

DIOXIN AND NO_x LOW TEMPERATURE CATALYTIC DEGRADATION

A. Bassetti¹, M. Bodini¹, M. Donegà², R. Miglio¹, W. Tirler², G. Voto²

¹ Snamprogetti SpA, via Maritano, 26 – 20097 S. Donato (MI) – ITALY

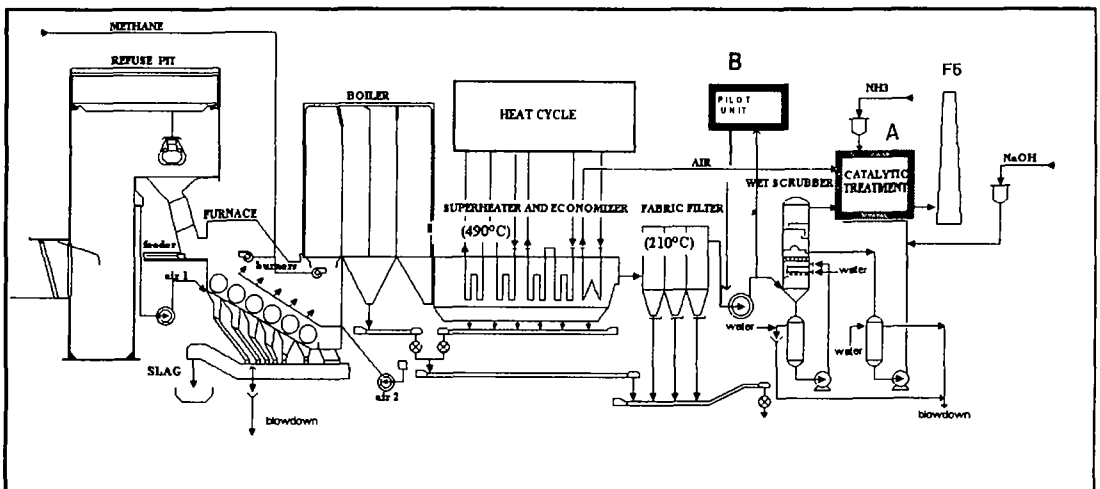
² Eco-Center SpA, via Lungo Isarco Sinistro, 37 - 39100 Bolzano – ITALY

1. Introduction

Town smog and acid rains, mainly produced by the atmospheric pollutants like SO_x, NO_x and particulate, are serious ecological problems. Those immediate effects as well as those of long time, associated to the chlorinated aromatic molecules (dioxines), are among reasons of public reluctance against MSW (Municipal Solid Waste) Incineration plants.

In recent years SCR technology installed after the flue gas scrubber has been successfully applied¹ for combined removal of NO_x and dioxines in the flue gas, as a final stage of the cleaning system. SCR catalyst operates at a temperature of about 300 °C, which requires installation of a heat exchanger and consumption of natural gas in order to heat the gas to said reaction temperature. This paper describes the performances of a catalyst pilot unit operated on gas taken out between the fabric filter and the flue gas scrubber of a full scale MSW Incinerator. The pilot unit (at position B in fig 1) is located downstream from the fabric filtration unit (FF) and operates at the same temperature of the exit gas from the filter, about 210°C. Results are compared with those of a conventional full scale SCR DeNO_x-CatOx unit located after the wet scrubber (at position A in Fig. 1) in the same plant.

Fig.1: Scheme of Bolzano MSW Incinerator with Catalytic units locations



By placing the catalytic reactor for combined dioxine and NO_x removal downstream of the dust filter without pre heating the gas, the use of a heat exchanger and the use of support fuel is avoided. On the other hand, the catalyst must be able to remove the dioxines and the NO_x in the

DIOXIN REDUCTION

flue gas exiting the dust filter at about 210° C with the content of HCl, SO₂, HF and volatile metals present in the flue gas before the cleaning train of the plant.

The pilot test demonstrated that this requirement may be met with a new type of monolithic base metal low temperature catalyst developed and supplied by Haldor Topsoe A/S.

2. Material and Methods

The cleaning train of the MSW Incineration Plant² has, after the waste heat recovery boiler, a FF for particulate separation, a two stage WS for acid gases and volatile metals removal and a final SCR DeNO_x-CatOx section, having 124.000 Nmc/h capacity and working at 300-350°C (position A) for NO_x and trace organic compounds removal. Moreover a DeNO_x pilot unit (ref. B) was installed and operated on a bypass flow downstream from the FF, at 200-220°C. The pilot unit mainly comprises a gas blower, a heater, an NH₃ feed system, a vertical catalytic bed with 3 catalyst blocks and auxiliary devices for measurement and control. It is able to treat about 100 Nmc/h of flue gas. Gas can be sampled for analysis before and after each of the blocks in order to evaluate in a systematic way GHSV, linear velocity and deactivation profile using NO_x as indicator. The catalyst is a monolithic type commercial SCR catalyst with metal oxides as the active components; it was developed and supplied by Haldor Topsoe A/S. Two flue gas sampling trains (for dioxin analysis) were located at the inlet and outlet of the catalytic contacting device for simultaneous sampling of streams. PCDD/Fs, PHAs and PCBs sampling, clean up and quantification were conducted in accordance with actual European Standard Protocols. Analysis of the 17 toxic isomers were performed with HRGC-HRMS. Transition metals were also determined by ICP-MS and ED-XRF in the inlet and outlet streams. Fresh and stabilised catalyst samples were characterised. Monitoring of macrocompounds: H₂O e CO_x and of inorganic micropollutants: HCl, SO_x, NO_x, CO, HF has been conducted with an on line FTIR analyser, able to switch periodically from the inlet, to the interlayer and to the outlet streams of the catalyst bed. FTIR NO_x results have been compared in a preliminary phase with those of other analytical devices (electrochemical, wet chemistry). There is an important issue of continuous monitoring all the component and this is the control of the real composition on the catalytic bed, which changes (i.e. H₂O content 15-40%v; HCl 200-1000ppm) with a cyclic periodicity as a function of waste quality to the combustion chamber and of maintenance operations of the plant (i.e. frequency of boiler soot blowing).

3. Results and Discussion

The average composition of both the inlet streams to the catalytic converters in A and B locations is detailed in Tab.1. The main differences are the acid gases and metals contents. A typical daily variability of outlet stream from the pilot unit is reported in Fig.2. Performances of the full scale catalytic unit (A) are proven. Catalyst durability at 300°C is demonstrated over some years. Emission levels for both dioxins (<0.05 ngTEQ/Nmc) and NO_x (<20 ppm) are stably about an order of magnitude below the law limit. The catalyst in location B undergoes more severe conditions. It should work at a temperature of about 100°C below the other unit and

Tab.1: average composition of flue gas

SCR-location		A	B
components			
H ₂ O	%v	15-20	15-20
O ₂	%v	9-11	9-11
CO ₂	%v	6-8	6-8
CO	ppm	<5	<5
Metals	ppm	<0,05	<0,2
Solid particles	ppm	<1	<1
HCl	ppm	<2	200-1000
SO _x	ppm	<10	10-200
HF	ppm	<0,2	1
NO _x	ppm	70-170	80-180
PCDD/F(TEQ)	ng/Nmc	0,2-0,5	0,2-0,5
IPA	ng/Nmc	2000	2000
PCB	ng/Nmc	20	20

DIOXIN REDUCTION

in the presence of potential poisoning for volatile metals. Acid gases concentration in addition has extremely high variability. Nevertheless the removal level of the NO_x (Fig.2) remained over 95%, with outlet concentration below 10ppm, and the PCDD/F removal it has even exceeded 95% (Fig.3) even in the tests with a remarkable dose of NH₃ (50% over stoichiometric). NH₃ excess has not had therefore meaningful effect on the level of dioxin degradation. In Fig. 4 the profiles of dioxin toxic isomers found on gases downstream from the two catalyst locations (ref. A and B) are compared; the patten is qualitatively similar even with delta of 100-120°C of reaction temperature. Life of the catalytic bed seemed to be satisfactory for the industrial applications and procedures for regeneration of the catalyst have been cheked and defined. Furthermore, no signs of plugging or pressure drop increase was found during 1000 hrs of operation.

4. Conclusions

In a preliminar pilot test of 1000 hrs duration with a new type of low temperature monolithic SCR catalyst supplied by Haldor Topsoe A/S, the feasibility of achieving simultaneously >70% NO_x reduction and 90% elimination of the dioxines at 210°C in the flue gas exiting the dust filter of a Municipal Waste Incineration plant has been demonstrated.

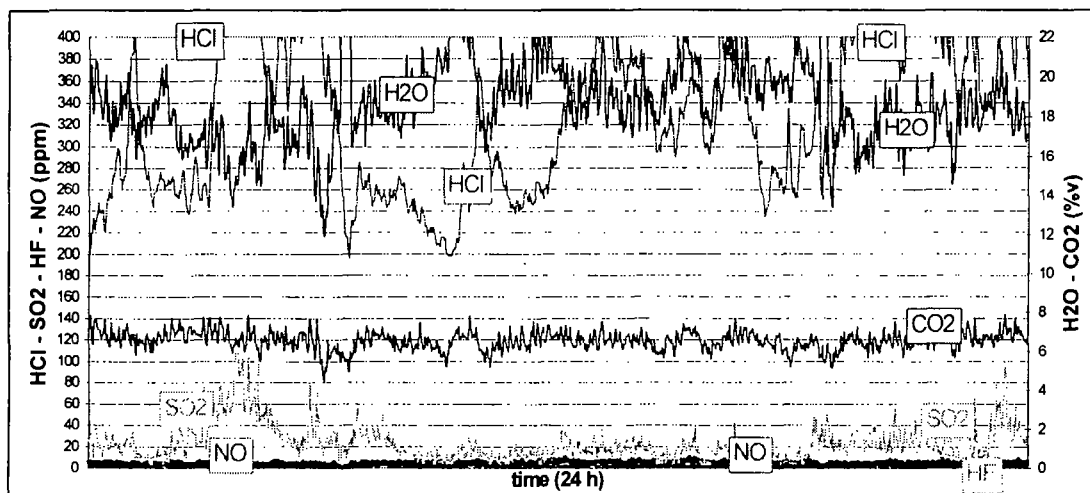
The advantages of the low temperature catalytic procedure, in the comparison of traditional SCR technology, are easy individuabile in energetic savings, since it is not necessary to burn methane for the re-heating of the exhaust gases; reduction of the environmental impact considering the CO₂ emitted for methane combustion.

By means of the combination in the cleaning train of the technologies: "Low Temperature catalytic degradation" and "SWS (Slurry Wet Scrubbing)"³⁻⁴, the achievement of "Zero Emission" would be really guarantee.

5 Acknowledgments

Authors wish to thank L.Breccia (General Impianti) for FTIR technical assistance

Fig.2: Daily variability of flue gas composition in SCR unit in location B (FTIR monitoring)



DIOXIN REDUCTION

Fig.3 Performances of pilot catalytic unit at 210°C (Inlet and outlet stream toxic isomer profiles)

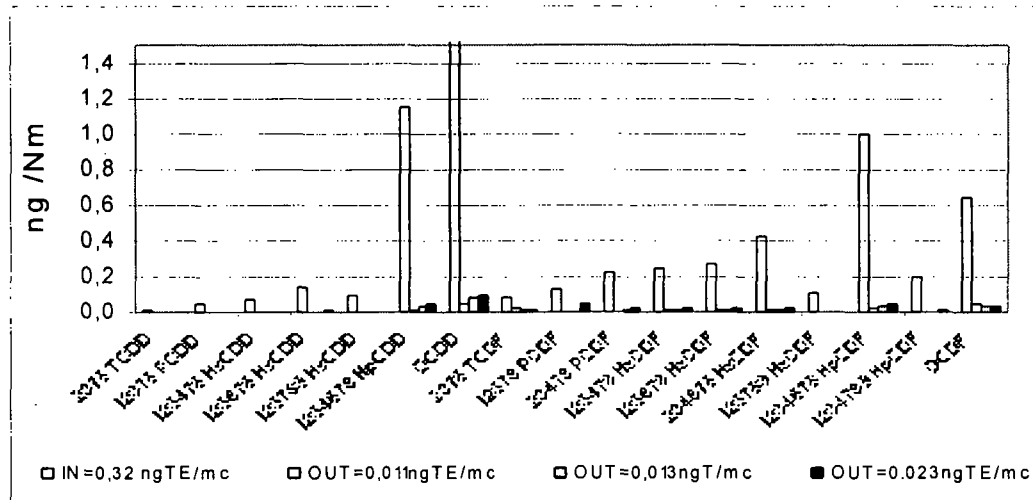
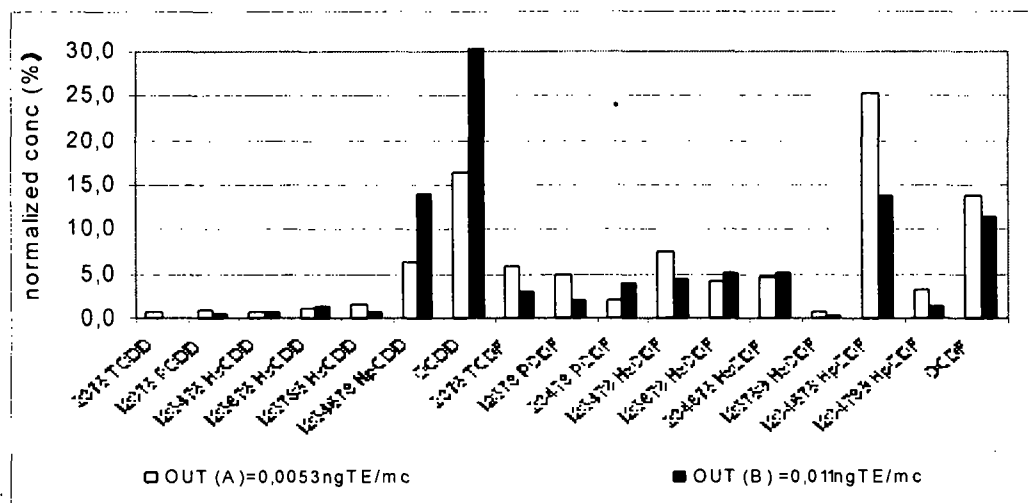


Fig.4 Normalised toxic isomer profile for outlet streams from: catalytic bed in A and B locations



6. References

- ¹ Boos et al.: *Chemosphere*, 29, 2051-2055 (1994);
Osada et al.: *Organohalogen Compounds*, 36, 249-252 (1998);
Oh et al.: *Chemosphere*, 38, 2097-2108 (1999);
Shin et al.: *Chemosphere*, 38, 2655-2666 (1999);
Shin et al.: *Environ. Sci. & Tech.*, 33, 2657-2666 (1999);
Unsworth *Organ. Compounds*, 40, 435-439 (1999)
- ² M.Grosso et al.: *Organohalogen Compounds*, 46, 146-149 (2000)
- ³ R.Miglio et al.: *Organohalogen Compounds*, 40, 445-449 (1999)
- ⁴ A.Bassetti et al.: *Organohalogen Compounds*, 45, 445-449 (2000)