THERMAL DESORPTION OF DIOXIN SURROGATES FROM MSWI DUST

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Abstract

MSWI dust samples (boiler, cyclone, baghouse) were thermally desorbed with the aim of monitoring a fluidised bed incinerator plant with a history of problematic dioxin (TOC and CO) emissions. Chlorobenzene isomers, as well as selected organic compounds (e.g. benzene, phenol, naphthalene, biphenyl, PAH, dibenzofuran) and their lower chlorinated congeners were analysed as possible dioxin surrogates[1].

The samples were characterised by means of Scanning Electron Microscopy (SEM), establishing particle size and shape as well as elementary composition. Other thermal analytical methods, such as Pollut-Eval analysis[3,4,6], Differential Thermal Analysis (DTA), and Thermogravimetric Analysis (TGA) coupled with Mass Spectrometry (MS) and dioxin analysis were also applied and confronted with results from the thermal desorption method.

Introduction

The plant under scrutiny consists of an internally circulating fluidised bed combustor, burning Municipal Solid Waste (MSW), assimilated commercial and industrial waste, hospital waste, sewage sludge, as well as leachates. Since starting its operations in 1999, it experienced various operating problems as well as serious dioxin emissions, even giving early in 2005 a rise to an emission value of almost 700 ng I-TEQ/Nm^3. Plant operating and combustion conditions were improved in collaboration with one of the authors; these measures, combined with injecting activated carbon into the flue gases, have solved the dioxin problem. A programme, optimising primary and secondary air control at times of overfeeding, aims at further reducing CO and TOC emission peaks and improving combustion efficiency. The plant features a fluid bed combustor followed by two empty radiation-cooling passes, one convection-pass waste heat boiler. Then twin cyclones collect coarse dust. A turbine distributes hydrated lime slurry and activated carbon (AC) is injected; the resulting residue is collected in a baghouse (BH) filter.

Materials and Methods

Thermal desorption of dust samples, collected from hoppers below the waste heat boiler, cyclone dust separator and baghouse filter was seen as a suitable means for monitoring both the previous situation (up to December 2005) as well as that at the start up of the renewed plant in September 2006. Five dust samples were collected in November 2005; supplemental baghouse samples were taken on 4, 6, 11 and 12 September 2006 while starting up, after an 8 months shutdown for further improvement. The samples were thermally desorbed in Markes Unity thermal desorption system (with cryofocusing trap) equipped with an autosampler (Ultra TD, Markes) and connected to a Finnigan Trace GC Ultra (Thermo Electron Corporation) and a Finnigan Trace DSQ mass-spectroscopic detector (Thermo Electron Corporation). For thermal analysis weighed samples were packed into cleaned glass thermal desorption tubes and plugged at both ends with glass wool, then treated in automated series of sample analysis.

Table 1. Conditions of analysis and instrumental settings

Tubes	Glass (4 mm I.D., 8.8 cm length)
Markes Unity	300°C×30 min, split 1:20, He
Cryo-trap	General purpose cold trap, graphitised carbon (Markes Int. Ltd.), -10°C → 345°C ×15 min
GC	CPsil8MS, 5% phenyl-groups column (30m × 0.25mm i.d., 0,5µm); temp. programm: 35°C (5 min)→ (8°C/min) → 100 (0 min)→ (12°C/min) → 280°C (10min), total 38 min; He, constant pressure 85kPa
MSD	Electron impact, 70 eV, full scan 50-450 amu

Conditions of analysis and instrumental settings are given in table 1. The compounds identified were quantified against chlorinated benzenes, spiked on an analytical sand matrix and desorbed under the same thermal conditions. Quantification was based on a relative response factors (RRF), decafluorobiphenyl being applied as internal standard.
The **Pollut-Eval method**[3,4,6] was used for continuous monitoring of desorption products (TOC by FID, CO_2 and CO by FTIR) from the samples when heated under nitrogen up to 650°C. The residue was cooled, and then reheated in air and the evolution of CO_2 and CO was monitored up to 850°C.

Table 2. Summary of some SEM-derived data (2005) – basis: no C and O

	Boiler	Cyclone		Baghouse 2005		Baghouse 2006	
		Average	St. Dev.	Average	St. Dev.	Average	St. Dev.
Ca	**40.9**	**43.5**	1.40	**55.1**	3.60	**30.1**	1.60
Si	14.5	12.3	0.30	4.60	0.77	5.49	0.31
Al	11.1	8.43	1.45	3.44	0.60	3.76	0.23
Fe	10.6	**7.10**	3.00	1.57	0.05	1.08	0.14
Mg	2.63	*0.96*	0.25	0.81	0.15	0.94	0.17
Ti	1.45	2.30	0.40	1.21	0.24	0.97	0.09
P	3.84	1.60	0.05	1.10	0.15	12.9	0.90
S	2.61	3.03	0.54	2.22	0.25	1.80	0.20
Cl	4.26	6.80	0.11	17.40	1.50	12.9	0.90
K	2.23	3.23	0.27	**4.45**	0.38	1.80	0.20
Na	3.29	2.35	0.66	2.36	0.12	2.86	0.32
Cu	**0.86**	**1.95**	0.59	**1.13**	0.08	**0.52**	0.09
Zn	1.16	4.16	0.49	1.66	0.25	0.62	0.12
Pb	0.07	1.79	0.75	**2.79**	0.68	*0.40*	0.25

Results and Discussion
SEM results. Particle size, morphology, as well as average elementary composition were established for all samples, using Scanning Electron Microscopy (SEM), combined with Energy Dispersive X-Ray spectroscopy. Table 2 gives all major elements and dioxin-relevant elements. Not shown are minor amounts of Cr, Mn, Ni. The data is compared with values from the International Ash Working Group[4]. Data exceeding the ranges cited are marked in **bold**, or in *italic* for low values. Boiler dust is rich in **Ca**, Si, Al and **Fe**. Note the high values for **Cu**, which is a partial explanation for the historically high dioxin values.
Pollut-Eval data yielded preliminary thermal desorption and oxidation values, including a FID, TOC and mineral carbon value[5] (table 3). **DTA** shows some *de novo* activity for baghouse samples only, especially boiler ash being lean in reactive carbon. For that reason in 2006 attention has further focused on these baghouse samples. **TGA.** Consecutive weight losses occur by sample drying, dehydration and carbonate decomposition, as follows from on-line MS monitoring of carrier gas effluent. Organic substances were barely detectable on-line.
Thermal desorption. The levels of non-chlorinated and chlorinated species, as recorded for the 2005 samples (table 4), were reproducible at the level of cyclones, yet for the baghouse samples studied their relative amounts are rather variable. The amount is still low (< 0.2 µg/g of non-chlorinated compounds) for boiler ash. The cyclone ash has a higher load, of 1.3 µg/g for non-chlorinated species and 0.3 µg/g for those chlorinated compounds studied. The latter are highest in baghouse dust, composed of fine dust (that non-collected by the cyclone), spent lime used to neutralise acid gases (HCl, SO_2, HF) and activated carbon, injected for capturing dioxins, PAH, and mercury.

Table 5 monitors the in-plant evolution of organics, compared to boiler dust as an internal reference (= 1). The ratio (chlorinated) / (non-chlorinated) considerably increases from boiler to baghouse. These rising numbers may be explained either by decreasing temperature, or by gradual further chlorination of products formed. The weight average level of chlorination of CBz + Bz continuously increases (proving it is not determined by the adsorption / desorption equilibrium). The neutralisation residues from late 2005 are compared to 4 recent ones in tables 6 and 7, suggesting that organic load was somewhat more important during the new start up in 2006. For chlorinated compounds (essentially chlorobenzenes), the situation was largely equivalent in 2005 and 2006. The amounts detected remain well below comparable results from *de novo* testing and compare with literature values for old incinerators: 0.22-1.9 µg CBz/g and 0.86-3.2 µg CPh/g[4].

Conclusions

Direct thermal desorption of MSWI dust samples (boiler, cyclone, baghouse) allows establishing the load of selected organic compounds that are either considered as dioxin surrogates or as indicators of combustion quality. A level of ca. 1 µg/g is indicated for benzene and naphthalene, of 1.7 to 4.6 for CBz in the baghouse dust (spent salts + AC). The method shows a load of CBz rising in a sequence boiler, cyclone, baghouse. Non-chlorinated organics are highest in the relatively coarse cyclone dust, possibly as a result of adding lime acting as a diluting agent. A balance shows a total output per Mg waste incinerated of 105 – 171 mg of the non-chlorinated compounds selected for analysis and of 30 – 63 mg of the chlorinated compounds selected, in this case chlorobenzenes basically.

In another paper, however, it is verified whether operating conditions (temperature, time) influence upon the results of the thermal desorption tests described and in how far. Desorbed compounds may vary in amount and distribution when these desorption parameters are modified: higher chlorinated compounds tend to desorb at a higher temperature only, yet may dechlorinate in the process. The orders of magnitude, however, seem to be established reliably.

Acknowledgements

Dr. Olie (Univ. Amsterdam) supplied dioxin values and Dr. X. Bourrat and Prof. Albéric (Univ. Orléans) Pollut-Eval results, both covered in distinct papers. Mr. O. Steenhaut (VUB, Brussels) conducted the SEM analyses.

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Table 3**.** Summary of some Pollut-Eval derived data and dioxin analyses, courtesy Orléans Univ. and Dr. K. Olie

	Boiler	Cyclone		Baghouse 2005		Units
Line		1	2	1	2	
FID – Desorbed	0.00	0.01	0.01	0.01	0.01	mg C/g
– Decomposed	0.01	0.45	0.27	0.07	0.10	mg C/g
Typical FID value*	0.16	0.24	0.24	0.36	0.36	mg C/g
Total TOC	0.01	0.15	0.13	1.53	0.79	mg C/g
Mineral Carbon	0.45	0.5	0.68	2.4	4.85	mg C/g
Typical MinC value*	3.3	13.6	13.6	24.3	24.3	mg C/g
PCDD	0.81	65.9	n.a.**	247.3	n.a.	ng/g
PCDF	0.845	88.2	n.a.	202.1	n.a.	ng/g
PCDD/F, I-TEQ	0.011	1.73	n.a.	3.23	n.a.	ng/g

* for mechanical grate stokers[2] ** n.a. – "not analysed"

Table 4. Data on the 2005 samples (L1, 2 = Line 1, 2). Baghouse = BH. All units **ng/g.**

	Boiler	Cyclone L1	Cyclone L2	BH L1	BH L2	BH 2006
Non-chlorinated compounds						average
Benzene	123	1060	1012	427	710	2160 +/- 700
Phenol	24	6.5	<1	<2.3	<0.9	<2.4
Naphthalene	17	130	180	295	2735	1000 +/- 220
Biphenyl	1.2	35	30	0.2	2.9	4.7 +/- 3.5
PAH*	0.4	24	30	3.2	1.9	0.2 +/- 0.1
Dibenzo-p-dioxin	<0.1**	<1.3	<1	<0.5	<0.7	<0.6
Dibenzofuran	1.3	3.8	9.1	<0.6	<0.6	0.6 +/- 0.4
Total non-chlorinated	167	1260	1262	725	3450	3160 +/- 600
Chlorinated compounds						
CBz	20	237	286	600	1832	1670 +/- 750
Total chlorinated	20	241	286	600	1833	1672 +/- 750
Ration chlorinated / non-chlorinated	0.12	0.19	0.23	0.83	0.53	-
WA chlorination level, CBz + Bz	0.26	0.56	0.53	1.16	1.58	-
WA chlorination level , CBz	1.84	3.08	2.39	1.99	2.20	-

* Desorption and recovery of PAH is very partial only, except for Acenaphthene and Acenaphthylene

** <0.1 – below detection limit, DL = 0.1 ng/g

Table 5. Relative in-plant dust values. Boiler dust = 1, WA = Weight average

	Boiler	**Cyclone L1**	**Cyclone L2**	**Baghouse L1**	**Baghouse L2**
Non-chlorinated	1.00	7.54	7.57	4.35	20.6
Chlorinated	1.00	12.05	14.30	30.0	91.6

Table 6. Mass flow of selected pollutants, average flows based on average annual outflows, in µg/Mg of waste.

	Boiler	**Cyclone**	**Baghouse**	**Total output**	**Unit**
Mass flow	21	67	24	112	kg per Mg waste*
Non-chlorinated	3.5	84.5	17 - 83	105 - 171	mg per Mg waste
Chlorinated	0.42	16 - 19	14 - 44	30 - 63	mg per Mg waste

* Mean of annual averages over a time period from 2000 to 2005

Table 7. Comparison of some TOC data, campaigns 2005 and 2006, µg/g

Data	Benzene	Naphthalene	Non-chlorinated	CBz
2005	0.6 +/- 0.2	1.5 +/- 1.7	1.9 +/- 0.7	4.6 +/- 3.6
2006	2.2 +/- 0.7	1.0 +/- 0.2	3.2 +/- 0.6	1.7 +/- 0.7