

CLEANING EFFICIENCY FOR PCDD/F, POP AND OTHER COMPOUNDS OF A SMALL DRY FLUE GAS CLEANING SYSTEM AT TWO LINES OF A MUNICIPAL SOLID WASTE INCINERATOR

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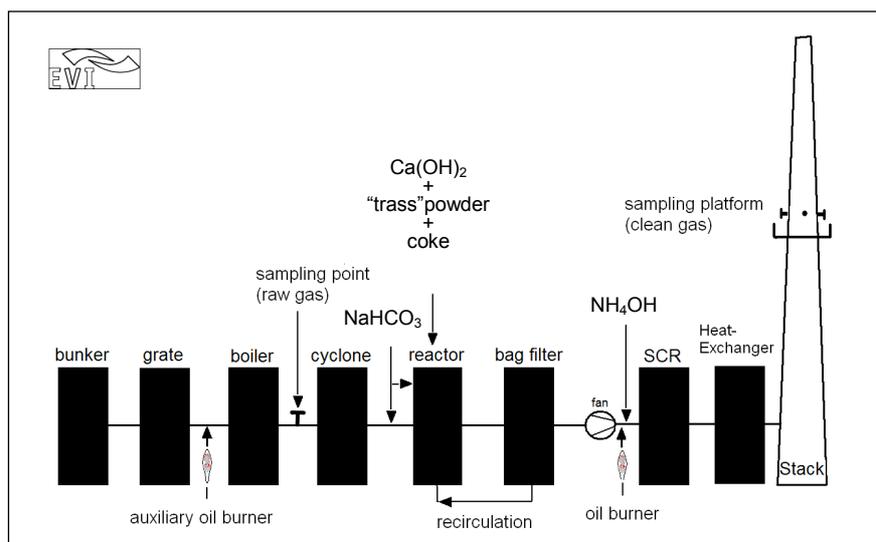
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Introduction

Emissions measurements in the raw gas and clean gas have been carried out at the 2 lines of the municipal solid waste incinerator EVI, Laar, Germany. With the data, the cleaning efficiency of the minimal but effective dry flue gas cleaning system was calculated as requested in the permit by the licensing authority. It can be shown, that the cleaning efficiency for PCDD/F and POP as well as for heavy metals was between 95 - 100%.

Plant description

EVI (Fig.1) has two identical combustion lines equipped with 3-zones grate design for the incineration of



approx. 25 Mg waste per hour ($H_u = 12$ MJ/kg), generating ~ 83 t steam (60 bar) per hour. The flue gas cleaning system is identical for each incineration line and consists of a double cyclone, NaHCO_3 -injection after the cyclones, an absorber reactor with injection of NaHCO_3 and injection of $\text{Ca}(\text{OH})_2$, "trass" powder with coke (HOK) (50/45/5%), a bag filter with PTFE/PI-fabric and with NH_4OH -injection in front of the low temperature catalyser (SCR-DeNOx). A part of the precipitated reaction products/sorbent from the bag filter is recycled into the reactor.

Oil firing with auxiliary burner in the post-combustion chamber and in front of the DeNOx is done only during the start-up procedure and if a temperature drop below 850 °C occurs. Clean gas is released into atmosphere via heat exchanger and 80 m-stack.

The emission limit values (ELV) due to permit for the plant, which are partially lower than ELV according to German regulations (17. BImSchV)¹, are shown in Table 1.

Table 1 Emission limit values (ELV) due to permit of EVI (selection) and in accordance to 17. BImSchV

component	unit	ELV due to permit	ELV 17. BImSchV
PCDDF I-TEQ	[ng/m ³ ,N]	0,005	0,1
benzo(a)pyrene (B(a)P)	[mg/m ³ ,N]	0,6E-06	0,05 *)
PCP (Tri - Penta)	[mg/m ³ ,N]	0,21	-
PCB (WHO)	[mg/m ³ ,N]	0,0015	-
sum Cd, Tl ¹⁾	[mg/m ³ ,N]	0,01	0,05
sum Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V, Sn ²⁾	[mg/m ³ ,N]	0,05	0,5
sum B(a)P,As,Cd,Co,Cr ³⁾	[mg/m ³ ,N]	0,05	0,05
Cd	[mg/m ³ ,N]	0,001	-
Sb	[mg/m ³ ,N]	0,0006	-
As	[mg/m ³ ,N]	0,0005	-
Cr	[mg/m ³ ,N]	0,002	-
Ni	[mg/m ³ ,N]	0,005	-
Hg	[mg/m ³ ,N]	0,01	0,03
dust	[mg/m ³ ,N]	2,5	10

1) according to §5, point 3a of German 17. BImSchV

2) according to §5, point 3b of German 17. BImSchV

3) according to §5, point 3c of German 17. BImSchV

*) sum B(a)P,As,Cd,Co,Cr (according to §5, point 3c of 17. BImSchV)

Materials and methods

The raw gas sampling point is located at boiler outlet in front of the cyclone, it does not comply with the requirements of EN 15259². The clean gas sampling point is in the stack at a height of 30 m. All requirements of EN 15259 are fulfilled for this sampling point. All sampling and calibration (AST/QAL2) of continuous emission monitoring systems (CEMS) has been carried out by Müller-BBM as a notified and accredited body in acc. to ISO/IEC 17025³. Sampling of PCDD/F, PCB (WHO), Chlorophenols (Tri- to PentaCPh) and benzo(a)pyrene (B(a)P) was performed over 6 h according to EN 1948-1, method B3, suitable for net measurements. Analysis of PCDD/F and POP has been done by mas GmbH^{*)} in compliance with EN 1948-2 and -3⁴ using HRGC/HRMS. Two samplings over 1.5 h for heavy metals and 0.5 h for dust were performed for each line. Sampling and analysis of heavy metals was done in accordance with EN 14385⁵ using ICP/MS and EN 13211⁶ for Hg (cold vapour AAS). Hg concentrations in the clean gas were obtained from the CEMS.

Results and discussion

As required by the authority, the cleaning efficiency of the MWI flue gas cleaning system had to be determined by measurement. Simultaneous sampling in the raw and clean gas were therefore carried out.

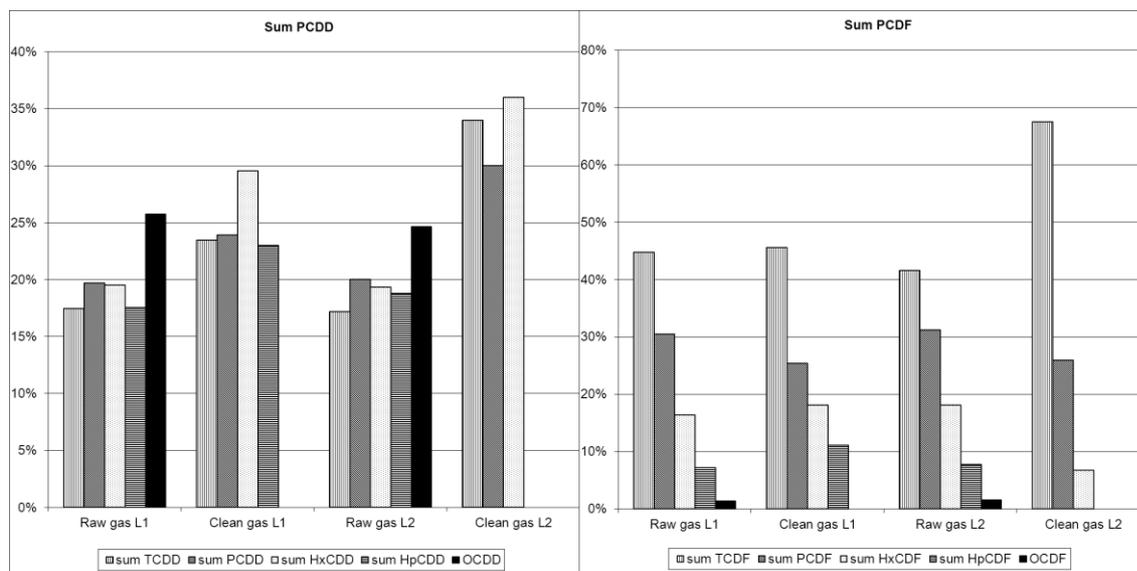
As expected, high levels of PCDD/F were found in the raw gas⁷ (line 1 / line 2: 1,3 / 2,5 ng ITEQ/m³N).

The concentration of PCB (WHO) and PCPh are also considerably increased. The sum of the 12 dioxin-like (dl) PCB (WHO) is 1,2 / 2,2 ng/m³N and the sum of Tri- to Pentachlorophenols adds up to 0,6 / 1,1 µg/m³N. Only concentrations of benzo(a)pyrene were below the limit of determination in the raw gas. The concentrations of the heavy metals were up to a magnitude higher than in the clean gas. The elevated values correlate with the high dust content in the raw gas of 1,5 g/m³N and 1,2 g/m³N respectively, assuming that POPs and heavy metals are largely formed on or bound at the dust particles^{8,9}.

The corresponding measurements in the clean gas of line 1 and line 2 showed very low levels of all selected compounds. As known from former¹⁰ and later measurement campaigns at this MWI, PCDD/F-concentrations were as low as 0,0011 / 0,0001 ng ITEQ/m³N and thus even lower than the results of a 3 years measurement campaign at another MWI plant with wet flue gas cleaning system as described earlier^{11,12}.

The cleaning efficiency for the PCDD/F congener groups and the single 2,3,7,8-substituted congeners was above 99,7 %. As can be seen in Fig. 2, the pattern of the PCDD/F distribution didn't change significantly from raw gas (e.g. decreasing from TCDF to OCDF) to clean gas (e.g. decreasing from TCDF to OCDF).

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In the tables 2 and 3, the data of the measurements in raw- and clean gas as well as the calculated cleaning efficiency is summarized. The cleaning efficiency of the flue gas cleaning system is at least 94%, being above 99% for the majority of the compounds investigated. Only the value for mercury at line 1 is lower (85%). A reason for this may be, that the injected amount of the Ca(OH)₂, “trass” powder and coke-mixture was lower than normal during the time of measurement. (line 1 = 138 kg/h; line 2 = 297 kg/h). The amount of this mixture injected into the absorbing-unit is automatically controlled via the mercury concentration in the clean gas as measured by the CEMS. Due to a temporary failure of the CEMS, leading to a lower Hg-value indicated, the amount of absorbing-mixture was reduced, resulting in the slight increase of the Hg- and B(a)P-emissions. As a consequence to avoid such higher values, the minimal amount of mixture injected was increased and the mercury threshold level for the additional mixture dosage was decreased. Especially the clean gas concentration of mercury is very sensible to the injected amount of the mixture and also the temperature in the absorbing-unit.

The cleaning efficiency for mercury at line 2 was 96% and with that as high as for POPs and heavy metals on both lines.

Table 2 results raw- and clean gas, cleaning efficiency line 1

compound	unit	Raw gas		Clean gas		cleaning efficiency [%]	
		mean concentration	expanded uncertainty *)	mean concentration	expanded uncertainty *)		
PCDD/F	I-TEQ	ng/m ³	1,3080	0,4009	0,0011	0,0002	99,92
B(a)P		mg/m ³	< 0,4E-06	< 0,1E-06	1,6E-06	0,2E-06	-***)
heavy metals	sum acc. 3a **)	mg/m ³	1,026	0,206	0,00008	0,00001	99,99
heavy metals	sum acc. 3b **)	mg/m ³	13,798	2,767	0,01932	0,00196	99,86
heavy metals	sum acc. 3c **)	mg/m ³	1,325	0,266	0,00136	0,00014	99,90
heavy metals	Cd	mg/m ³	1,019	0,204	0,00007	0,00001	99,99
heavy metals	Tl	mg/m ³	0,008	0,002	0,00001	0,00000	99,89
heavy metals	Sb	mg/m ³	4,264	0,855	0,00072	0,00007	99,98
heavy metals	As	mg/m ³	0,124	0,025	0,00031	0,00003	99,75
heavy metals	Cr	mg/m ³	0,176	0,035	0,00089	0,00009	99,49
heavy metals	Ni	mg/m ³	0,057	0,110	0,00277	0,00028	95,12
heavy metals	Hg	µg/m ³	109,7	22,2	16,5	2,6	85,00
PCP	tri-penta	µg/m ³	0,61	0,19	0,04	0,01	93,78
PCB	WHO-PCB	ng/m ³	1,183	0,363	0,025	0,005	97,89
dust	total dust	mg/m ³	1526,611	612,422	0,075	0,075	100,00

*) includes sampling and analysis, level of confidence 95 %, coverage factor k = 2

**) according to §5 of German 17. BImSchV

***) could not be calculated

Table 3 results raw- and clean gas, cleaning efficiency line 2

compound	unit	Raw gas		Clean gas		cleaning efficiency [%]	
		mean concentration	expanded uncertainty *)	mean concentration	expanded uncertainty *)		
PCDD/F	I-TEQ	ng/m ³	2,4670	0,7566	0,0001	0,0000	100,00
B(a)P		mg/m ³	< 0,4E-06	< 0,1E-06	< 0,1E-06	< 0,1E-06	- ***)
heavy metals	sum acc. 3a **)	mg/m ³	1,585	0,318	0,00002	0,00000	100,00
heavy metals	sum acc. 3b **)	mg/m ³	14,585	2,926	0,00716	0,00073	99,95
heavy metals	sum acc. 3c **)	mg/m ³	1,813	0,364	0,00109	0,00011	99,94
heavy metals	Cd	mg/m ³	1,580	0,317	0,00001	0,00000	100,00
heavy metals	Tl	mg/m ³	0,005	0,001	0,00001	0,00000	99,82
heavy metals	Sb	mg/m ³	5,336	1,070	0,00042	0,00004	99,99
heavy metals	As	mg/m ³	0,119	0,024	0,00015	0,00002	99,87
heavy metals	Cr	mg/m ³	0,109	0,022	0,00083	0,00008	99,24
heavy metals	Ni	mg/m ³	0,069	0,014	0,00059	0,00006	99,15
heavy metals	Hg	µg/m ³	97,9	19,9	4,3	3,0	95,66
PCP	tri-penta	µg/m ³	1,08	0,33	0,04	0,01	96,41
PCB	WHO-PCB	ng/m ³	2,195	0,673	0,000	0,000	100,00
dust	total dust	mg/m ³	1197,919	480,704	0,075	0,075	99,99

*) includes sampling and analysis, level of confidence 95 %, coverage factor k = 2

**) according to §5 of German 17. BImSchV

***) could not be calculated

As a main important result of the effective dry flue gas cleaning system it can be shown that the very low emission limit values (ELV) due to permit are consequently realized at both incinerator lines of EVI.

Acknowledgements

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References:

1. Verordnung über die Verbrennung und die Mitverbrennung von Abfällen in der Fassung der Bekanntmachung vom 14. August 2003 - 17. BImSchV) (8/2003); *BGBl. I*: 1633, zuletzt geändert am 27.01.2009, *BGBl. I*: 129, 131
2. Air quality – Measurement of stationary source emissions – Requirements for measurement sections and sites and for the measurement objective, plan and report; German version EN 15259 (2008)
3. DIN EN ISO/IEC 17025; General requirements for the competence of testing and calibration laboratories; German version ISO/IEC 17025; (2005)
4. DIN EN 1948/1-4; Stationary source emissions – Determination of mass concentration of PCDDs/PCDFs and dioxin-like PCBs, Part 1: Sampling; Part 2: Extraction and clean-up; Part 3: Identification and qualification; German version EN 1948 (2006); Part 4: Sampling and analysis of dioxin-like PCBs; German version EN 1948 (2010)
5. EN 14385; Stationary source emissions – Determination of the total emissions of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl and V; German version; (2004)
6. EN 13211; Stationary source emissions – Manual method of determination of the concentration of total mercury; German version; (2001)
7. Hunsinger H, Jay K, Vehlow J (2000); *Organohalogen Compounds Vol. 46*:86-89
8. Stieglitz, Vogg (1987); *Chemosphere 16*, 1917-1922
9. Vogg (1995); *Organohalogen Compounds Vol.22*: 31-48
10. Gass HC, Schneider C, Sünderhauf W, Pot E (2011); *31st International Symposium on Halogenated Persistent Organic Pollutants POPs*; Brussels, Belgium
11. Gass HC, Jager E, Menke D, Lüder K (1998); *Organohalogen Compounds Vol. 36*: 175-78
12. Gass HC, Sünderhauf W, Rotard W, Jager J (2000); *Organohalogen Compounds Vol. 46*: 154-157