SLURRY WET SCRUBBING: AN EFFECTIVE OPTION FOR SIMULTANEOUS PCDD/F, Hg AND ACIDIC GASES REMOVAL

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1. Introduction

Prevention, control and abatement capability of flue gas treatments at Waste Incineration plants for Energy conversion should necessarily undergo a process of continual improvement in order to meet the requirements of the Environment utmost respect. The efforts of the research in this field are to develop more efficient and reliable systems, together with sophisticated sampling and analytical monitoring devices, in order to achieve and guarantee the target of *Zero emission.*
In this framework, conventional air pollution control technologies, developed so far, are suitable only for specific kind of contaminants abatement. Hence, in order to remove all the contaminants and reach the highest overall efficiency, it is necessary to foresee a series of different devices and/or stages. This paper describes the experimental and modelling activities we have done with the aim of introducing organic microcontaminants removal functionality in a Wet Scrubber (WS), widely used as pollution control equipment and generally as the preferred way for acidic emissions reduction. A conventional two-staged WS unit can reliably reach outlet concentration for HCl and SO2 of 5 and 20 mg/Nm^3 respectively and 0.01 mg/Nm^3 for Hg but does not reduce PCDD/F concentration of the inlet stream. Furthermore investigations have been focused on design criteria of a Slurry Wet Scrubber (SWS) [1-3], which is an evolution of a WS unit where the scrubbing liquor is a slurry. The slurry is basically a low concentrated homogeneous suspension of lipofilic solids in water. The SWS is a promising option for the contemporary removal of acidic gases (HCl, SOx, HF...), heavy metals (Hg, Cd...) and organic microcontaminants (PCDD/F, PCB ...). Different configurations of WS are filed in patents and are known in the current state of the art (such for instance plate type columns, Venturi or Vortex scrubbers[4], bubble columns, jet-loop reactors and spraying towers) but very few are those employed for the aforementioned specific application[5-8]. Dioxin removal levels in addition are often difficult to be assessed, because performances are the result of superimposition of equipment design factors effects, constructive material interferences (memory effects) and non stationary flue gas compositions.

2. Materials and Methods

SWS configuration effects on the PCDD/F removal performances were assessed by making several measurements with a bench scale unit [9] installed and operated on a by pass stream of the flue gas cleaning system of the MSW Incineration Plant in Bolzano- Italy[10].
Some flue gas/slurry contacting configurations have been selected as a result of a preliminary technological assessment; the choice has been guided and influenced by factors as easiness of scaling up and operation, erosion and fouling minimisation, capital, operating and maintenance costs reduction. In addition, by considering that the purpose of gas/liquid contactors is to *maximise the gas-liquid* interphase area per unit volume, the configuration that provides the highest interphase area (jet-loop reactor) was selected and proven as a reference.
The experimental unit includes: a flue gas/slurry contacting device (glass made), a fun for flue gas extraction, a pump for scrubbing liquor circulation when necessary, a slurry/cool water heat

exchanger for temperature control and auxiliary devices for indication and control of operative conditions, such as temperature, pressure, gas and slurry flow rates, pH, make up and purge flow rates. Two flue gas sampling trains (silanised glass probes) were located at the inlet and outlet of the contacting device. Experimental procedure was as follows: operative conditions (temperature, gas flow rate, scrubbing slurry hold-up or flow rate, pH, slurry concentration, and so on) were held constant to properly condition the system; afterward simultaneous samplings were started at the inlet and outlet of the contacting device. PCDD/F analysis were carried out according to EN 1948 method. Analysis of the 17 toxic isomers were performed with HRGC-HRMS. Specific samplings of gas were taken for Hg and acidic gases analysis. For a correct balance Hg and anions (sulphite, sulphate, chloride, fluoride...) were analysed in the recycling liquor too, by potentiometric titration and ion exchange cromatography respectively. Fresh and exhausted activated carbon samples were characterised by laser scattering diffraction and transmission microscopy for the evaluation of granulometry distribution and by X-Ray Fluorescence (XRF) analysis for determination of the saturation level with heavy metal, especially Hg. Tests of inertization with a cement based mixture were performed on flyash and residues from scrubber blowdown in the presence of elevated activated carbon content. Mechanical and chemical leaching tests were executed in order to verify the conversion of the effluents to harmless matter or eventually to correct doses of additional chemicals.

Mathematical models have been implemented in order to describe fluid dynamics and mass transport effects. The model parameters were fitted to experimental data in order to obtain a suitable tool to scale up the selected configurations and optimise their performances. For one configuration (jet loop reactor), Computational Fluid Dynamics (CFD) simulations have been made to describe the complex fluid dynamics of the system, using an Eulerian/Eulerian multiphase approach. Simulations domain consists of the ejector and the vessel and the main scope was the characterisation of bubble bed length and bubble hold-up into the vessel (fig.2).

3. Results and Discussion

Experimental unit inlet stream is characterised by a total particulate matter below 1 mg/Nm^3 and by a PCDD/F content in the range 0.2 – 0.5 $ngTEQ/Nm^3$. Further detail shows that PCDD/F are mainly in the gas phase, only a fraction lower than 15% is associated to the particulate matter. Average concentrations of HCl and SOx are around 500 and 40 mg/Nm^3 respectively, Hg concentration shows very high fluctuation from 0.03 to 0.30 mg/Nm^3. It should be underlined that when the SWS is used it shows PCDD/F removal functionality meanwhile it does not reduce, but even improves, the acidic gas and Hg abatement capacity of the unit. Dioxin removal efficiency depends on both the configurations and adopted operative conditions. First of all we made a series of tests with a jet-loop reactor (using an ejector as gas distributor in a bubble column vessel working at low gas/slurry ratio) for a proof of concept and in order to verify the upper limiting performances of a slurry scrubbing. This device is characterised by the highest (~500 m^2/m^3 measured by the sulphite reaction[11]) gas/liquid interphase area among the contacting devices.

Results of tests done at different temperature levels, activated carbon content, solid particles dimensions and gas/slurry ratios validated the mathematical model. Furthermore, a sensitivity analysis has been made to check the simulated performances of the system while changing model parameters and operating conditions (fig. 1). According to modelling results and experimental evidences dioxin outlet loading can be reduced even below 0.005 $ngTEQ/Nm^3$ (removal >99%), with Hg e HCl below 0.001 and 1 mg/Nm^3 respectively.

Other experimented configurations were the spraying tower (one ejector as slurry sprayer) and the slurry bubble column. For comparison we have also verified the performances of a conventional plate type scrubber, operated with slurry of activated carbon. Each SWS configuration shows advantages and specific limitations, but more in general the effects of the main operative parameters are the same. Dioxin removal level can reach over 95%, dosing a minimum target concentration of activated carbon, reducing temperature and particles diameter and working with elevated L/G ratios. We did not observe either transport of carbon particles in the outlet gaseous stream or solids flotation, even when working with very high flow rates (1-2 m/sec as superficial gas velocities). Activated carbon samples, after being used in very drastic conditions (elevated flow rate of slurry circulation) maintained their original properties. Microscopy did not evidence agglomeration phenomena, expected as a consequence of the high salinity of the circulating liquor and by the content of organic and inorganic compounds adsorbed on the solids. Tests of inertization/stabilization of dusts and solid residues from the waste water treatment, to which elevated quantity of activated carbon were added, are under study in order to give formulations for production of chemical and mechanical stabilised solid effluents. Elementary analysis (by XRF) of exhausted activated carbon samples revealed that several heavy metals have been adsorbed together with organic microcontaminants, this lighten the waste water treatment to which the column purge must be sent. Addition of sulphur derived molecules (for instance commercial TMT-15, thiourea) to the scrubbing liquor produces stabilised compounds of the heavy metals. Hg and Cd, the principal volatile metals removed in the wet treatment are in this way simultaneously precipitated as sulphates and adsorbed on activated carbon, so they are almost completely removed from the purge stream of the SWS.

4. Conclusions

Operative experience shows that SWS system, as long as proper slurry scrubber design is applied,

may be considered an effective option for dioxin reduction and it may also be used to contemporary control PCDD/F, heavy metals and acidic gases emissions. Hence it represents an alternative solution respect to other dioxin removal technologies, such as dry active carbon injection or catalytic convertors. The SWS system gives significant improvements in Hg reduction too. Dioxin outlet loading is reduced below 0.005 ngTEQ/Nm^3, with Hg e HCl below 0.001 and 1 mg/Nm^3 respectively. Hg is almost completely removed from the water too, its residual level in water is below 0.01 ppm without any other additional treatment .

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6. References

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Fig.1

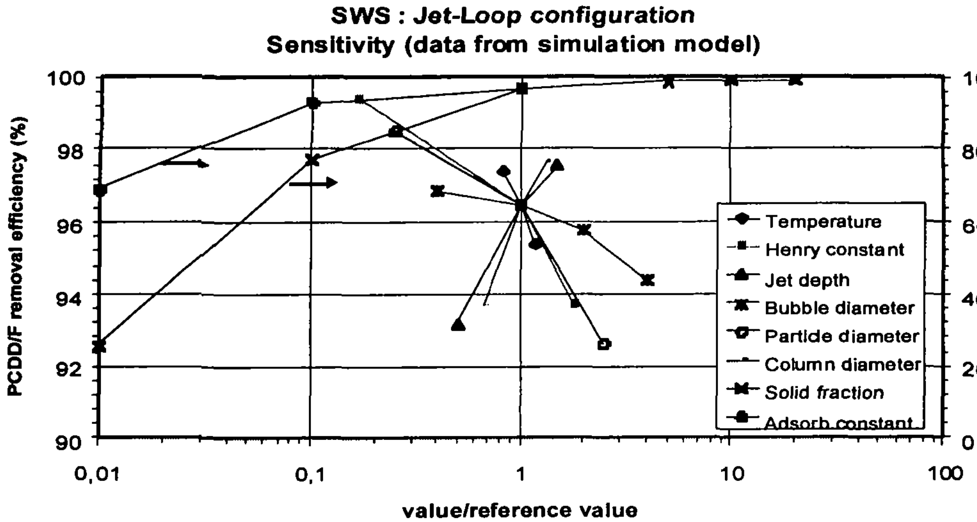

Fig.2: Liquid volume fraction field with 2 different liquid flow rates: a) 2 m^3/h; b) 8 m^3/h.