

THE FLUX AND MASS BALANCE OF PCDD/Fs AROUND COLD SIDE HEAT RECOVERY SECTION AND FABRIC FILTRATION IN A MSW INCINERATION FULL SCALE PLANT.

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Introduction

The emissions of PCDD/Fs in the flue gas and particulate matter from municipal solid waste incineration processes can be attributed to one or more formation pathways, active during combustion and flue gas cooling down for energy recovery and/or emissions control. Several formation mechanisms have been proposed, involving various gas phase reactions at high temperatures ($> 900^{\circ}\text{C}$)¹ as well as heterogeneous catalyzed reactions on flyash particles in the lower temperature regions ($200\text{-}400^{\circ}\text{C}$)^{2,3}. When conditions for achieving a high efficiency of combustion are maintained, the first pathway is of minor importance whilst the heterogeneous post-furnace formation is considered the most relevant⁴. The mechanisms claimed involve the catalytical synthesis of PCCD/Fs on the flyash surface through rather complex chemical routes, either from residual carbon and organic or inorganic chlorine (de-novo synthesis) than from various chlorinated organic precursors, potentially arising from incomplete combustion.

The predominance of post-furnace formation has a significant influence on process design and operating conditions maintained over the cool side of the energy recovery section and the particulate removal equipment. Here, particles retained on the tubes and walls of the boiler and collected flyash by the control device might remain for long residence times in the temperature range where significant formation rates are expected, thus potentially enhancing the PCDD/Fs content of the gaseous emissions and of the resulting flyash to be disposed off. Since few data derived from real plants⁵ are available on this field of interest, an extensive research study on a full scale MSW incinerator was conducted for evaluating PCDD/Fs presence and their corresponding mass fluxes over the whole plant. Present work reports the main results obtained across the cool side of the boiler and the fabric filter, and outlines some important implications derived for their design and operating conditions.

Materials and methods

The evaluation was conducted at the waste to energy facility of the Bolzano Province in Italy. The plant is designed on two parallel lines, with a total capacity of up to 400 t/day of urban waste with average lower heating value between 1500 and 3000 kcal/kg. The line utilised for the study has a mass burn waterwall furnace with a roller type combustion grate ("Düsseldorf system") and a secondary combustion chamber; energy is recovered through a water tube boiler and a steam turbine, providing up to 3.3 MW of electricity and up to 8 Gcal/h for district heating at the design

Emission Control and Abatement Technologies II

refuse feed rate. Flue gas cleaning is performed by a fabric filter and a two-stage wet scrubber, in line with a final SCR (Selective Catalytic Reduction) unit for NO_x and trace organics (mainly PCDD/Fs) conversion. The incineration units are integrated with a wastewater treatment plant, for all the liquid effluents and scrubber blowdowns, and with a stabilisation/solidification unit for the inertization of flyash and sludge residues.

Flue gas was sampled in four different points, located at the boiler cold side inlet, across the fabric filter unit and at the stack; a grab sample of the mixed residues (whole boiler and fabric filter flyashes) was collected, simultaneously with flue gas sampling, at the conveyor discharge point in the final storage bin of the total flyash.

PCDD/Fs sampling, clean up and quantification were conducted in accordance with actual European Standard Protocols⁶. Flue gas sampling was performed by the filter-cooler method and conducted with an automatic, continuous adjusting isokinetic sampling system (Zambelli, Italy). Quartz fiber filtration media, spiked with Sampling Standard EF-4138, Cambridge Isotope Laboratories Inc.(CIL), was adopted for particle collection, in line with a water cooled condenser and methoxyethanol filled impingers as absorption traps. Special precautions were followed for maintaining the filter casing below 125 °C, in order to prevent any de-novo reaction. The extraction standard, EDF-4139 (CIL), was split and distributed according to the suspected amount of compounds in the different sampling train compartments for every sampling point. Extraction of filter media was done by soxhlet with toluene, extraction of aqueous liquid by liquid/liquid extraction with dichloromethane. An automatic three column system (Dioxin Prep, Fluid Management System Inc.) was used for chromatographic clean up. Prepacked teflon disposable columns, containing multilayer silica, alumina and carbon, were utilised. Prior to the quantification procedure, the syringe standard (ED-4140, CIL) was added. Quantification of PCDD/F was done by HRGC-HRMS (AutoSpec Ultima Micromass), at a resolution greater than 10.000 (5% valley). The analytical system was calibrated by calibration standard CS1 through CS5 (EDF-9999 CIL five-point calibration range). For improved isomer identification two GC-columns, one with apolar stationary phase (Restek RTX 5 MS) and one with a polar (Restek RTX 200) were used.

Results and discussion

Flue gas concentrations of PCDD/Fs resulting for all sampling points are reported in Table 1, in terms of total values and I-TEQ. Along the flue gas pathway, concentration levels measured at the exit of the hot side of the boiler clearly increase across the cooler side of the heat recovery section (superheater and economiser), with a subsequent slight reduction within fabric filtration and a very significant removal over the last treatment units (wet scrubber and SCR), with emissions well below the limit of 0.1 ng I-TEQ/m³, established for the plant by the local authorities. All the values for the boiler-fabric filter section are included in the lower range of measurements reported for similar full scale evaluations⁷⁻¹¹. The increase in the cold side of the boiler (roughly 8 ng/m³, equivalent to 0.23 ng I-TEQ/m³), rather well documented in other full scale studies⁷⁻⁹, is observed both in the vapour and in the particulate phase, although most of it occurs in the gas fraction, and has to be attributed to formation mechanisms through de-novo synthesis: temperature levels between 485°C at the inlet and 210°C at the outlet and gas residence times required for optimum heat transfer are well within the range of values claimed for the intervention of these mechanisms^{2,3}. Across the fabric filter, in spite of a high particulate removal efficiency (in excess of 99.9%, with TSP outlet concentrations normally below 1 mg/m³), only a minor reduction of PCDD/Fs is observed (around 10% or 30% in terms of I-TEQ values), with a removal efficiency

Emission Control and Abatement Technologies II

of 90% for particle bound concentrations and a slight increase of the vapour phase levels. Once again, the operating temperature levels of the filter (210°C-215°C) and the residence time of the particles on the fabrics lead to the intervention of de-novo synthesis, already observed for these particulate control devices in similar operating conditions^{10,11}. The formation through de-novo mechanisms is also supported by preliminary evaluations of the carbon content of particulates sampled at the boiler cold side and fabric filter inlets: measured values between 0.07% and 0.3%, whilst indicating a very good burn out of organics in the furnace, are included in the range reported for the potential intervention of the postulated mechanisms¹¹.

Table 1. PCDD/F concentrations in flue gas (all values in normal conditions, dry gas at 11% O₂)

Sampling point	Concentration (ng/m ³)			I-TEQ concentration (ng/m ³)
	Total	Vapour	Particulate	Total
Boiler exit	1,89	1,28	0,61	0,04
Fabric filter inlet	9,99	7,68	2,31	0,27
Fabric filter outlet	9,04	8,82	0,22	0,19
Stack	0,24	n.a. ⁽¹⁾	n.a. ⁽¹⁾	0,005

⁽¹⁾ Not determined separately

A more detailed evaluation of the results obtained, with particular respect to the PCDD/Fs formation, can be derived from mass balance calculations. Mass fluxes of PCDD/Fs in the flue gas around the sections investigated (cold side of the boiler and fabric filter) were obtained from concentrations and flow rate measurements, whilst the flux contained in the flyash produced was calculated from the PCDD/Fs content of the mixed flyash sample, collected from the final storage bin, and its corresponding production rate. The resulting mass balance, reported graphically in Figure 1, provides for a global production of 550 µg/h of PCDD/Fs: 300 µg/h derive from the cold side boiler section and 250 µg/h from the fabric filter, with a relative contribution fairly comparable between the two sections. PCDDs are formed in slightly lower amounts with respect to PCDFs, with total productions of 210 µg/h and 340 µg/h, respectively. Within the energy recovery section the majority of the mass flux produced is measured in the vapour phase, both for PCDD/Fs than for the single families, indicating the potential of soot blowing operations and high temperature levels in determining consistent stripping phenomena from the surface of the particles, where formation by de-novo synthesis takes place. The predominance of less volatile hepta and octa CDDs in flyash separated across the boiler and of more volatile tetra to hexa CDFs in flue gas condensate at boiler exit, evaluated with preliminary measurements, should adequately support this hypothesis. For the fabric filter unit, instead, the major PCDD/Fs production, as well as for the single families, corresponds to the solid particulates, with a vapour phase production significantly lower: most of the compounds formed are contained in the removed flyash, characterised by a concentration of around 6000 ng/kg of PCDD/Fs (3000 ng/kg of PCDFs and 3000 ng/kg of PCDDs), corresponding to 120 ng I-TEQ/kg. Nevertheless, almost all of the flue gas mass flow rate of both families leaves the filter with the vapour phase, due to the high particulate removal efficiency maintained by the control device.

The evaluations conducted point thus out a production of PCDD/Fs in the cold side of the heat recovery section and in the fabric filter, where temperature levels and residence times are included in the range of activity of de-novo synthesis formation pathways. A further sampling campaign will be conducted on the plant for confirming and extending the main observations reported. Nevertheless the results obtained rise some significant implications for process operation, related

Emission Control and Abatement Technologies II

to the increase in the PCDD/Fs content of flyash to be disposed off and to the partial utilisation of the high removal capabilities of the fabric filter, equipped with very efficient Gore-Tex[®] bags, for controlling properly also PCDD/Fs emissions. Some important indications derived from the study are thus related to the possibility of enhancing the performance of the plant by operating the filter at a lower temperature level, preferentially below 200°C, and by modifying the frequency of boiler soot blowing and of the cleaning cycle of the filter bags. From the design point of view, improvements in the cold side heat recovery section might also include modifications for reducing residence times and flyash accumulation. The results confirm also the effectiveness of the SCR unit, located before the stack, for the conversion of trace organohalogen compounds, emitted in concentrations well below the limit of 0.1 ng I-TEQ/m³.

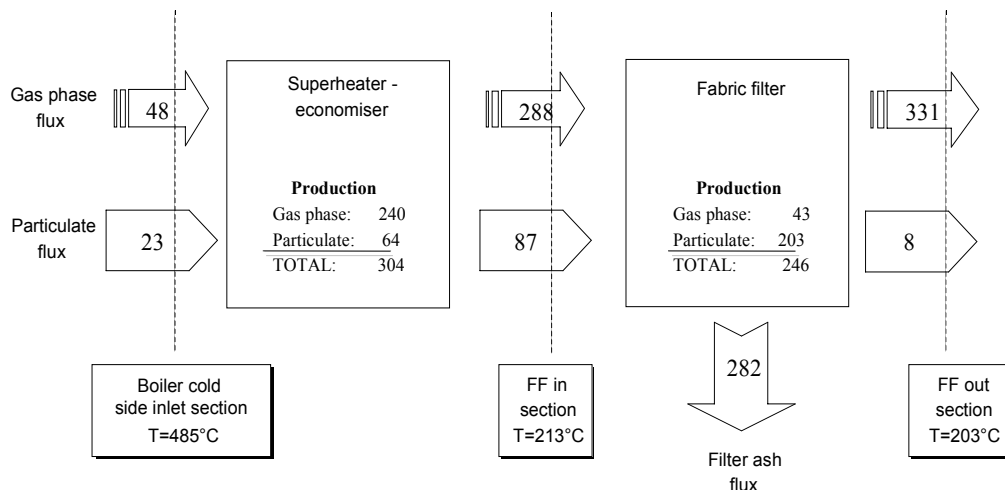


Figure 1. PCDD/Fs mass balance (all values in µg/h).

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