

PCDD/Fs release during normal and transient operation of a full scale MSWI plant

Mario Grosso¹, Stefano Cernuschi¹, Elisabetta Palini¹, Marco Lodi², Giulio Mariani²

¹Politecnico di Milano, Milano

²Istituto di ricerche farmacologiche Mario Negri, Milano

Introduction

The purpose of the present work is the evaluation of the total dioxin release in the environment and corresponding mass partitioning in all gaseous, liquid and solid residues produced in a full scale municipal solid waste (MSW) incineration plant. The integrated approach followed in the evaluation is addressed by recent regulatory issues contained in the Integrated Pollution Prevention and Control Directive¹ (“IPPC Directive”), where adoption of overall limits for pollutants release in the environment from industrial plants is foreseen for the near future.

The evaluation was conducted at a MSW incineration plant in operation since the end of the 1970s and recently upgraded for complying with more restricted emission limits established by recent legislation. Measurement campaigns were performed in order to assess dioxin mass flows both in steady state operation and during a simulation of transient conditions of shut-down and subsequent start-up of the plant. The potential dioxin reformation phenomena and release downstream of wet scrubbing, already documented by recent studies^{2,3,4,5}, were also investigated.

Methods and materials

The plant (Figure 1) is designed on three parallel mass burning furnaces with energy recovery for a total burning capacity of 225 t/day of municipal solid waste (MSW), including a maximum of 12 t/day of treated hospital waste.

Flue gas treatment was originally equipped with an electrostatic precipitator (ESP) and a two stage wet scrubber (WS) for each line. Recently it has been upgraded to enhance its gas treatment capability: a dry system (common to all three lines) was installed, consisting of online injection of hydrated lime and activated carbon (AC) upstream of a fabric filter (FF). Prior to stack release to the atmosphere, flue gas is mixed with pre-heated air to increase its temperature. Treatment of scrubber liquid blowdowns is provided through a wastewater treatment plant.

The present study was conducted with two subsequent sampling campaigns. The first one (baseline I) was oriented to the evaluation of dioxin emissions during steady-state operation. The second one was conducted to investigate transient conditions. However, a new baseline steady-state situation (baseline

II) was also evaluated, owing to some significant modifications in flue gas cleaning system operation: addition of AC in the second stage of the wet scrubber, injection of a lime-carbon mixture (Sorbalit ®) together with AC upstream of a fabric filter and improvement of fabric filter efficiency through the use of new bags with more efficient filtering medium.

Both campaigns were extended over a week, with flue gas samplings conducted simultaneously in the sections upstream and downstream of the fabric filter and at the stack (Figure 1). Composite weekly samples of solid and liquid residues (slag and boiler ash, ESP ash, FF ash, sludge and treated wastewater) were prepared by mixing grab samples collected daily.

PCDD/Fs samplings and analyses were performed in accordance with current European Standard Protocols⁶, following procedures already described in detail in previous papers^{7,8}. Major plant operating parameters, as well as mass quantities of waste burned and output residues, were acquired from plant monitoring and control systems.

Transient simulation in the second campaign was conducted in series on furnace 1 and 3 (line 2 was not in operation), with the total duration of each shut-down and start-up operation of nearly 8 hours. The simulation procedure was as follows: waste feeding was stopped, and the backup oil burner was fired in order to maintain the combustion temperature above 850°C; when the grate was free of residual waste, the temperature was gradually decreased to around 400°C and then increased once again to above 850°C, when furnace waste feeding was restarted. Sampling of flue gas was performed during the whole transient procedure, while solid residues were sampled taking into consideration the retention time typical of each single device.

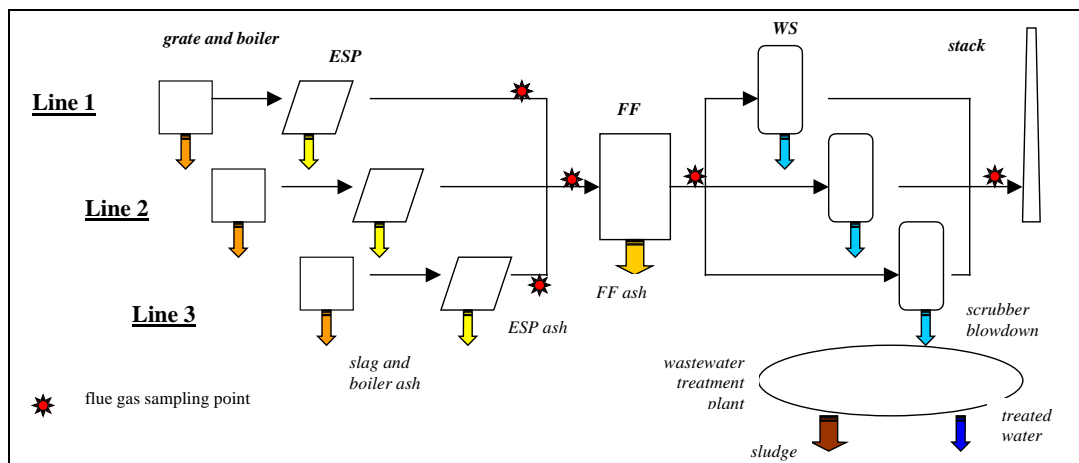


Figure 1: Layout of the plant with the location of the flue gas sampling points

Results and discussion

PCDD/Fs measured in all flue gas sampling points and in solid and liquid residues during steady-state operation and transient conditions are reported in Table 1, in terms of toxic equivalent units (I-TEQ) and of total concentration.

Most relevant differences in dioxin contaminations detected in steady operation are related to the flue gas. In fact, in the first campaign stack emission exceeded the regulatory limit ($0.1 \text{ ng}_{\text{I-TEQ}} \text{m}^{-3}$) and a measurable increase of concentration across wet scrubber was observed, probably due to a dioxin release from plastic materials (memory effect). In the second campaign the addition of AC in the wet scrubber has led, as expected, to a decrease in stack concentration below the emission limit and to a simultaneous increase in scrubber blowdown values.

With respect to solid and liquid residues, the most contaminated fluxes result, on average, FF ash and wastewater sludge. The lower PCDD/Fs content detected in FF ash in the second campaign might be explained by a “dilution effect” due to a greater dosage of the reactants (Sorbalit and AC) compared with the previous campaign (addition of nearly $14 \text{ kg t}_{\text{MSW}}^{-1}$ instead of $9 \text{ kg t}_{\text{MSW}}^{-1}$). No apparent improvement in FF removal efficiency for PCDD/Fs is thus attributable to the use of the new sorbent mixture, as further demonstrated by comparable values of flue gas concentration measured across the filter during both campaigns.

During the second campaign the contamination of furnace slag and of flue gas at ESP outlet, collected separately for each line, indicates a worse performance of line 1, still equipped with the original counter-current design furnace, than line 3, recently upgraded with a modern co-current design furnace.

REMEDATION METHODS AND CONTROL TECHNIQUES

Table 1: Dioxin concentrations in flue gas, solid and liquid residues.

Concentration	STEADY-STATE				TRANSIENT	
	baseline I		baseline II		II	
	I-TEQ	PCDD/Fs	I-TEQ	PCDD/Fs	I-TEQ	PCDD/Fs
<u>Solid residues ⁽¹⁾ ($\mu\text{g kg}_{\text{DS}}^{-1}$):</u>						
Slag and boiler ash 1	0.03 ⁽²⁾	2.38 ⁽²⁾	0.14	10.09	0.07	3.70
Slag and boiler ash 3			0.02	0.97	0.03	2.03
ESP ash 1	0.17	13.32	1.15	159.38	0.75	76.79
ESP ash 2	2.67	264.96	n.d.	n.d.	n.d.	n.d.
ESP ash 3	0.62	45.68	2.78	270.34	2.75	309.64
FF ash	3.41	190.59	1.53	114.70	3.43	275.92
Sludge	3.70	217.50	2.62	255.59	1.89	124.54
<u>Liquid residues (ng l^{-1}):</u>						
WS blowdowns	0.02	0.94	2.04	113.88	n.d. ⁽⁵⁾	n.d. ⁽⁵⁾
Treated water	0.009	0.045	n.d. ⁽⁵⁾	n.d. ⁽⁵⁾	0.073	3.18
<u>Flue gas ⁽³⁾ (ng m_n^{-3}):</u>						
Outlet ESP 1	5.98 ⁽⁴⁾	300.9 ⁽⁴⁾	9.82	747.25	10.69	490.88
Outlet ESP 3			2.99	151.35	30.19	1854.64
Outlet FF	0.22	13.59	0.30	14.39	n.d. ⁽⁵⁾	n.d. ⁽⁵⁾
Stack	0.81	38.52	0.05	2.27	0.39	9.37

⁽¹⁾ concentrations referred to dry matter

⁽²⁾ only one sample for the three lines

⁽³⁾ concentrations referred to dry gas, normal conditions (273 K, 1013 hPa) at 11% O₂

⁽⁴⁾ only one flue gas sampling point, upstream the FF

⁽⁵⁾ not determined

The simulation of partial shut-down and start-up operation of the plant was conducted with the same procedure for both lines, as described above. The post-combustion temperature profile, measured during the entire simulation (Figure 2), shows that line 3 transient conditions were characterised by longer duration and lower minimum temperature.

For line 1 no significant variations in PCDD/Fs concentration levels were detected in flue gas compared to steady-state operation. On the other hand, a ten-fold increase of concentration values at ESP outlet was measured for line 3: this might be attributable to the potential intervention of PCDD/Fs reformation phenomena, due to the presence of all the conditions for the process to take place. A key factor seems to be the production of soot during oil burner operation, as pointed out by recent studies^{2,3,4}. Fresh soot particles together with the presence of chlorides released by boiler deposits⁵, within the appropriate temperature window (200°C - 450°C), could lead to formation pathways observed in similar operating conditions.

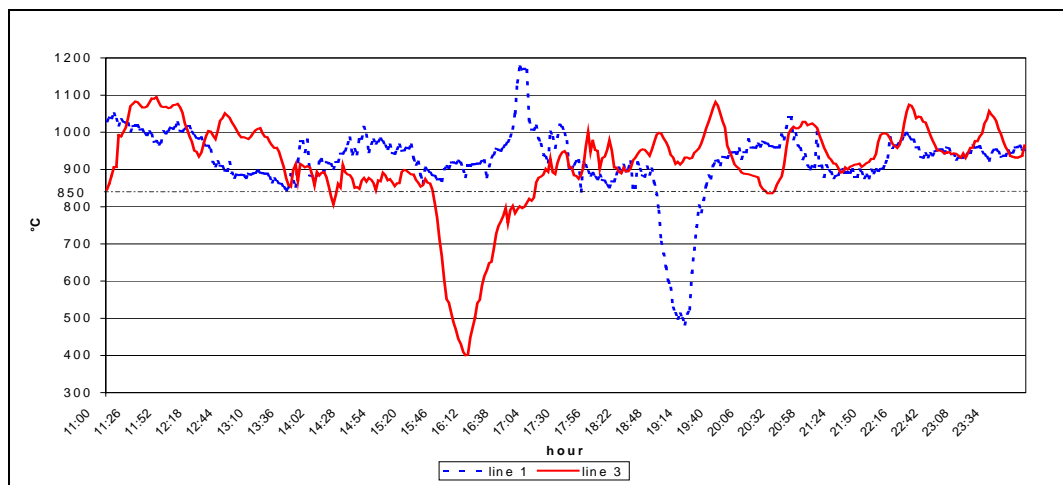


Figure 2: Post-combustion temperature profile for the two lines during transient simulation

Shifting of the homologue distribution patterns (Figure 3) from the more dominant lower chlorinated PCDF, typical of flue gas during normal conditions, towards the higher chlorinated PCDD during transient conditions, suggests once more the potential dioxin reformation on soot particles. Another characteristic indicator of a significant PCDD/Fs reformation, already reported in similar evaluations^{2,3,4}, is the decrease in PCDF/PCDD ratio from 1.7, during normal operation, to 0.6, during transient conditions. Despite the AC injection in the scrubber, transient conditions result in PCDD/Fs stack concentration exceeding the current emission limit.

For solid and liquid residues, PCDD/Fs contamination levels are essentially comparable with steady-state measurements, with the only exception of FF ash where both total and I-TEQ concentration values result significantly increased.

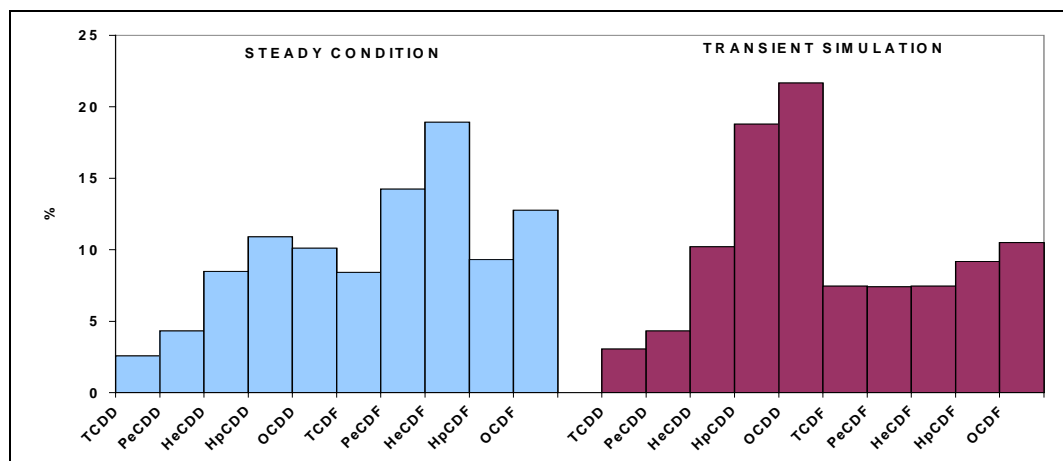


Figure 3: Homologue distribution flue gas at ESP outlet of line 3

Dioxin specific mass fluxes released with the different residues produced by the plant are reported in Table 2, in terms of I-TEQ and total PCDD/Fs values. During steady-state conditions a total and essentially constant release in the environment of nearly $45 \mu\text{g}_{\text{I-TEQ}} t_{\text{MSW}}^{-1}$ was estimated in both campaigns. Partitioning of mass fluxes within the residues (Figure 4) results in significant contributions mainly associated with FF and ESP ashes and with slag, and is influenced by the modifications in flue gas treatment introduced between the two campaigns. The most significant differences are a lower release through stack flue gas and the corresponding increased release with treated water, resulting in the second campaign from AC addition in the scrubber. The difference in slag mass flux could be attributed to the heterogeneity of the material and to the consequent wide range of PCDD/Fs concentration values typically observed for this residue.

During transient operating conditions dioxin total release increases by almost 50%, mainly due to the higher contamination of FF ash and stack flue gas; however, most of the mass flux is still released with slag, FF and ESP ash.

Table 2: Specific mass flows of dioxins released into the environment

Specific emission [$\mu\text{g } t_{\text{MSW}}^{-1}$]	STEADY-STATE				TRANSIENT	
	baseline I		baseline II		II	
	I-TEQ	PCDD/Fs	I-TEQ	PCDD/Fs	I-TEQ	PCDD/Fs
Slag and boiler ash	3.6	332.0	11.3	797.6	7.0	409.6
ESP ash	10.8	1000.7	9.5	1129.1	7.6	825.8
FF ash	24.1	1348.1	21.9	1642.4	47.1	3782.1
Sludge	1.8	106.8	1.8	172.1	1.5	102.1
Treated water	0.03	0.16	n.d. ⁽¹⁾	n.d. ⁽¹⁾	0.3	13.2
Flue gas at the stack	4.9	234	0.3	14.9	2.6	61.4
TOTAL RELEASE	45.3	3021.9	45.0	3769.4	66.1	5194.3

⁽¹⁾ not determined.

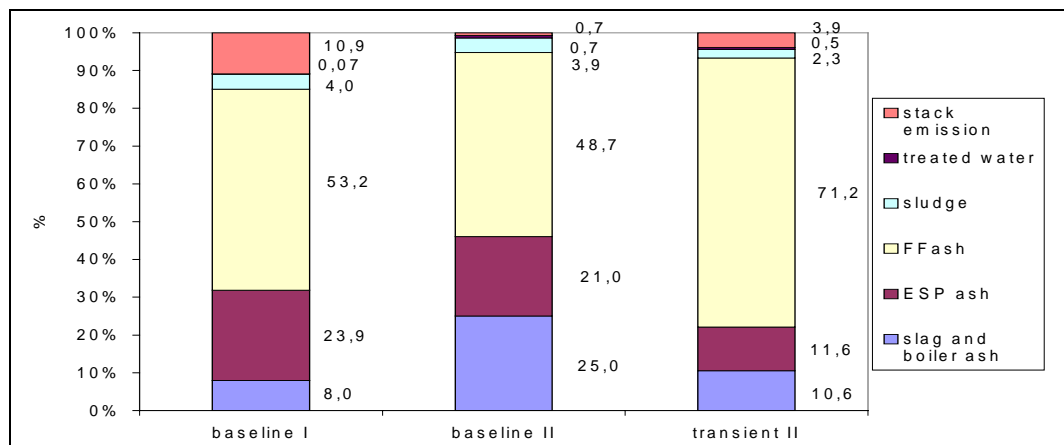


Figure 4: Distribution of dioxin emissions in the environment, in terms of TEQ.

Conclusions

PCDD/Fs total release during steady-state operation is included in the range of values normally reported for similar facilities. Transient behaviour investigated results in a measurable increase of flue gas concentration in the raw gas. This further supports the contribution of potential PCDD/Fs formation pathways arising from non optimum combustion conditions.

Since a great deal of attention is dedicated to furnace and flue gas treatment design, oriented to comply with restrictive stack emission limits, most of the PCDD/Fs release is essentially associated with solid and/or liquid residues, due to dioxin transfer from flue gas.

Future regulations, in accordance with integrated policies for pollution prevention and control, will require, as far as is technically feasible, flue gas treatment devices oriented to the minimization of PCDD/Fs mass release through residues. This can be achieved by using control technologies based on conversion rather than transfer of the dioxin flue gas load, such as catalytic oxidation⁹.

Acknowledgement

The authors wish to thank the plant operators for their useful cooperation.

References

1. European Union, 1996. Council Directive 96/61/EC
2. H. C. Gass, K. Luder, M. Wilken, (2002), Organohalogen Compounds
3. M. Wilken, F. Marsch, G. Dehoust, (2003), Organohalogen Compounds, 63, 29-32
4. H.O.Nordsieck, K.N.Etscheidt, R.Zimmermann,(2003),Organohalogen Compounds,63, 33-36
5. H. Hunsinger, H. Seifert, K. Jay, (2003), Organohalogen Compounds, 63, 37-40
6. Determination of the mass concentration of PCDD/Fs, Reports EN 1948-1,2 and 3, CEN 1996
7. M.Giugliano, S.Cernuschi, M.Grosso, E.Aloigi, R.Miglio (2001),Chemosphere, 43, 743-750
8. M.Giugliano, S.Cernuschi, M. Grosso, E.Aloigi, R.Miglio(2002),Chemosphere, 46, 1321-1328
9. M. Grosso, S. Cernuschi, M. Giugliano, M. Donegà, W. Tirlir (2003), Organohalogen Compounds, 63, 106-109