

DIOXIN-EMISSIONS FROM A MSWI RELATED TO MEMORY-EFFECTS IN A 2-STAGE WET SCRUBBER

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Summary

During the start-up of the recently refurbished MSWI-plant of ISVAG (Wilrijk, Belgium), an extensive campaign was launched to monitor the emission of dioxins. The resulting data indicate that virtually all current dioxin release is due to memory effects situated in the wet scrubber, which was unaffected by the refurbishment and located after a new semi-dry scrubber with bag-housefilter. The data obtained provides valuable information leading to a better understanding of this memory effect.

Prior Experience with Memory Effects

Dioxin emission values from MSWI-plant tend to react slowly to changes in feed quality, operating conditions, or boiler fouling. Some of this inertia is due to gradual and delayed dioxin formation in boiler and flue deposits, another part is related to a gradual release of dioxins from plastic and rubber parts in the wet and cold part of the plant. Dioxins may be ad- or absorbed during start-up, bag house short-circuiting, etc., and slowly released later, increasing the flue gas dioxin load by as much as one or two orders of magnitude.

Geuzens, Vanderreydt et al. found a measurable decrease in dioxin concentration while monitoring the start-up of the MIWA-incinerator plant (St Niklaas, Belgium) by comparison of dioxin values before and after a wet scrubber^[1,2]. During the commissioning of the Amsterdam incinerator plant, however, it was found that dioxin load may also increase during scrubbing^[3]. Kreiszi et al.^[4] systematically tested synthetics, such as polypropylene and butyl rubber and ascribed the above effects to a strongly temperature (and concentration) dependent absorption and desorption of PCDD/F.

History of the ISVAG-plant

Since the ISVAG-plant was first put into operation in 1980, it was revamped several times in order to cope with the gradually more and more stringent emission codes.

Table 1: History of the composition of the ISVAG-plant

I	1980-94	mechanical grate furnace – cooling tower – electrostatic precipitator (ESP) one common stack, no emission monitoring
II	1994-97	mechanical grate furnace – cooling tower – ESP (new) – 2 stage wet scrubber - one common stack with common emission monitors
III	1999-00	mechanical grate furnace (new) – boiler – urea injection (SNCR) – ESP – semi-dry scrubber – activated carbon injection – bag house – 2 stage wet scrubber (cleaned) - two separate stacks with separate emission monitors

Plant capacity, however, remained the same at 120,000 TPA (for a LHV of approx. 10 MJ/kg). Table 1 provides a brief plant history, including a concise description of the set-up of the two, in principle, identical incinerator lines.

During the most recent refurbishment the wet scrubber was cleaned to minimize its memory effect. A three-step cleaning strategy was implemented:

- replacing all packing material (representing 96.5% of the contaminated surface)
- cleaning of the interior of the scrubber (removal of sludge and remaining solids)
- rinsing all cold parts (i.e. the quench, the acid and the alkaline column) with a water-activated carbon mixture for approx. 6 weeks at ambient temperature (using Norit SA Super in a concentration of approx. 4.6 g/l)

Subsequently, lines one and two were put into operation in early November 1999 and early February 2000, respectively.

Experimental Study

During period II ('94-'97), a total of six dioxin measurements were performed in the common stack of the plant. The measurements were well distributed over time and were taken according to the condensation method with a sampling time of six hours and using 'Tenax' as adsorbents.

Approximately 20 days after the start-up of each line in period III ('99-'00), a measurement campaign was initiated consisting of two dioxin measurements per stack, per week. Each measurement was taken according to the condensation method with a sampling time of six hours and using 'XAD-2' as adsorbents. Sampling was conducted according to norm EN 1948-1, and PCDD/F analysis were performed by GC/HRMS according to norm EN 1948 2,3.

For line one, the results of 28 such measurements are available (11/99-3/00). For line two, the results of 15 such measurements are available (2/00-5/00). In addition, the results of several 'simultaneous' measurements are available, taken according to the same method but with samples at different locations in the plant (exit bag house, stack).

The result of each measurement comprises the total dioxin emission and the fingerprint. Different independent and certified labs were used to perform sampling and analysis.

Results

During the first stages of the start-up, the plant was run on natural gas for significant periods to dry and bake the refractory stones, rinse the boilers, and perform warm-commissioning of the air pollution control equipment. To take into account the influence of operating time on the memory effect, the results of the dioxin measurements are represented using the following adapted time scale:

$$\text{time} = 1 \times (\text{\#hours of waste incineration}) + 0.75 \times (\text{\#hours with natural gas operation}).$$

The multiplication factor of 0.75 was estimated, based on the ratio of flue gas flow rates under normal operation (waste incineration) and during operation on natural gas.

For period II, five out of six dioxin measurements are considered (one was an outlier and is excluded). The emission values range from 1.3 to 2.5 ng I-TEQ/Nm₃ and a virtually identical 'dirty 17' fingerprint is observed. As shown in Figure 1, the average distribution of congeners in the period of '94-'97 agrees well with that of other MSWI.

It is plausible that the memory effect observed during period III stems mainly from period II and that the fingerprint measured during this period is representative of the dioxins absorbed in the material of the wet scrubber. Thus, Figure 1 provides an 'image' of the dioxins absorbed, ie the 'memory' of the 2-stage wet scrubber.

The numbers on the horizontal axis correspond to the following congeners respectively: 2,3,7,8-TF; 2,3,7,8-TD; 1,2,3,7,8-PeF; 2,3,4,7,8-PeF; 1,2,3,7,8-PeD; 1,2,3,4,7,8-HxF; 1,2,3,6,7,8-HxF; 1,2,3,7,8,9-HxF; 2,3,4,6,7,8-HxF; 1,2,3,4,7,8-HxD; 1,2,3,6,7,8-HxD; 1,2,3,7,8,9-HxD; 1,2,3,4,6,7,8-HpF; 1,2,3,4,7,8,9-HpF; 1,2,3,4,6,7,8-HpD; OCDF; OCDD. The above applies to all figures in the presentation.

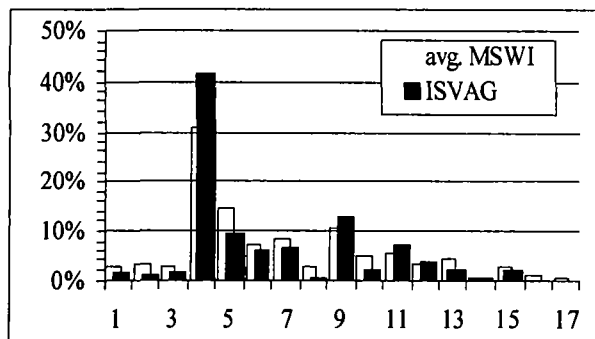


Figure 1: ISVAG fingerprint in period II

Figure 2 shows the decrease in dioxin release from both stacks during period III. The upper curve corresponds to line 2, while the lower one corresponds to line 1. Although the decrease of the dioxin emission exhibits the same time dependency, it is clear that line 2 has a much higher initial value. Figure 2 thus clearly demonstrates a decreasing memory effect.

Figure 2: Decrease in dioxin release on lines 1 and 2.

Figure 3: Average fingerprint of lines 1 and 2 and during period II.

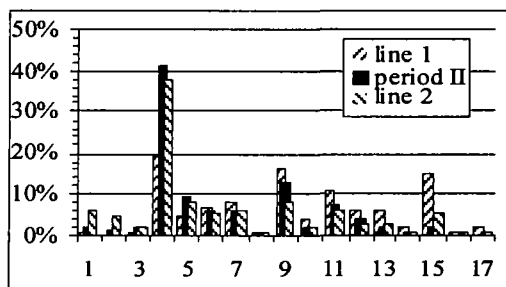
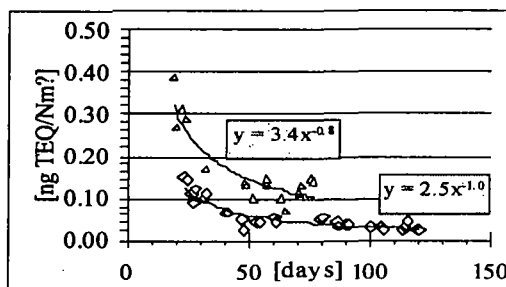


Figure 3 compares the average fingerprints of lines 1 and 2 with that observed during period II. It is observed that the fingerprints on both lines are fundamentally different from each other and that both are independent of time. Also, it illustrates the good agreement of the fingerprint of line 2 with that of period II.

Table 2 shows the results of the simultaneous measurements, with in column two the number of days since initial start-up.

Table 2: Simultaneous measurements (emissions in [ng I-TEQ/Nm³])

	time [days]	exit bag house ^(*)	stack ^(*)	fuel
line 1	27	0.014	0.11	waste
line 2	48	< 0.01	0.14	waste
line 1	37	0.001	0.094	natural gas

Dioxin levels at the bag house exit are far below the current emission standard. In addition, the last two columns indicate the existence of a memory effect in the wet scrubber, with, at that time, an approximate dioxin concentration of 0.09 – 0.13 ng I-TEQ/Nm³. Operation on natural gas in the same time period confirms this value.

Figures 4 and 5 show the fingerprints obtained during simultaneous measurements on both incinerator lines.

Figure 4: Fingerprint of simultaneous measurements on line 1

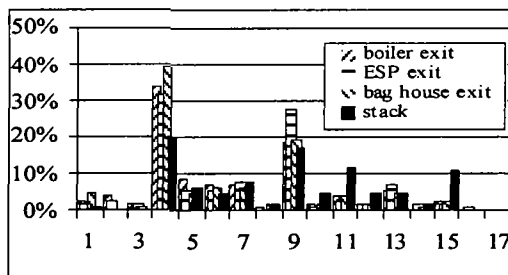
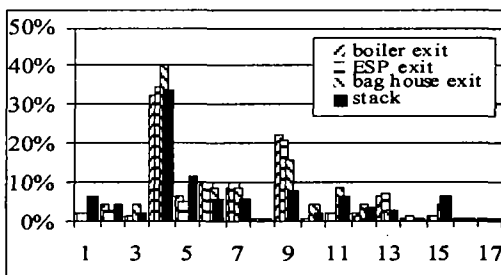


Figure 5: Fingerprint of simultaneous measurements on line 2



It is observed that the fingerprints corresponding the first three locations (boiler exit, ESP exit and bag house exit) are similar for both lines. This is to be expected since they correspond to the dioxins that are being formed during the actual incineration process and since this process is being conducted in an identical manner for both lines.

The very low dioxin concentration at the bag house exit (Table 2), the increasing concentrations over the scrubbers (Table 2) with decrease over time (Figure 2), and the different fingerprints obtained before the wet scrubbers and in the stack (Figure 4 and 5), the stack emissions are proven to be the result of the memory effect only. This conclusion is further supported by the fingerprints given in Figure 3, showing similar fingerprints during phase II and line 2.

Further study is required to establish an explanation for the observation that dioxins released from the wet scrubber of line 1 have a fundamentally different fingerprint than those released by the wet scrubber of line 2. Chlorination or dechlorination of PCDD/F because of differences in pH in the scrubbers, wall temperatures of the scrubber, or differences in packing material are possible explanations. A systematic analysis of past operating data is currently underway to further clarify the observed phenomena.

Conclusions

1. The memory effect from the wet scrubber is well established by two time series of dioxin values as well as from simultaneous measurements at various plant locations. Its contribution to the emission of 0.09 – 0.13 ng TEQ/Nm³ constitutes virtually the entire dioxin release.
2. On both incinerator lines, the decrease in dioxin emission is almost proportional to (time)⁻¹.
3. The two lines show a different fingerprint; further study is required for explaining this feature.
4. The fingerprint of line 2, on which the memory effect is strongly present, agrees well with that from before the last refurbishment.

References

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