

## Dioxin Studies on a MSW-Incinerator.

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### Introduction

Dioxin values were recorded by various control laboratories, before, during and after revamping the Ghent incinerator plant. The values obtained on both lines and at different locations in the flue gas ducts are discussed, as well as their characteristic fingerprint, along with the measures taken to reduce the dioxins by primary and (especially) by secondary measures.

Dust samples were taken at various plant locations, analysed and subjected to 'de novo' testing. Some samples are rather highly loaded, others show high 'de novo' activity. The resulting values and fingerprints and the distribution gas/solids are discussed.

### Materials and methods

Fly ash samples were collected at various locations in the incinerator. Dioxins analyses were performed by registered Belgium laboratories (SGS and VITO). De novo tests were performed by Dr Stieglitz in Karlsruhe as described in reference (1).

### Results and discussion

#### *Historical construction phases*

##### 1970: Construction of the incinerator

- Design characteristics: 5.5 ton of waste / hour with a heating value of 15.500 kJ/kg.
- Countercurrent flow of gases and liquid; CEC Grate.
- Quench tower upon the combustion chamber, followed by injection of tertiary air to regulate the temperature. No longer in use. Electrostatic precipitator (2 fields). Still in use.

##### 1996: revamping of the incinerator.

- New SEGHERS grates were installed (surface: 20.2 m<sup>2</sup>).
- The walls were covered with SiC firebricks
- A semi-dry reactor (lime injection) was installed after the EF, followed by a baghouse filter, a dry scrubber (NaOH injection) and a demister.

##### *Some important working parameters are:*

- Primary air flow : 16.000 to 18.000 Nm<sup>3</sup>/hr. Secondary air flow : 15.000 to 20.000 Nm<sup>3</sup>/hr.
- Air flow cooling side walls : 2.000 to 4.000 Nm<sup>3</sup>/hr.
- Throughput : 5 à 6,5 t/hr depending upon waste heating value.
- Thermal capacity : 15 à 20 MWth depending upon waste heating value.
- Temperature exit quench tower : 320 °C. Temperature exit semi-dry reactor: 175 °C
- Temperature in stack: 80 °C
- Lime injection : about 1,5 m<sup>3</sup>/hr at 6 wt.% Ca(OH)<sub>2</sub>.
- Active carbon injection : about 10 kg/hr.

Nowadays the incinerator is equipped with Best Available Technology flue gas cleaning (semi-dry removal of acidic compounds (HCl, HF, SO<sub>2</sub>) and adsorption on activated carbon for dioxins and heavy metals removal). This allowed to reduce dioxin emissions from 10-100 ng/Nm<sup>3</sup> in the '70 down to 0.01 - 1 ng/Nm<sup>3</sup> today.

### ***Dioxins measurements and fingerprints.***

Dioxins were measured in 1997, 1998 and 1999 at various locations in the incinerator: after the quench tower, after the electrofilter, after the baghouse filter and in stack. Some typical values are given in Table 1, together with the dust content of the flue gases when available.

In December 98 the Flemish Authorities decided to close temporarily the incinerator because of several measurements exceeding the norm fixed at 0.1 ng/Nm<sup>3</sup>. A series of measures were taken to reduce dioxin concentration in the flue gases, among other:

- Replacement of the bags of the baghouse filter
- Coating of the bags with lime before start up
- Cleaning up (baghouse filter, electrofilter, quench tower, wet scrubber demister and stack)
- Replacement of the damaged parts of the demister
- Overhauling poppetvalve to bypass to minimize dust breakthrough
- Verification of burners to ensure a minimum temperature of 850°C during start up and shut down. Operators were trained to reduce manually air injection during start up at places useless for the combustion this to avoid excess cooling.
- Thresholds for the by pass activation were redefined (working temperature widened between 150°C and 250°C )
- Active carbon injection was put on the maximum
- Distribution of active carbon in the pipe was optimised by putting a conical piece at the injection point
- Reduction of cold air leakage through the ash pit and the last section of the grate to reduce CO peaks.

Measurements performed in 99 show that the emission standards are respected at present.

<b>OVEN 1</b>					
<b>Datum</b>	<b>ngTEQ/Nm<sup>3</sup>, dry, 11%O<sub>2</sub> After Quench</b>	<b>ngTEQ/Nm<sup>3</sup>, dry, 11%O<sub>2</sub> After EF</b>	<b>ngTEQ/Nm<sup>3</sup>, dry, 11%O<sub>2</sub> After baghouse</b>	<b>ngTEQ/Nm<sup>3</sup>, dry, 11%O<sub>2</sub> In Stack</b>	<b>Dust, mg/Nm<sup>3</sup> In stack</b>
<b>24 April 97</b>	20.50	5.590	0.03	<b>1.620</b>	4.44
<b>25 April 97</b>	10.60	9.40	0.023	<b>1.180</b>	2.94
<b>22 August 98</b>	0.570	0.330	0.160	<b>0.120</b>	1.50
<b>29 September 98</b>			0.470	<b>0.130</b>	2.29
<b>4 April 99</b>				<b>0.095</b>	N.A.

Table 1. Dioxin concentration at various locations for Oven 1.

The temperature just after the quench (320°C) and the working temperature of the electrofilter (300°C; difficult to reduce without entailing clogging problems) lie in a dangerous range for dioxin formation. As soon as combustion stops dioxins start reforming along three pathways (1) rapid gasification of carbon in particles entrained with the off-gases (2) slow gasification of carbon in particles deposited in the pipework (3) condensation of chlorophenols and other precursors via catalytic routes.

Fingerprints (isomer distribution) were calculated for both ovens. Three examples are given below. Only the dirty seventeen's are given, so each graph was determined by dividing the concentration

of one congener (in ngTEQ/Nm<sup>3</sup>) by the sum of the concentration of the dirty seventeen's (in ngTEQ/Nm<sup>3</sup>). Some trends can be extracted from these fingerprints:

- in all cases the most predominant congener is 23478-PeCDF which accounts for about 40% of the total toxicity.
- dioxin concentration is less reproducible than these of furan.

### **De novo tests**

Dust collected in the Electrofilter and in stack were submitted to a "de novo" test (=annealing test). During this test, the sample is heated at 300°C for two hours in a flow of air. PCDD/F, PCBz, PCPh, PCB, PAH, ... are analysed before and after exposure. The dioxin formation potential of the dust can thus be assessed. Results are presented in Table 2.

	TE ng/g	PCDD	PCDF	PCBz	PCPh
V43 in Electrofilter 1997 (a)	41.4	1526	747	1402	936
V43 (b) 1997	193.3	2260	3374	21455	458
V43 (c)	0.067	1,96	3,20	9852	0
V44 in stack 1997 (a)	48.0	2201	1260	1531	360
V44 (b)	94.47	2155	1670	2215	149
V44 (c)	0.25	6,3	7,51	7595	275
EU37 in baghouse (a)	1.65	56,9	40,5	917	1887
EU37 (b)	80.6	883,2	2333	13107	907
EU37(c)	0.34	3,61	6,07	2161	3
EU38 in Electrofilter (a)	1.72	59,92	41,07	53	32
EU38 (b)	2.12	46,96	46,42	459	6
EU38 (c)	5.07	79,97	163,4	10429	401
EU39 in by pass (baghouse) (a)	4.72	145,3	159	197	153
EU39 (b)	5.94	148,0	83,1	132	2
EU39 (c)	135.6	3194	2833	397	0

Table 2. TE, PCDD/F, PCBz and PCPh loads of some samples before and after annealing. (a) before annealing (b) after annealing, solid phase (c) after annealing, gas phase; the baghouse material is a mixture of lime & fly-ash; the electrofilter deposits underwent a long residence time, whereas the material from the by-pass deposited in a duct, normally dead.

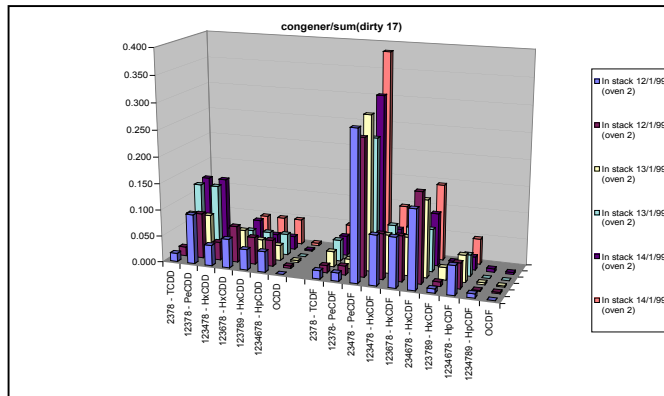
The fly ash and the fly dust collected in 1997 are both heavily loaded with dioxines (41 and 48 ng TEQ/g respectively), what makes an efficient dust separation essential in order to respect the norm of 0.1 ng/Nm<sup>3</sup>. This implies: perfect working of the baghouse filter (no holes !), no by pass activation over the baghouse, and perfect working of the demister. The samples collected in 1999 are quite homogeneous and are in the same order of magnitude as the fly ash analyses of Prof. Hagenmaier.

### **Acknowledgements.**

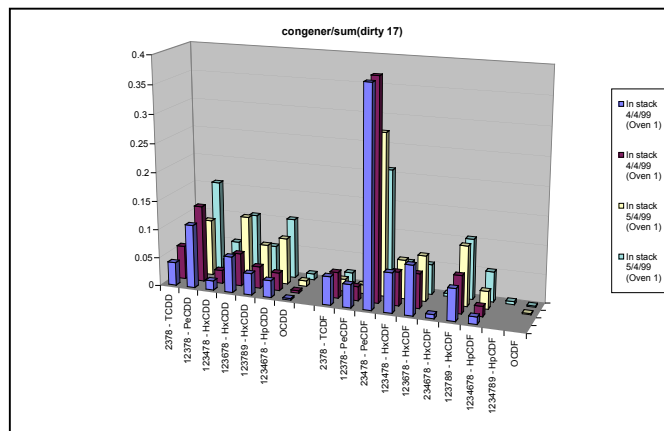
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### **References**

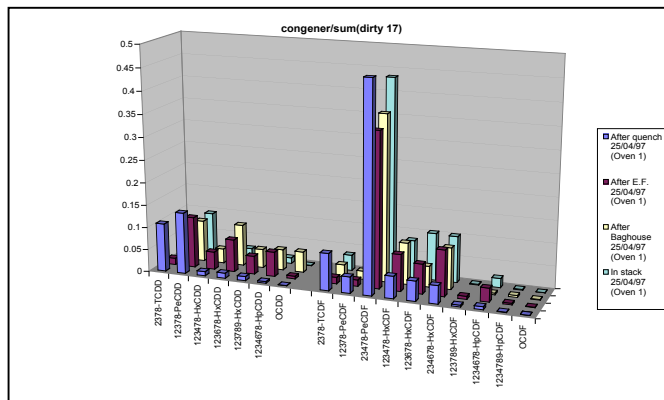
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Graph 1. Isomer distribution in stack. Oven 2, 1999



Graph 2. Isomer distributions in stack. Oven 1, 1999



Graph 3. Isomer distribution at various location, 1997