany, and Veritas, Lyon, France, as indicated.

### Other Results

In addition to the benefits of PCDD/F destruction, other benefits were realized as well.

- The total number of cleaning cycles of the fabric filter is less than 1/10 compared to the previous filter material.
- The consumption of additive is 20 to 30% less compared to previous operation.

## MUNICIPAL SOLID WASTE INCINERATOR, CITY OF HARELBEKE, BELGIUM

### Plant Description

The MSWI City of Harelbeke processes municipal waste from the surrounding communities of Kortrijk, Belgium. The plant started up in 1987, and is owned and operated by IMOG[2]. The waste is processed in two CEC "Seeghers" furnaces, each of them with a designed incineration capacity of 40,000 tons of municipal and industrial waste per year. The boiler steam production is 22 t/h. An ESP first dedusts each furnace line. The gas streams of the two lines are then merged into one common APC line, consisting of a quench, an acid scrubber and basic scrubber (3 separate towers), a fabric filter, and a one-layer honeycomb catalytic reactor for NOx control. The plant configuration is shown in Fig. 4.

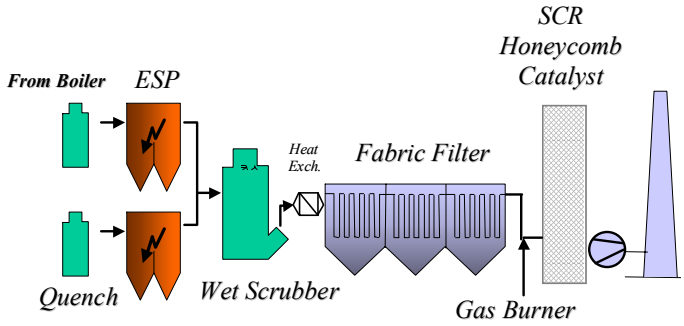


**Figure 4.** Plant configuration for the IMOG waste incinerator

### Regulatory Situation in Belgium

In the Flanders region of Belgium where IMOG is located, municipal waste incinerators are not allowed to operate unless the PCDD/F regulatory limit of 0.1 ng I-TEQ/Nm$^3$ is met. Continuous

[2] IMOG: **I**ntercommunale **M**aatschapij voor **O**penbare **G**ezondheid in het gewast Kortrijk

sampling and bi-weekly analysis for PCDD/F are performed to ensure compliance with the regulation during all stages of operation, including startup and shutdown. If an incinerator is found to be out of compliance, immediate measures to solve the problem must be enacted. An incinerator can be closed down if satisfactory progress toward compliance is not demonstrated. As a result of regulatory and enforcement actions to reduce PCDD/F emissions, 6 incinerators were closed down in 1997 after a measurement campaign of 19 incinerators; the remaining 13 incinerators instituted measures to control emissions (1). By 1998 the remaining incinerators were in compliance with the regulatory limit. By 2000, the average annual emissions of PCDD/F from all municipal waste incinerators in Flanders were reduced from more than 120 g/yr to less than 1 g/yr (1).

**Alternatives Considered**

IMOG's initial approach to control PCDD/F was to add PAC into the wet scrubber. The best emission results for PCDD/F obtained at the stack were < 0.1 ng I-TEQ/Nm³, although it was very difficult to maintain the emissions constantly below the level of 0.1. This was due to the difficulty of retaining the PAC in the wet scrubbers and in the demister.

Based on these experiences it was decided to add a fabric filter with the REMEDIA™ D/F Catalytic Filter System for particulate control and destruction of PCDD/F. The new system began operation in January 2000. Due to contractual reasons, the fabric filter was operated with the injection of SORBALIT® for the first 8 months. In September 2000, the authorities permitted IMOG to run the fabric filter without the injection of SORBALIT, leaving the destruction of PCDD/F to be solely controlled by the REMEDIA™ D/F Catalytic Filter System.

**Emission Measurements**

At IMOG, like all other MSWIs in the Flanders region of Belgium, the PCDD/F concentration at the stack is measured in two ways:

- The continuous sampling system (AMESA), where a cartridge is changed every two weeks and analyzed in a laboratory, and
- The 6-hour measurement (according to EN 1948) performed by an accredited measuring institute two to four times a year.

Figure 5 shows the emission of PCDD/F from February 2000 until December 2000. From a concentration of 0.045 in February, the AMESA values decrease to 0.0011 ng I-TEQ/Nm³ in December. There is good agreement between the AMESA system and the 6-hour measurements.

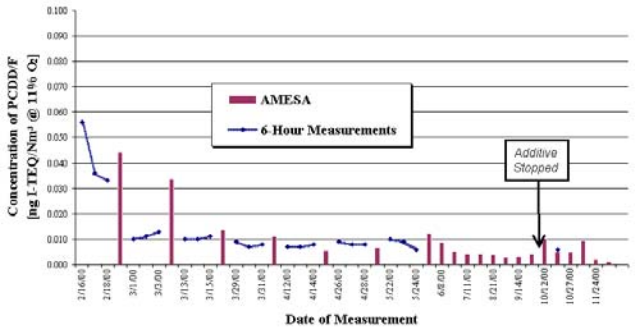


**Figure 5.** PCDD/F concentrations in the stack, and comparison of the continuous sampling system (AMESA) and 6-hour measurements.

Several 6-hour measurements at the fabric filter inlet and outlet were performed in 2000. The inlet concentrations of PCDD/F ranged between 1.26 and 2.4 ng I-TEQ/Nm³. The outlet concentrations with the REMEDIA™ D/F Catalytic Filter System were below the measurement detection limit of the

6-hour measurement[3], which was 0.006 ng I-TEQ/Nm³ (blank level). The overall removal efficiency on a TEQ basis was 99.5 to 99.7%. No change in PCDD/F concentration was detectable after the catalytic reactor, as shown in Fig. 6.

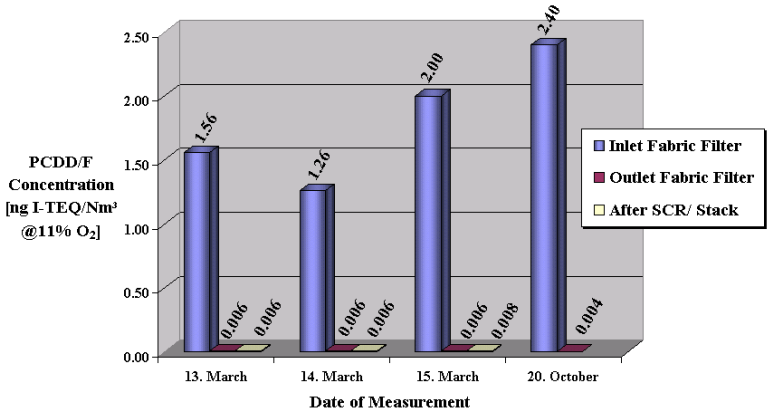


**Figure 6.** PCDD/F concentrations at fabric filter inlet, fabric filter outlet, and stack (6-hour measurements). The catalytic reactor is represented as "SCR" for selective catalytic reduction of NOx.

The REMEDIA™ D/F Catalytic Filter System has been in operation over a period of more than 5 months (14 months total), without the injection of carbon-based additives. The PCDD/F emissions are dramatically lower than 0.1 ng I-TEQ/Nm³.

### Other Results

The particulate emissions at the stack range from 0.2 to 0.6 (mg/Nm³). Also, due to the operation of the fabric filter without additive, the weekly amount of dust collected dropped from 6700 kg to 15 kg.

## MUNICIPAL WASTE INCINERATOR, CITY OF ROESELARE, BELGIUM

### Plant Description

The IVRO municipal waste incinerator is located in Roeselare, Belgium. The plant configuration is shown in Figure 7. The plant was built in 1976 and consists of two incinerator lines, each having its own air pollution control train consisting of an electrostatic precipitator, dry lime scrubber, and fabric filter. Each incinerator and flue gas cleaning line feeds into one common stack.

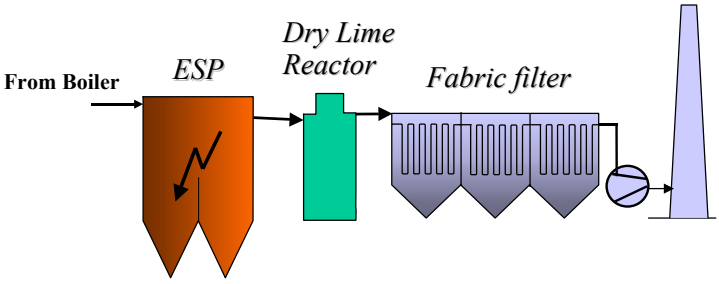


**Figure 7.** Plant configuration for the IVRO municipal waste incinerator.

Over the years the capacity of each incinerator line has increased from 3.2 tons of waste per hour to 4 tons of waste per hour. In 1996, new PCDD/F regulations were enacted, prompting IVRO to install a powdered activated carbon (PAC) injection system.

[3] The PCDD/F concentrations measured by SGS were 0.001 and 0.002 ng/m³

## Alternatives Considered

The PAC system was used at temperatures of 200-230ºC. At these high temperatures corrosion can be kept to a minimum; however, there is an increased risk of fire in the fabric filter. To avoid the risk of fires and plant shutdowns, IVRO began to look for alternatives to PAC. In 1997, catalytic filters were installed in three compartments in the existing Line 2 fabric filter. Tests were conducted to verify that the filters could destroy PCDD/F below the regulatory limit of 0.1 ng I-TEQ/Nm$^3$. Upon successful verification, in 1998 IVRO equipped the remaining 17 fabric filter compartments of both lines with catalytic filters.

## Emission Measurements

Figure 8 shows PCDD/F inlet ("raw gas") concentrations and outlet ("clean gas") emissions at IVRO since installation of the catalytic filters. Emissions have been well below the 0.1 ng I-TEQ/Nm$^3$ regulatory limit over a period of 42 months. Figure 9 shows the homologue distribution of PCDD/F in the raw and clean gas for one specific measurement performed on the fabric filter of Line 1. Figure 10 shows the distribution of all toxic isomers in the raw and clean gas for this same measurement on Line 1. The reduction of gas-phase PCDD/F is greater than 99.29% for all toxic isomers.

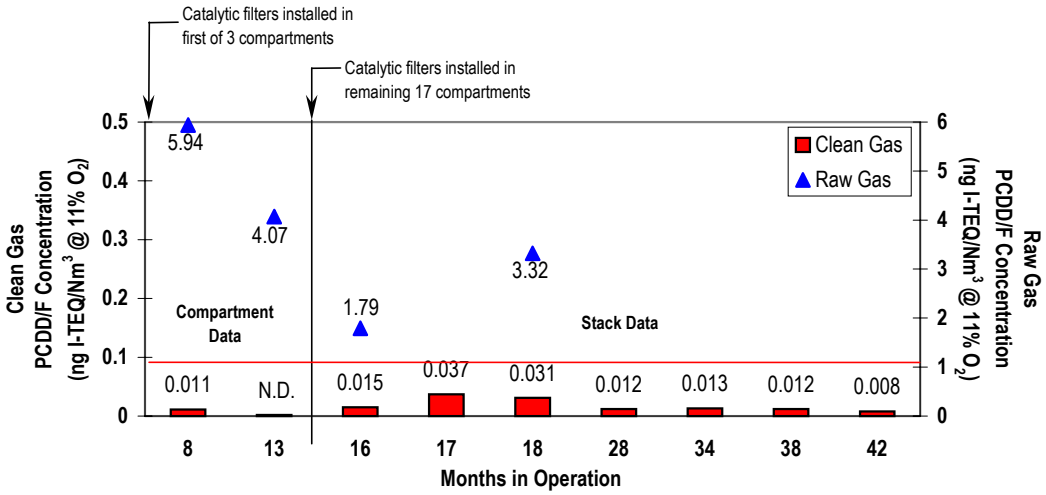


**Figure 8.** PCDD/F concentrations (TEQ) in the raw and clean gas. Raw gas values represent gas phase PCDD/F only; the total raw gas concentrations are 34% higher on average. Clean gas values represent total (solid + gas phase) PCDD/F. Compartment data from Line 2. N.D. indicates values below the detection limit of 0.004 ng I-TEQ/Nm$^3$ for the total TEQ concentration.

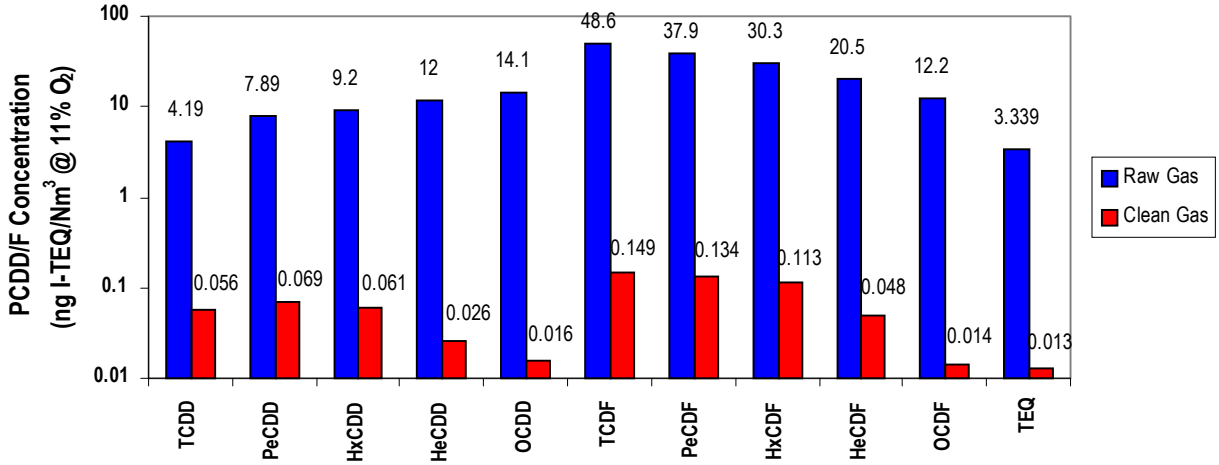


**Figure 9.** PCDD/F concentrations in the raw and clean gas for all homologue groups – non-TEQ basis (Line 1). Raw and clean gas values represent gas phase PCDD/F only. The overall TEQ concentration is also represented.

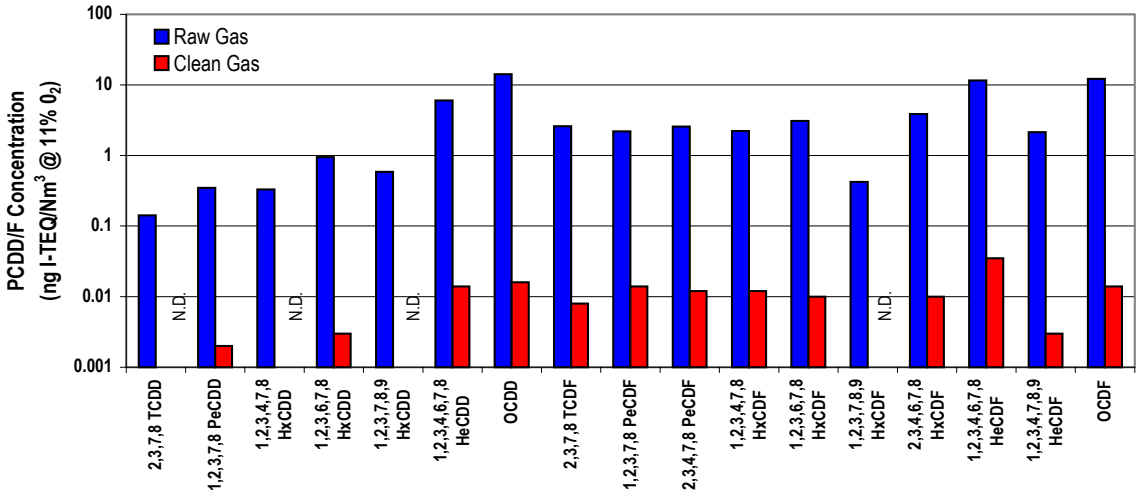


**Figure 10.** PCDD/F concentrations in the raw and clean gas for all toxic isomers – non-TEQ basis (Line 1). Raw and clean gas values represent gas phase PCDD/F only. N.D. indicates values below detection limits of 0.001 ng/Nm$^3$ for the TCDD isomer and 0.002 ng/Nm$^3$ for the HxCDD/F isomers.

## Other Results

Over a period from August – September 1997, particulate concentration measurements were conducted at the outlet of a compartment in the Line 2 fabric filter. This compartment was the first in which catalytic filter media was installed. The particulate emissions ranged from < 0.2 – 0.4 mg/Nm$^3$ (at 11% $O_2$). In January 1999 the particulate concentration in the raw gas was measured as 2.1 g/Nm$^3$ at 11% $O_2$. Thus, the particulate removal efficiency at IVRO has been demonstrated to be > 99.98%. In a study by Bonte et al. (2), the amount of PCDD/F destroyed by the catalytic filters was quantified. On a non-TEQ basis, the overall removal efficiency was **99.57%** (99.52% on a TEQ basis), the percentage adsorbed on the filters was **0.01%**, and the percentage destroyed was **99.56%**.

## CONCLUSIONS

The REMEDIA™ D/F Catalytic Filter System was introduced in 1997. This system is an evolution of two proven technologies: catalysis and surface filtration. A GORE-TEX® membrane captures sub-micron particulate including heavy metals, and the catalytic felt destroys gaseous PCDD/F by means of a catalytic reaction. The performance of the system was monitored at three European municipal waste incinerators.

Significant results have been achieved in combination with the catalytic membrane filter material, e.g.:

At **Ronaval Thonôn-les-Bains** the following results were achieved:

- A significant reduction of PCDDF from 1.9 to 0.0047 – 0.0260 ng I-TEQ/Nm³ @11% $O_2$.
- The total number of cleaning cycles decreased to less than 1/10 compared to the previous filter material.
- The consumption of additive is 20 to 30% less compared to previous operation.
- The potential risk of fire in the fabric filter was prevented.

At **IMOG Harelbeke**:

- An overall removal efficiency of PCDD/F of 99.5 to 99.7% was achieved.
- The particulate emissions at the stack ranged from 0.2 to 0.6 mg/Nm³.
- The operation of the fabric filter without additive resulted in significant savings on additive consumption and disposal.
- Consistent performance below the PCDD/F regulatory limit was demonstrated.

At **IVRO Roeselare**:

- The PCDD/F emissions have been well below the regulatory limit of 0.1 ng I-TEQ/Nm³ @ 11% $O_2$ over a period of 42 months.
- The reduction of gas-phase PCDD/F is greater than 99% for all toxic isomers.
- The reduction in PCDD/F was shown to be a result of catalytic destruction with only 0.01% adsorbing on the filters.

## ACKNOWLEDGMENTS

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## KEY TO ABBREVIATIONS

| | |
|---|---|
| APC | air pollution control |
| ESP | Electrostatic Precipitator |
| $Nm^3$ | normal cubic meter |
| ePTFE | expanded polytetrafluoroethylene |
| I-TEQ | amount of 2,3,7,8 tetrachlorodibenzo-p-dioxin equal to the total PCDD/F calculated using International Toxicity Equivalency Factors |
| MSWI | municipal solid waste incinerator |
| ng | nanogram |
| PAC | powdered activated carbon |
| PCDD/F | polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans |
| SCR | selective catalytic reduction |
| t/h | tons per hour |

## REFERENCES

1. FRANCOIS et al., "Reduction of the PCDD/PCDF Emission in the Flemish Region (Belgium)," Organohalogen Compounds, Vol. 45, 2000, pp. 352-355.

2. BONTE et al., "Catalytic Destruction of PCDD/F in a Fabric Filter: Experience at a Municipal Waste Incinerator in Belgium," International Conference on Incineration and Thermal Treatment Technologies, Philadelphia, May 14-18, 2001.



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