FORMATION AND SOURCES

PCDD/F- EMISSIONS DURING COLD START-UP AND SHUT-DOWN OF A MUNICIPAL WASTE INCINERATOR

Horst C. Gass¹, Karl Lüder², Michael Wilken³

¹MPU-Meß- und Prüfstelle Technischer Umweltschutz GmbH, Kolonnenstr. 26, D-10829 Berlin (HC.Gass@MPU-GmbH.de)

²MVB Müllverwertung Borsigstraße GmbH, Borsigstr. 6, D-22113 Hamburg (Lueder@MVB.HEW.de) ³MWC Michael Wilken Consulting, Florastr. 8, D-12163 Berlin (MWCBerlin@AOL.com)

Introduction

Since 1994 close to 250 PCDD/F clean gas samples were taken at the municipal solid waste incinerator MVB Borsigstr. GmbH, Hamburg, in several campaigns at up to five sampling points simultaneously. The results of all official PCDD/F-measurements at the stack were in compliance with the German standard for waste incinerators of 0.1 ng I-TEQ/Nm³. Most of the data even remained under the annual average of 0.05 ng I-TEQ/Nm³ which is in effect for this plant, but some single data were close to 0.1 ng I-TEQ/Nm³. As already reported at DIOXIN 2000, under normal plant operation conditions the clean gas emissions are significantly higher than those obtained simultaneously after the bag house as the first flue gas treatment step /1/. It was concluded that the contamination of the final flue gas treatment system and the long lasting memory effect could be possibly attributed to off-normal conditions. A subsequent analysis of the extensive plant operation and dioxin data could not explain the observed phenomena for upsets, shutdown operations, soot-blowing, non-stationary plant operation and unexpected failure or malfunction of plant components as described from Clarke /2/. Only the start-up procedure after a plant revision (cold start) remained as a possible reason which was not investigated so far at this plant. Therefore several measurement campaigns during the cold start-up were performed on both lines of MVB. Samples were taken simultaneously in the first flue (second level above oil burner in the post combustion chamber), the raw gas after the boiler (directly after the fourth flue), the semi-clean gas after the bag house and in the clean gas (see fig. 1). Additionally the shut-down procedure was also investigated in one campaign.

Methods and Materials

All measurements and analysis were performed according to EN 1948 /3/ with the exception that the sampling time was shortened and adjusted to the different phases of the start-up procedure. The detection limit was 0.001 ng I-TEQ/Nm³ for all 2,3,7,8-substituted isomers. All data are standardized to 273 K and 1013 hPa at 11 % O₂. A detailed plant description can be found in /4/.

Results and Discussion

The shut-down procedure can be divided into the phases

- stop of waste feeding,
- closing of waste feeder,
- waste burn-out on the grate.

During one shut-down operation the PCDD/F-concentrations were determined simultaneously at the sampling locations of raw gas, flue gas after bag house and clean gas in the above mentioned

ORGANOHALOGEN COMPOUNDS Vol. 56 (2002)

FORMATION AND SOURCES



Figure 1. plant scheme and sampling locations

phases. Prior to the shut-down a control measurement under normal operation conditions was performed in the raw gas.

Only the final stage of the shut-down procedure showed some elevated levels in the raw gas. But at the sampling locations downstream no increase of the PCDD/F-levels could be observed in comparison to the standard operation conditions.

phases of shut-down procedure	Sampling locations			
	after boiler	after bag house	clean gas	
normal operation conditions	0.72		_	
stop waste feeding	0.48	0.013	0.021	
closing of waste feeder	0.68	0.009	0.010	
waste burn-out on the grate typical PCDD/F-concentrations	1.76	0.016	0.014	
normal plant operation		0.01	0.02	

Table 1. PCDD/F concentrations [ng I-TEQ/Nm³ at 11% O_2] in the different phases of a shut-down procedure at the different sampling locations

The start-up after a plant revision (cold start) at this municipal waste incinerator follows also a certain procedure and is divided into the steps:

- Oil burning with a maximum fuel feed rate until the minimum furnace temperature for the incineration of waste (850 $^{\circ}$ C) is reached

• Start of waste feeding when furnace temperature has at least 850°C in the first flue; increasing feed rate until design load is reached

• Designed feed rate (normal operation)

In cases that the refractory material has been replaced or repaired (long time plant revision) an additional drying phase at lower temperatures for several hours is added prior to the oil burning phase

	sampling locations				
Phases of cold start-up	1. flue	after boiler	after bag house	clean gas	
drying phase (only after long time plant revision)		20-35.2	2.5	0.23	
oil burner operation	2.2 - 9.6	41 - 267	5-26.6	0.08 - 0.72	
Start waste feed Average concentration in the following days	1.1 – 8.7	16 – 64	3.9 – 16.5	1.35 - 4.3 1.1 (3 days) 0.21 (4 days)	
typical PCDD/F-concentrations				0.1 (8 days)	
normal plant operation		0.7	0.01	0.02	

Table 2. PCDD/F concentrations [ng I-TEQ/Nm³ at 11% O_2] found in the different phases of the cold start-up at the different sampling locations

to carefully temper the new refractory material. Due to the plant configuration and standard start-up operation, during the oil burning phase no coke is added prior to the bag house in order to avoid ignitions of the coke due to the high oxygen level and the small particle load in this phase.

A total of 5 cold start-ups have been investigated for their dioxin emissions in all different phases simultaneously at the different sampling locations and are compared to the typical concentrations obtained over the past years during normal plant operation in the designed range.



Figure 2. PCDF/PCDD ratio in the raw gas during shut-down and start-up procedures

ORGANOHALOGEN COMPOUNDS Vol. 56 (2002)

FORMATION AND SOURCES

In all measurements a very strong increase of the flue gas concentrations after the boiler could be observed mainly in the phase when only the oil burner are in operation. Due to the lack of coke prior to the bag house in this operation phase the gas reaching the wet scrubber system contains now about 1000 times higher concentrations than under stable normal operation conditions.

With the waste feeding the PCDD/F-levels after the boiler are still elevated, probably influenced by memory effects of the oil burner phase. Although the coke addition up-front of the bag house is going into operation at the same time, the PCDD/F-levels after the bag house are still in the same order of magnitude. With a time delay of a few hours an increase of the clean gas concentration is observed which is considerably above the long time average and even exceeds the German emission limit. Because the PCDD/F removal in the wet scrubber system is mainly a storage phenomena, in the following days the average clean gas concentration (determined in continuous long time samples) on in elevated level, indicating the long lasting memory effect /5,6,7/. A load calculation based on the average clean gas concentrations in the following days shows that one cold start-up alone is equivalent to approximately half a year of normal plant operation.

A good indicator for the possible formation processes of the PCDD/F in all phases is the ratio PCDF/PCDD. Figure 2 shows this ratio for all investigated shut-down and start-up procedures. During normal operation conditions with complete burn-out the ratio in the raw gas at MVB is around 10. The lowest ratios in the first flue and raw gas are always found during oil burner operation. This indicates massive contaminations of the boiler surface with soot particles and formation parameters indicate good combustion conditions the ratio is nearly unchanged probably due to the high inventory of the soot deposits in the boiler. Therefore it can be assumed that the contamination caused by the oil burner operation might have an impact for several days until the typical PCDF/PCDD ratio of around 10 is achieved. Further optimization of the cold start-up procedure with inert additivs during oil burner operation resulted in a sustainable reduction of the PCDD/F concentration in the clean gas under the German regulatory level.

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