PCDD/PCDF AND OTHER MICROPOLLUTANTS IN MSWI ASHES AND CRUDE GAS DURING SHUT-DOWN AND START-UP PROCESSES

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Introduction

During shut-down and start-up of MSWI plants, combustion conditions are impaired in comparison to normal operating conditions, even if back-up burners maintain high temperatures in the combustion chamber. PCDD/PCDF concentrations in MSWI crude gas are known to be elevated during and after transiently impaired combustion conditions due to memory effects[1,2]. Shut-down of continuously operated MSWI plants is not very frequent, but all MSWI plants have to be shut down for review at regular intervals.

Gass et al. reported on many crude gas and stack gas PCDD/PCDF measurements after plant revisions (cold start) and after short time shut-downs at MVB, a MSWI plant located in Hamburg, Germany[3]. Due to the coincidence of high PCDD/PCDF concentrations during start-up and memory effects in the scrubber, the normal start-up procedure showed to affect PCDD/PCDF concentrations in the gas purification plant for extended periods of time if no additional adsorbents were used. In one campaign additionally the shut-down procedure was investigated[4].

In the frame of a research project on the minimisation of PCDD/PCDF load in boiler ashes and filter dusts from MSWI plants, one aim of our study was to evaluate whether the results reported from MVB plant can be reproduced at another municipal waste incinerator and to evaluate the impact of the shut-down and start-up conditions on the PCDD/PCDF concentrations in boiler ash and ESP dust.

Methods and Materials

Sampling was performed at a 10 t/h grate incinerator of a German MSWI plant. The plant's back-up burners are operated with light fuel oil. Crude gas was sampled downstream of the ESP between the external economiser and the wet scrubber. With regard to the low dust concentration (typically less than 10 mg/m³) and the complex flow field at the sampling point, we dispensed to isokinetic sampling. Apart of this, sampling and analysis were performed according to DIN EN 1948 (condensation + XAD2 adsorption method). PAH, chlorobenzenes and chlorophenols were determined by GC-MS from the same samples as PCDD/PCDF. All results were standardised to 273 K and 1013 hPa. Simultaneously to gas sampling, boiler ash and ESP dust samples were collected. The plant scheme and sampling locations are shown in figure 1.

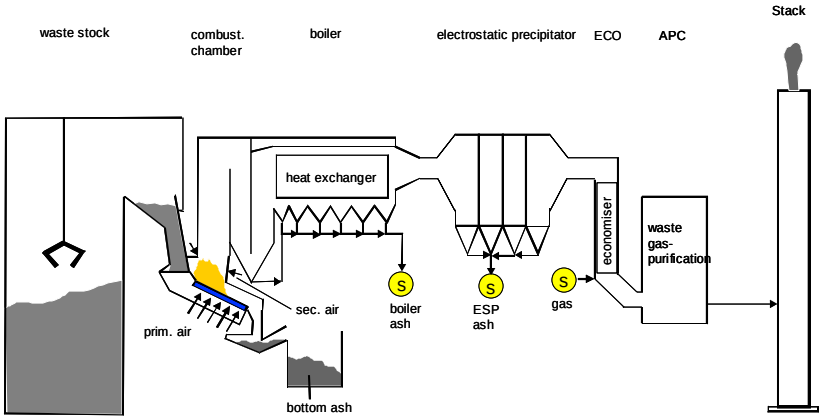

Figure1: Plant scheme and sampling locations (s)

Results and Discussion

1) Plant Shut-Down

The shut-down of a MSWI plant can be divided into two phases, phase a) being the time interval between stopping of the waste feed until the moment when the back-up burners are being fired. The second phase (b) lasts until the grate is free of residual waste. Both phases last approximately one and a half hour each. During the shut-down procedure in both phases samples were taken. Additional to the PCDD/PCDF-concentrations in the gas-phase the concentrations of the sum of PAK larger than 200 amu, the sum of PCBz (Cl2-Cl6) and the sum of PCPh (Cl1-Cl5) were determined. Prior to the shut-down reference samples under normal operating conditions had been taken on several days. The results are given in table 1.

Table1: Concentrations of organic pollutions in the crude gas after dedusting and in the ESP ash during a shut-down procedure

phase of shut-down procedure	**flue gas (after ESP and economiser)**				**ESP ash**
	PCDD/PCDF [ng I-TEQ/m³]	PAH > 200 amu [ng/m³]	Sum PCBz (2-6) [ng/m³]	Sum PCPh (1-5) [ng/m³]	PCDD/PCDF [ng I-TEQ/kg]
reference samples (mean ±SD, n=5)	4,1 ±1,2	40 ±9	260 ±66	1600 ±450	610 ±340
a) waste feed stopped, back-up burners not yet fired	4,4	36	250	594	710
b) burner operation until residual waste burn-out	2,6	47	209	708	600

During the shut-down procedure both PCDD/PCDF, PAH and chlorobenzenes concentrations in the crude gas are within the range observed at that plant at normal combustion conditions. The chlorophenols concentrations, however, are somewhat lower. The crude gas HCl concentration was between 500 and 800 mg/m³ before waste feed was stopped. The concentration went down to 200 mg/m³ within phase a) and then it dropped down to 60-70 mg/m³ when the back-up burners were fired. Throughout phase b) the HCl concentration remained above 45 mg/m³, probably due to releases from chloride containing deposits. Obviously, the amounts of chlorides deposited on the walls and on the heat exchanger tubes are sufficient to produce appreciable amounts of chlorinated compounds even if HCl concentrations in the gas have dropped to quite low values.

Similarly to the PAH, chlorobenzenes and PCDD/PDCF concentrations in the crude gas, the PCDD/PCDF load of the ESP dust is not affected by the shut-down procedure in a significant way.

2) Start-up Procedure

After plant revision, start-up is a slow process, because rapid changes in temperature have to be avoided in order to save the refractory lining materials used in the combustion chamber. After warming up by steam the combustor is aerated. Combustion chamber temperature then gradually is raised by increasing the back-up burners feed rate. Waste is fed when the minimum combustion chamber temperature required (850°C) is reached. Fig. 2 shows combustion chamber temperature, waste and back-up burner feed as well as the CO, HCl and PCDD/PCDF concentrations. Additionally, the PAH, PCBz and PCPh concentrations of the gas samples as well as the PCDD/PCDF concentrations in ESP ash and boiler ash are given in table 2.

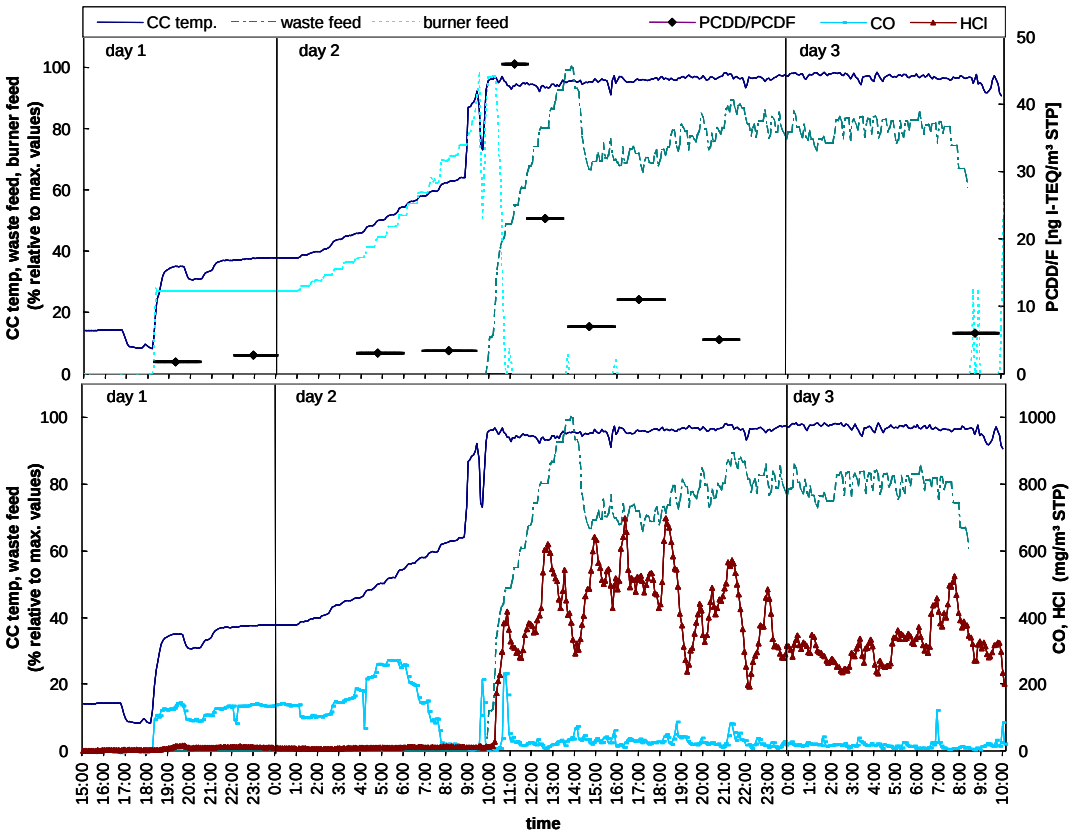

Figure 2: PCDD/PCDF, HCl and CO crude gas concentrations at start-up of the MSWI plant

During the heat-up period, the HCl concentration in the crude gas is lower (5-15 mg/m³ STP) than during shut-down after burn out of residual waste on the grate. As long as the combustion chamber has not reached sufficiently high temperature, CO and PAH concentrations are high, indicating rather poor combustion conditions. PCDD/PCDF crude gas concentrations during the heat-up period are only a little lower than at normal operation with waste as the fuel. Obviously, the rather bad combustion conditions during heat-up with fuel oil combined with residual deposits in the cleaned combustion chamber and boiler are sufficient for formation of halogenated PIC.

Immediately after waste is fed, PCDD/PCDF concentrations both in the crude gas and in the ESP ash are increased by a one order of magnitude comparing to normal operating conditions.

Table 2: PCDD/PCDF, PAH, PCBz and PCPh concentrations in the crude gas and PCDD/PCDF concentrations in ESP ash and boiler ash during start-up

sample #,	**flue gas (after ESP and economiser)**				**ESP ash**	**boiler ash**
phase of start-up	PCDD/PCDF	PAH > 200 amu	Sum PCBz (2-6)	Sum PCPh (1-5)	PCDD/PCDF	PCDD/PCDF
procedure	[ng I-TEQ/m³]	[ng/m³]	[ng/m³]	[ng/m³]	[ng I-TEQ/kg]	[ng I-TEQ/kg]
reference samples (mean ±SD, n=5)	4,1 ±1,2	40 ±9	260 ±66	1600 ±450	610 ±340	126 ±90
#1 heat-up	1,7	4740	370	17730	-	-
#2 heat-up	2,7	8070	750	28730	-	-
#3 heat-up	3,0	5160	1330	29880	-	-
#4 heat-up	3,4	1100	13500	7090	-	-
#5 waste fed	46	5230	2720	28500	-	-
#6 waste operated	23	840	1600	15200	5400	200
#7 waste operated	7,2	170	540	6070	1800	49
#8 waste operated	11	130	780	9690	2900	66
#9 waste operated	4,9	78	480	7630	1100	68
#10 waste opd.	6,2	52	410	8960	-	-

PCDD/PCDF concentrations both in the crude gas and in the ESP ash clearly remain elevated during 12 h after switching to waste as the fuel. Even 24 h after start of waste feed, the PIC concentrations are slightly higher than at normal operation. As boiler ash PCDD/PCDF concentrations vary by large depending on the section of the boiler being rapped at the sampling interval, no statistically significant changes can be detected during the start-up procedure.

Concerning the minimisation of ESP ash PCDD/PCDF load, ESP ashes from start-up procedures should be selected for an extended period of time and treated, e.g. by re-burning.

It should be mentioned, that the elevated crude gas PCDD/PCDF concentrations do not imply stack gas emissions are exceeding the emissions allowed. E.g. adsorption steps in flue gas cleaning process are capable to manage even high peaks in crude gas concentrations.

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References

1. Zimmermann R., Blumenstock M., Heger H.J., Schramm K.-W. and Kettrup A. (2001) Emission of Nonchlorinated and Chlorinated Aromatics in the Flue Gas of Incineration Plants during and after Transient Disturbances of Combustion Conditions: Delayed Emission Effects. Environ. Sci. Technol. 35, 1019-1030
2. Weber R., Sakurai T., Ueno S. and Nishino J. (2002) Correlation of PCDD/F and CO values in a MSW incinerator-indication of memory effects in the high temperature/cooling section
3. Gass H.C. and Lüder K. (2002) Stellt der Anfahrbetrieb aus kaltem Anlagenzustand eine PCDD/F-Belastung bei der thermischen Abfallverwertung dar?. 7. Fachtagung Thermische Abfallbehandlung 20, 87-96
4. Gass H.C., Lüder K. and Wilken M. (2002) PCDD/F-Emissions during Cold start-up and shut down of a municipal waste incineration. Organohalogen Compounds 56, 193-196