

PCDD/F EMISSIONS RELATED TO THE OPERATING CONDITIONS OF THE FLUE GAS CLEANING SYSTEM OF MWI-AMSTERDAM

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ABSTRACT

An overview is given of the results of two optimization programmes aimed at reducing the PCDD/F emissions of MWI-Amsterdam. Special attention was given to minimize the *de novo* synthesis in the first electrostatic precipitator (fly ash removal). Means to enhance the absorption of PCDD/Fs in the spray dry absorber were also investigated. Finally, the effect of adding Activated Carbon to the second scrubber is reported on.

INTRODUCTION

Municipal Solid Waste (MSW) produced in the Amsterdam area has been incinerated in three successive Municipal Waste Incinerators (MWIs) from the year 1919 onwards. The first MWI was in service until 1969 and was replaced by a - for those days - modern MWI called "AVI-North". Given the increasing amounts of MSW and more stringent environmental legislation the Amsterdam City Council decided in 1985 to close the existing "MWI-North" on January 1st, 1993 and to put a newly built MWI in operation on that same date. The initial layout of this third MWI, called "MWI-Amsterdam", had to meet the following demands:

- four incineration lines, each with a daily capacity of 600 metric tons
- flue gas cleaning corresponding to the German TA-luft '86, the most stringent demand in Europe at that time (but contained no limits for emission of PCDD/Fs)
- zero waste water discharge

In 1989, the Amsterdam City Council Board, in providing the necessary financial backing, gave its explicit approval to the construction of the MWI-Amsterdam. Each line of the contracted MWI consisted of:

- horizontal double-motion overthrust grate
- 3-draught-radiating with post-connected convection steam boiler
- 1-field electrostatic precipitator (fly ash to be used as an filler in asphalt)
- Spray absorber with post-connected 3-field electrostatic precipitator
- bottom ash processing (crushing, sieving, separation of ferrous and non-ferrous metals)

As a result of the detection of increased levels of PCDD/Fs in cow's milk grazing in the vicinity of Dutch MWIs, in 1989 a new Dutch emission directive (RV '89) was enacted containing a maximum permitted emission of PCDD/F of 0.1 ng I-TEQ/Nm³ for MWIs to be constructed after 1990. Existing MWIs were 'forced to exert themselves' to achieve this value of 0.1, with an allowed maximum of 0.4 I-TEQ ng/Nm³. The permit of MWI-Amsterdam prescribes less than 0.3 ng I-TEQ/Nm³. Faced with this new PCDD/F emission standard, the Amsterdam City Council decided to enlarge the already contracted layout with an additional flue gas cleaning consisting of a DeNO_x (SNCR), active carbon injection in spray absorber, 2-step scrubber followed by an Electro-Dynamic Venturi (EDV) scrubber for aerosol separation.

Constructed with this double flue gas cleaning (originally semi-dry with retrofitted wet scrubbers) MWI-Amsterdam was put in service in January 1993. The resulting PCDD/F emission was expected to be less than 0.3 ng I-TEQ/Nm³. The total investment amounted to 0.5 billion US-dollar.

PCDD/F EMISSIONS IN THE FIRST OPERATIVE YEAR (1993)

From January 1993 a number of emission-monitoring programmes were performed in order to check whether specifications of contractors and permits of the authorities were met. In general the installation performed extremely well, achieving emission levels far below the permits except for PCDD/F-emission. As a consequence this aspect got increasing interest as the year went by and most of the other initial operating problems were solved. To illustrate the effort that was made to solve the problem of PCDD/F-emissions: in total 82 gas samples were analyzed for PCDD/Fs in 1993 only. Apart from stack-emissions, the performances of the various segments of the flue gas cleaning device were measured. **Figure 1** gives a schematic overview of the consecutive FGC-devices of MWI-Amsterdam. The bold characters denote the four locations at which flue gas samples were taken for PCDD/F-analysis.

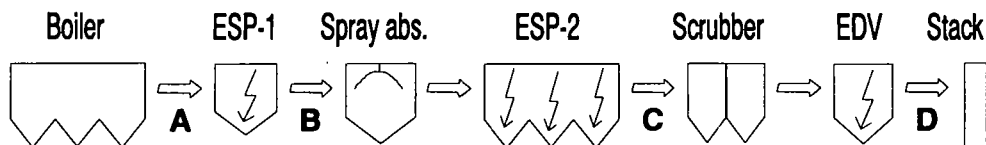


Fig. 1 Schematic overview sampling positions during the 1993 measurements.

Apart from formal permit-verifications, measurement-programmes were performed to unravel the effect on the PCDD/F-emission by

- optimization of the SNCR,
- replacement of co-injection of "Herd-Ofen-Koks (HOK)" by Activated Carbon (AK) in the spray absorber,
- additional injection of Activated Carbon in the second scrubber.

The overall results of the PCDD/F-measurements are summarized in **Table 1**. It is shown that the levels of PCDD/F in the stack-emissions are well above the permit-level of 0.3 ng/Nm³ I-TEQ. The PCDD/F-levels directly after the boiler are reasonable (3.4 ng/Nm³), but - apparently due to *de-novo* synthesis - increase in the ESP to some 5.8 ng/Nm³ at ca. 230 °C. Furthermore, the removal efficiency of the various segments of the flue gas

cleaning, was found to be insufficient to reduce the PCDD/F stack emission (2.1 ng/Nm^3) to the permitted level. Operating the wet scrubber with up to 60 g/l AK did have some positive effect, but the resulting emission at the stack (1.6 ng/Nm^3) was still too high.

POSITION:	A (n = 5)	B (n = 4)	C (n = 29)	D (n = 44)
Overall result	3.4 ± 1.5	5.8 ± 1.0	4.2 ± 3.4	2.1 ± 1.4
no AK in Scrubber			3.1 ± 1.6	2.4 ± 1.4
AK in Scrubber			5.9 ± 4.4	1.6 ± 1.3

Tab. 1 Results of the 1993 measurements. (Units: TEQ ng/Nm^3)

PCDD/F EMISSIONS IN THE SECOND OPERATIVE YEAR (1994)

Aim and character of the measurement programme

Using the results of the 1993 measurements the combustion process as well as the flue gas cleaning systems were optimized and a new series of PCDD/F-measurements was commenced in april 1994. The optimized parameters were:

- reduction of the excess oxygen (from 11% to 9% v/v)
- cleaning system of the convection bundles
- fixed set-point of the lime milk dosage (containing 6 g/l AK) in the spray absorber
- primary field of ESP-2 switched off to obtain higher residence times for the AK in the gas-phase

The 1994 measurement programme aimed at obtaining insight into the effect of the following parameters on dioxin emissions at several sampling positions in the installation:

- optimization measures as described above
- *de novo* synthesis of PCDD/Fs in ESP-1
- PCDD/F-reduction in the spray absorber
- PCDD/F-reduction in the scrubbers and EDV

In order to obtain the essential information, the 1994 measurements were performed at selected operating conditions (optimized as described):

run a: normal operation

run b: ESP-1 switched off

run c: ESP-1 switched off; no AK-dosage in the spray-absorber

run d: AK-dosage in the second scrubber (including one measurement with ESP-1 switched off)

During these runs simultaneous samples were taken at the positions A, B, C and D. In order to obtain mass balances of PCDD/Fs the production-rate of residues of ESP-1 (fly ash, denoted as 1 in Fig. 2), ESP-2 (FGC-salt: "2") and the scrubbers (untreated waste water: "3") as well as the total gas flow were measured and sampled. In addition, the input water of the spray absorber (consisting of treated waste water from the scrubbers and lime milk) was analyzed for PCDD/F-content. As the contribution of this flow was shown to be negligible these results are omitted in this paper.

EMCO

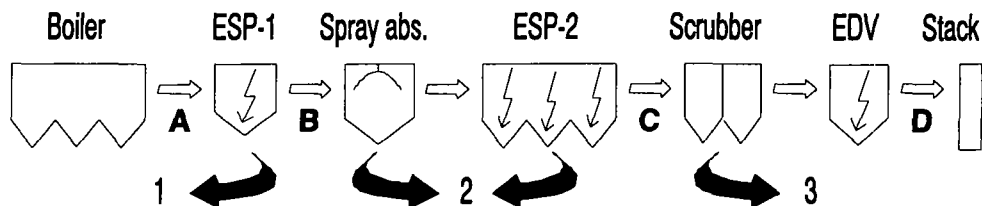


Fig. 2 Schematic overview sampling positions during the 1994 programme.

Evaluation of the results

An overview of the results (both PCDD/F concentrations in flue gases as PCDD/F mass balances) is given in Table 2. Based on these results several conclusions were drawn:

POSITION:	A	B	C	D	1	2	3
run a	1.4 ± 0,11 (164 ± 13)	2.3 ± 0,10 (266 ± 12)	0.4 ± 0,05 (43 ± 6)	1.1 ± 0,07 (128 ± 8)	(176 ± 11)	(152 ± 19)	(0.6 ± 0,24)
run b	2.0 ± 0,23 (228 ± 26)	2.4 ± 0,24 (271 ± 28)	0.5 ± 0,16 (57 ± 18)	1.1 ± 0,08 (132 ± 9)	(81)	(427)	(0.7 ± 0,30)
run c	2.3 ± 0,26 (263 ± 30)	3.0 ± 0,51 (346 ± 59)	1.5 ± 0,29 (177 ± 33)	2.7 ± 0,10 (315 ± 11)	(31)	(248)	(1.2)
run d			0.4 ± 0,05 (45 ± 6)	0.2 ± 0,03 (22 ± 4)			(67 ± 12)

Tab. 2 Results of the 1994 measurement programme.
(bold: TEQ ng/Nm³; brackets: mass balance in TEQ µg/h)

- 1) The levels of PCDD/Fs (1.4 - 2.3 ng/Nm³) at sampling position A (boiler emission) show that the adapted primary combustion measures in this modern installation (optimized conversion in the secondary chamber and reduced residence times of the flue gases at the temperature range 400 - 250°C) greatly reduce the *de novo* synthesis in the boiler.
- 2) At the operating temperature of ESP-1 - i.e. 230°C - and normal operation (run a) the *de novo* synthesis accounts for more than a 3-fold increase of the total amount of PCDD/Fs, based on the balance of PCDD/F upfront and downstream of ESP-1. Switching off the voltage of ESP-1 results in a distinct decrease of the *de novo* synthesis in ESP-1. This effect was anticipated as fly ash is a known¹ catalyst for the formation process of PCDD/Fs. Since, due to gravitation, still 50% of the fly ash precipitates, the *de novo* synthesis is not entirely annihilated under these circumstances.
- 3) Based on levels of PCDD/Fs (I-TEQ ng/Nm³) in the flue gas upfront and downstream of the spray absorber, a removal efficiency of roughly 80% is achieved both in run a and b. Hence, no additional absorptive effect was established in the spray absorber and ESP-2 when ESP-1 was switched off (run b). Note that

additional absorption was anticipated by the elevated levels of - carbon containing - fly ash in the spray absorber and ESP-2.

The results of run c indicate that fly ash cannot replace AK entirely as an absorbent in the spray absorber: operating the spray absorber without administering AK (but with elevated levels of fly ash) reduced the removal efficiency to 50%. In sum, none of the runs achieved a removal efficiency of 90%, a value which - according to literature² - in theory is achievable using a spray absorber with post-connected ESP.

- 4) Taking into account the mass balances of PCDD/Fs, a remarkable increase of PCDD/Fs was observed over the spray absorber and ESP-2 during run b. Although laboratory experiments³ have revealed that the chlorination of phenol does occur at 150°C using HCl as a catalyst, *de novo* synthesis is very unlikely at the operating temperature (150 °C) of the spray absorber and ESP-2, this phenomenon cannot be explained. A closer investigation of the amount of, and PCDD/F levels in, the ESP-2 residues is in progress at the moment.
Yet, the total production of PCDD/Fs during run b (640 TEQ µg/h) and c (595 µg/h) - by summation of residues 1, 2 and 3, and stack gas emission d - do not differ significantly. As in run c only the removal efficiency of the spray absorber was changed compared to run b, similar total productions of PCDD/F might be expected. Hence, the measured production of PCDD/F in the spray absorber and/or ESP-2 seems to fit.
- 5) Comparing the flue gas entering the wet scrubbers with the stack gas, an - on average 2-fold - increase of PCDD/F levels is observed. Furthermore, the analyses of the waste water leaving the scrubbers indicate that the removal efficiency of these scrubbers is insignificant. As a net increase of PCDD/Fs upon passing the wet flue gas cleaning system did not appear in the 1993 measurements, we suggest that the observed increase in the 1994 measurements has to be ascribed to memory effects. It should be noted that the average scrubber entrance levels of PCDD/Fs at sampling point C (4.2 ± 3.4) of the 1993 measurements is markedly higher than the scrubber entrance levels (1.1 - 2.7) of PCDD/Fs during the 1994 measurements (due to the measures that were taken since 1993). Memory effects due to absorption-desorption equilibria of PCDD/Fs that are absorbed to the coated walls of the scrubbers was reported earlier⁴.
- 6) Operating the second scrubber with 70 g/l AK results in a decrease of PCDD/Fs levels in the stack gas relative to sampling position C. Apparently this is due to the absorption by AK, as the concentration of PCDD/F in the waste water of the scrubbers amounts roughly to 100 times the levels obtained at normal operation. Moreover, we believe that even lower stack gas levels can be obtained under prolonged operation of AK in the second scrubber, since memory effects tend to decrease in time. Note that additional proof for the existence of memory effects can be derived from the mass balance of run d, in which a doubling of the PCDD/F-levels seem to occur between sampling point C and D. We suggest that the presence of AK in the second scrubber absorbs PCDD/F formerly absorbed at wall and coatings.

CONCLUSIONS AND DISCUSSION

Given the results of the 1994 measurement programme it can be concluded that within the framework of the present flue gas cleaning devices of MWI-Amsterdam emission levels below the permitted 0.3 I-TEQ ng/Nm³ can be achieved. Assuming that the observed increase of PCDD/Fs in the flue gases whilst passing the scrubbers is ascribed to memory effects, several options may well lead to permanent emission levels of < 0.3 ng/Nm³:

- Elimination of *de novo* synthesis in ESP-1 by either quenching the flue gas entrance temperatures to less than 200°C, or replacing ESP-1 by a connecting tube between the boiler and the spray absorber. Depending on the requirement for separate collection of fly ash and spray absorber salts, ESP-1 may be replaced by a cyclone.
- Separate injection of AK and lime milk in the spray absorber to increase the PCDD/F removal efficiency of this device to 90% or more (note that during all the measurements discussed in this paper AK was mixed with lime milk prior to injection).
- Operation of the second scrubber with added suspended AK.

The ultimate effect of any of these options is unclear in terms of fulfilment to the permitted emission levels of < 0.3 ng/Nm³. As the first option requires extensive retrofitting and the last option is generally believed to be prone to operating difficulties, MWI Amsterdam prefers optimization of the AK injection in the spray absorber to be enforced first. Simultaneously, closer investigation of the feasibility of the other options can be performed.

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