Destruction of the flame retardant hexabromocyclododecane in a full-scale municipal solid waste incinerator

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Abstract

Hexabromocyclododecane containing polystyrene foam obtained from the building and construction market has been co-incinerated in a full-scale waste incineration plant. The co-feeding of 1 and 2 wt% of polystyrene foam had no influence on the operation of the plant. The bromine content increased the raw gas hydrogen bromide concentration slightly. The air emission, including that of dioxins and bromine, was not altered and so was the quality of the solid residues. The hexabromocyclododecane concentrations in the solid residues were almost identical, regardless of whether or not and how much polystyrene foam was added. The obtained destruction efficiency was >99.999% independent of the amount of added polystyrene foam. This finding indicates a virtually total destruction of hexabromocyclododecane.

Keywords

Hexabromocyclododecane (HBCD) destruction, polystyrene foam, municipal solid waste incineration, polystyrene foam co-incineration, dioxins, mixed halogenated dioxins

Introduction and objectives of the trials

Polystyrene foams (PSFs) are widely used for heat insulation purposes in buildings. According to information provided by the two organisations CEFIC (2014), The European Chemical Industry Council, and EXIBA (2014), the European Extruded Polystyrene Insulation Board Association, the PSF types EPS (expanded polystyrene) foam and XPS (extruded polystyrene) foam represent 37% of the insulation market in Germany; the annual production in Germany of both types of foams was in the order of 12 Mill. m^3 in 2008.

Because of legislative demands, organic heat insulation foams are, to a great extent, flame retarded. The two industry organisations estimate that this is the case for approximately 77% of the EPS and 94% of the XPS consumption. The chemical compound used for decades by most foam suppliers is hexabromocyclododecane (HBCD), very much owing to its long-term proven fire prevention performance. HBCD is a brominated aliphatic cyclic hydrocarbon with a bromine content of 74.7%. It has been classified in 2008 as a persistent, bioaccumulative, and toxic (PBT) compound under the REACH Regulation (European Parliament and Council, 2007), and it currently undergoes the REACH authorisation process with a sunset date of 21 August 2015. In addition, it has recently been classified as a persistent organic pollutant (POP) under the UNEP Stockholm Convention (UNEP, 2014). From these proceedings it can be expected that in the coming years the use of HBCD as a flame retardant will be globally terminated.

Concerns arise when PSF reaches the end of its useful life and becomes waste. Owing to the hazardous nature of its ingredients, re-use as well as recycling have been prohibited (UNEP, 2014) and landfilling in a number of European countries is not allowed any longer. Hence, the only disposal option is thermal treatment. Depending on the type of material and regulations in place, thermal treatment will have to take place in a municipal solid waste incinerator (MSWI) or in a hazardous waste incinerator (HWI).

Detailed information about the thermal destruction of potentially hazardous compounds in waste incineration can be obtained from investigations on a laboratory scale, in test rigs, in semi-technical test facilities, and in full scale waste incineration plants. Tests at smaller scales require less effort, are less costly, and can be performed under well-defined conditions. However, the direct translation to technical applications may be limited when scale-up or fluctuations of parameters, such as heating value of the waste,

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are considered. Hence, it was decided to run co-incineration trials with HBCD containing EPS and XPS foams in a state-of-the-art MSWI. The design objectives of these trials were to:

- investigate the influence of PSF on the operation of the plant, including combustion efficiency and energy recovery;
- document the compliance with the emission limits at high PSF feed rates by means of the existing air pollution control (APC) system;
- study the formation of chlorinated, brominated, and mixed halogenated dibenzo-p-dioxins and dibenzofurans (PCDD/F, PBDD/F, and PXDD/F, respectively), in the following called dioxins if all groups of compounds are considered;
- obtain reliable information about the destruction efficiency of HBCD.

First results of the test trials have been published in a technical report (PlasticsEurope, 2014) and in a separate summary report (Dresch et al., 2014).

Thermal stability of HBCD

HBCD is the preferred flame retardant for PSF. The compound does not form a chemical bond with the matrix material. Technical HBCD comprises varying shares of α-, β-, and γ-isomers, which isomerise at temperatures exceeding 110°C (Heeb et al., 2010). For this reason no isomer-specific analysis of HBCD was executed.

HBCD starts to disintegrate at approximately 240°C. It releases bromine radicals by homolytic cleavage, which abstract hydrogen from the polystyrene molecules, thus forming HBr (Beach et al., 2008). Specific organic destruction products have not been identified; it is estimated that traces of brominated aliphatic compounds may be formed at higher temperatures (Abdallah et al. 2008).

Recently, test results have been published on the co-incineration of refuse-derived fuel (RDF) and polystyrene, flame retarded with HBCD, in a small laboratory-type rotary kiln incinerator (Takigami et al., 2014). The authors claim a destruction efficiency of 99.9999%, but do not provide all details for verification. However, the fact that the blank tests and the co-incineration tests showed identical HBCD concentrations in all residue streams indicates a virtually total destruction of HBCD. Traces of PBDD/F were analysed in a few tests with high HBCD input, but no effect could be observed in view of the PCDD/F and dioxin like polychlorinated biphenyls (dl-PCB) emission.

Test materials

PSF insulation foams

The waste burnt during the test trials was municipal solid waste (MSW) collected in the Würzburg region, which is served by the incineration plant. Neither commercial and industrial waste nor

Table 1. Characteristics of the PSF test materials.

	Units	EPS	XPS1	XPS2
Density	kg m^{-3}	15	38.5	35.5
Board sizes				
Length	mm	1,000	1,265	1,265
Width	mm	500	615	615
Thickness	mm	100	50	50

EPS: expanded polystyrene; XPS: extruded polystyrene.

sewage sludge were included. The average lower heating value of such MSW is 10.4 MJ kg^{-1} with short-term variations of ± 5%. The lower heating values of the two types of polystyrene (PS) foams were 38 MJ kg^{-1} (EPS) and 39 MJ kg^{-1} (XPS). The highest addition of PSF was 2 wt%, which increased the fuel heating value by 0.78 MJ kg^{-1}. This increase does not exceed the set value of the heat load of the furnace and in fact no notable changes in the operation parameters occurred during the co-incineration tests.

The PSF supplied by the manufacturers had typical market quality and was delivered as complete boards with dimensions typical for material coming back from demolition sites. The XPS foams were blown with CO_2, the EPS ones with pentane, which has already been completely released during the manufacturing and storage stages. The dimensions and the density of the boards are listed in Table 1.

Since the PSF materials were not made up with any construction and demolition waste, their content of heavy metals was very low, as is documented in Table 2. The limit of quantification (LOQ) of strontium was 2 mg kg^{-1} and that of the other metals was 1 mg kg^{-1}. The table also contains concentration ranges of these metals in MSW (Belevi and Moench, 2000; Chandler et al., 1997), which are typically higher by a factor of 10 up to 100. Hence, any influence of heavy metals can be neglected.

The content of chlorine, bromine, fluorine, and sulphur was measured, too. The respective data are referenced in Table 3. For all analysed concentrations, the standard deviation was 10%, and the LOQ was 50 mg kg^{-1}. The table also contains concentration ranges of the same elements in MSW, gathered from the references cited for Table 2.

The highest additional element input is expected for bromine, of which the typical concentration in MSW is in the order of 100 mg kg^{-1} (Vehlow and Mark, 2000). Even with a PSF addition of 2 wt%, the bromine content only gets approximately doubled, which should not have any significant effects neither on the raw gas quality nor on the emissions.

HBCD in PSF

The analysis of HBCD in polymers is complicated since, although HBCD is not chemically bound to the polymer matrix, its total separation without any impact on the molecule can be problematic. The results obtained from three independent laboratories are

Table 2. Concentration of selected metals in the PSF and in MSW.

	Cu	Mn	Ni	Sr	Ti	Zn
	mg kg⁻¹	mg kg⁻¹	mg kg⁻¹	mg kg⁻¹	mg kg⁻¹	mg kg⁻¹
EPS	12	8	5	3	10	100
XPS1	11	5	4	2	7	79
XPS2	14	11	14	18	46	21
Std. dev. (%)	21	19	24	20	30	32
MSW	200–1,000	200–500	20–130	100–150	1,000–2,000	600–2,000

EPS: expanded polystyrene; MSW: municipal solid waste; XPS: extruded polystyrene.

Table 3. Halogens and sulphur concentration in the PS foams and in MSW (data in mg g⁻¹;).

	Br[a]	Cl	F	S
	mg kg⁻¹	mg kg⁻¹	mg kg⁻¹	mg kg⁻¹
EPS	4,100	460	<50	50
XPS1	7,400	250	<50	<50
XPS2	15,300	<50	<50	320
MSW	20–150	5,000–8,000	100–150	1,000–3,000

[a]Br concentration of PSF is an average value and has been measured by several laboratories.
EPS: expanded polystyrene; MSW: municipal solid waste; XPS: extruded polystyrene.

compiled in Table 4. The table also contains the concentrations communicated by the manufacturers as well as the figures calculated from the bromine analysis.

The results showed much higher variations than could be expected for analytical data provided by experienced commercial laboratories. Especially the data sent in by laboratory 1 were partly close to 50% of the other ones only. All other values looked more homogenous and were included in calculating mean values to be used for the calculation of the HBCD destruction. These mean values and the respective standard deviations are included in the last column of Table 4.

HBCD in MSW and air

The MSW burnt during the test trials has not been analysed for HBCD, because taking waste samples would have been an impossible and sensible task considering the effort needed for its practical execution.

Published data on HBCD concentrations in MSW are not available. The option selected here was to identify waste fractions that are known to contain HBCD. These are mainly industry textiles and small electrical and electronic waste equipment. A number of recently published articles on MSW composition in Germany (EAW, 2013; Landratsamt Kitzingen, 2013; SHC, 2012; Siepenkothen, 2010; Statistisches Bundesamt, 2014) indicates an average share of textiles of (3.5 ± 0.5) wt% and of electrical and electronic waste of (0.66 ± 0.11) wt%.

A Japanese publication reported HBCD concentrations in waste industry textiles of (33 ± 8) g kg⁻¹ (Kajiwara et al., 2009),

however, this type of textiles only contributes very small amounts to the textiles ending up in MSW, whereas clothing, the main fraction, is not flame retarded (UNEP, 2011). Estimating a maximum share of 5% of HBCD containing materials in the textiles fraction, the concentration of HBCD in MSW would arise to approximately 50 mg Mg⁻¹.

According to a Swiss publication, the HBCD concentration in electrical and electronic waste is 17 mg kg⁻¹ (Morf, 2005). This figure accounts for another approximately 100 mg of HBCD added per 1 Mg of MSW by this waste fraction.

The combustion air can be another potential HBCD input into the incinerator. Swedish air samples taken in urban areas ranged from 76 to 610 pg m⁻³, whereas in remote areas <1 to 25 pg m⁻³ were found (Remberger et al., 2004). Data from the Great Lakes district in the USA varied between 0.2 and 11 pg m⁻³ (Hoh and Hites, 2005) and air sampled inside a Japanese house contained 13–15 pg m⁻³ (Takigami et al., 2007).

The incineration of 1 mg of MSW requires approximately 4500 m³ of combustion air. Even at the highest HBCD concentration in air of 610 pg m⁻³, the combustion air would only add <3 μg to the content of HBCD per mg of incinerated MSW. Hence, for the calculation of HBCD destruction, the input of HBCD by MSW and by the combustion air will be neglected.

MSWI plant

The waste incineration plant selected for the present tests, the MSWI Würzburg, Germany, has already been used for co-incineration tests with waste plastics from the packaging sector in 1993/1994 (Mark, 1994), with automotive shredder residues (ASR) in 1997 (Mark, 1998), and with waste from electrical and electronic equipment (WEEE) in 2005 (Mark et al., 2006). The previous test results hence allow a comparison with the actual ones.

Line 1 of the plant, where the tests took place, is equipped with a grate system combining a water-cooled reciprocating part and a reverse acting part at the backend. The throughput is 10 Mg h⁻¹ and the residence time of the waste on the grate is approximately 2 h. The line has a cyclone downstream of the boiler for separation of coarse fly ash followed by a calcium-based dry scrubbing system and a back-end selective catalytic reduction (SCR) for NO$_x$ abatement. A scheme of line 1 is shown in Figure 1.

Table 4. HBCD concentrations in PSF (comparison of calculated and analysed data with those provided by the manufacturer; all data in g kg^{-1}; mean value with standard deviation; [a]: not included in mean value calculation).

	Laboratory 1[a]	Laboratory 2	Laboratory 3	Calculated from Br	Manufacturer's data, (EXIBA, 2014)	Mean value
EPS	3.4	5.7	6.0	5.5	7.0	6.1 ± 0.7
XPS1	6.7	11.6	10.0	9.9	13	11.1 ± 1.5
XPS2	13.5	20.0	22.0	20.5	24	21.6 ± 1.8

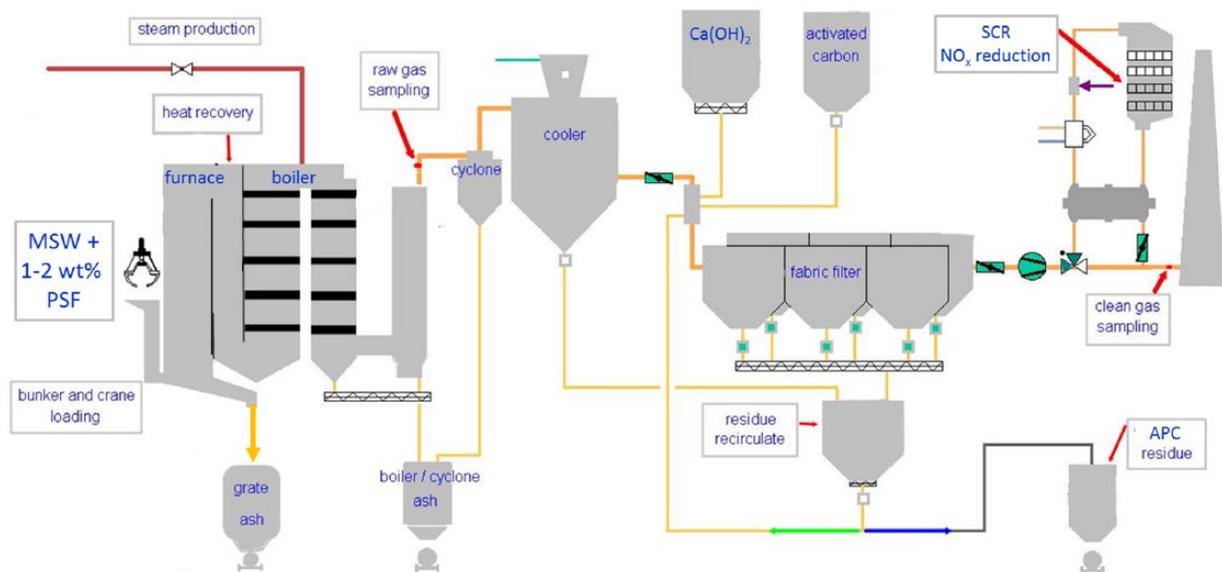EPS: expanded polystyrene; XPS: extruded polystyrene.

Figure 1. Schematic diagram of line 1 at the Würzburg MSWI.
APC: air pollution control; MSW: municipal solid waste; PSF: polystyrene foam; SCR: selective catalytic reduction.

Test programme and conditions

The programme consisted of a 1 week testing period whereby the test conditions offered an almost clean boiler operation, since the line had just gone through the regular maintenance shutdown. As in previous investigations, each testing condition lasted for 24 h, starting the first day with a base test (condition A) where only MSW was burnt, followed by the co-incineration tests (condition B and C), and ending with another base test (condition A). For all co-incineration tests, sampling was performed several hours after the start of PSF feeding to establish stable combustion conditions in the furnace. Two sampling periods were executed per test condition and day, the first one lasting for 6 h (tests A1, B1, C1, and A3) followed by a second one for comparison and lasting for 4 h.

The operating conditions were coded as follows:

A. base test –A1, A2.
B. medium level of 1 wt% PSF addition – B1, B2.
C. higher level of 2 wt% PSF addition – C1, C2.
A. base test – A3, A4.

The mix of the three PSF types was in all co-incineration tests set to 50% of EPS and 25% of each XPS type (see Table 1).

During all test runs, the plant was operated in its normal mode and all parameters were kept as constant as possible for a full-scale plant. The soot blowing of the boiler was performed outside of the sampling periods.

PSF handling and MSW mixing

A defined protocol was followed for the dosing of the PSF. The weight of every crane grab was measured by a load cell and recorded by the crane operator. The quantity of PSF, which needed to be manually loaded on top of the MSW in the feed hopper, was then taken from a list with pre-calculated amounts of EPS, XPS1, and XPS2 boards corresponding to the actual waste input.

Sampling strategy

Raw and clean gas sampling was carried out by an external contractor. The sampling points indicated in Figure 1, were for:

- the raw gas at the end of the boiler;
- the clean gas in front of the stack;
- dioxins and for metals at the same level as those for the online sampling, but the probes were about 2 m away from each other.

The sampling periods were from 08:00 to 14:00 and from 14:00 to 18:00 every day of the test runs.

Solid residue sampling was carried out on the following streams.

- Grate ash, taken from the ash discharging belt downstream of the grate ash water quench tank.
- Combined fly ashes (from the fourth flue gas section of the boiler and from the cooler) taken from a discharge silo.
- Fabric filter ash taken out of the ash conveyor.

The grate ash sampling followed the protocol recommended by the International Ash Working Group (Chandler et al., 1997). It was executed four times per hour during the gas sampling periods. The grate ash discharge conveyor was stopped and samples of 20 kg each were taken from the entire cross section of the conveyor. The total amount of grate ash taken per day was in the order of 600–800 kg.

Unburnt matter, metals, and bulky materials were manually separated and their weight was recorded. The grate ash was sent to a laboratory for analysis.

Table 5. MHKW operation parameters (averaged for each test condition).

	Unit	A1/2	B1/2	C1/2	A3/4
Throughput MSW	Mg h⁻¹	9.5	9.2	10.0	9.2
PSF	kg h⁻¹	0	120	220	0
Primary air	m³ h⁻¹	26,500	25,800	25,900	25,500
Secondary air	m³ h⁻¹	13,600	12,900	12,900	12,800
T	°C	912/924	913/912	900/903	933/932
O₂	vol%	7.8	7.5	7.9	7.7
Steam	Mg h⁻¹	27.3	26.9	26.5	27.8

MSW: municipal solid waste; PSF: polystyrene foam.

Test results

Operational performance

The plant operation data, averaged for each test condition, are listed in Table 5. These values were calculated starting 1 hour after the PSF feed had been introduced to the feeding hopper.

The primary and secondary air distributions were standard for MHKW operations. There was no process control change in the air management. The air distribution was as follows: Zone 1 (drying zone), zone 2 (main combustion zone), zone 3 (main combustion zone), zone 4 (post combustion zone), and zone 5 (final residue treatment zone), which were set to 8.3%, 35.5%, 39.8%, 13.1%, and 3.3%, respectively.

Raw and clean gas composition

Raw gas and clean gas monitoring was carried out by an external contractor, too. The data for selected ingredients, averaged during the test period, are listed for the tests A1, B1, and C1 in Table 6. The data in this table, as well as all following gas concentrations, are standardised to 273.2 K, 101.3 kPa, and 11 vol% O_2.

The CO and TOC values indicate an excellent burnout, the only changes during the co-incineration tests are seen for HBr, which was significantly increased. This increase had no influence on the lime consumption for acid gas neutralisation; the stoichiometric ratio varied around 1.3 to 1.4.

The clean gas concentrations of the regulated components have always been well below the air emission limits, as can be seen from their compilation in Table 7, which lists the averaged values measured by the plant's online emission control system. These data were confirmed by the analysed gas samples, which were taken during the tests A1, B1, and C1. The sampling time

Table 6. Raw gas concentration of selected gases (averaged during the test period, HCl and HBr values are averages of 6 to 11 half hourly gas samplings).

	CO	TOC	HCl	HBr	HF	SO₂	NOₓ
	mg m⁻³	mg m⁻³	mg m⁻³	mg m⁻³	mg m⁻³	mg m⁻³	mg m⁻³
A1	17 ± 4	<2[a]	781 ± 135	1 ± 0.7	2.5 ± 0.7	76 ± 8	380 ± 16
B1	20 ± 8	<2[a]	565 ± 310	2.7 ± 0.6	0.9 ± 0.4	101 ± 63	345 ± 38
C1	21 ± 3	<2[a]	632 ± 180	5.8 ± 2.1	0.8 ± 0.3	129 ± 64	330 ± 25

[a]Below LOQ.

Table 7. Emission data monitored by the emission control system (data in mg m⁻³).

	Dust	CO	TOC	HCl	SO₂	NOₓ	NH₃	Hg
A1	0.1	12.5	<0.1	5.0	6.3	60.0	0.5	<0.01
A2	<0.1	14.6	<0.1	5.2	1.6	62.0	0.4	<0.01
A3	<0.1	10.7	<0.1	7.3	3.1	62.5	0.3	<0.01
A4	<0.1	9.0	<0.1	7.5	0.8	58.6	0.2	<0.01
B1	1.4	15.4	<0.1	4.9	1.7	76.0	0.2	0.01
B2	<0.1	16.9	<0.1	5.1	0.5	56.4	0.4	<0.01
C1	<0.1	18.3	<0.1	6.0	3.0	64.0	0.4	<0.01
C2	<0.1	14.3	<0.1	4.7	1.3	57.0	0.3	<0.01
Emission limit	10	50	10	10	50	200		0.03

Table 8. Emission data analysed from gas samples (too small sample numbers for error calculation.

	Unit	A1	B1	C1	Emission limit
Dust	mg m^{-3}	<0.3	0.45	<0.3	10
HF	mg m^{-3}	0.42	0.37	<0.25	1
HBr	mg m^{-3}	<0.25	<0.28	0.3	n.a.
Hg	µg m^{-3}	0.8	0.3	0.1	30
Cd+Tl	µg m^{-3}	0.6	0.5	0.5	50
Sb+As+Pb+Cr+Co+Cu+Mn+Ni+V	µg m^{-3}	55	20	15	500

n.a.: not available.

Table 9. Raw gas concentrations of PCDD/F, PBDD/F, and PXDD/F.

	Unit	A1	B1	C1
PCDD/F	ng(ITEQ) m^{-3}	1.84	3.05	3.31
PBDD/F	ng m^{-3}	<0.5[a]	<0.5[a]	<0.5[a]
PXDD/F	ng m^{-3}	11.6	59.4	110.8

[a]Below LOQ.
ITEQ: international toxic equivalents.

was always 30 min. These samples were also analysed for HF, HBr, and the heavy metals regulated by the EU Waste Incineration Directive (European Parliament and Council, 2000). The results and the respective emission limits are shown in Table 8.

Dioxins

Today a state-of-the-art MSWI plant has a typical PCDD/F inventory in the raw gas downstream of the boiler of 1–5 ng m^{-3} in terms of international toxic equivalents (ITEQ). Raw gas sampling for dioxin analysis took place during the entire 6 h sampling period following the provisions as set forth by the EU Waste Incineration Directive. Data are provided in Table 9 for test runs A1, B1 and C1.

The measured PCDD/F concentrations were in the same order of magnitude as typically found in the Würzburg MSWI. They match previous raw gas PCDD/F concentrations of 2.75–4.58 ng(ITEQ) m^{-3} measured in 1993/1994, when mixed plastic waste from the packaging sector was co-incinerated (Mark, 1994) and 1.8–6.7 ng(ITEQ) m^{-3} in the campaign in 1997 when ASR were co-fed (Mark, 1998; Mark et al., 1998). In both test campaigns, the addition of plastic waste did not change the PCDD/F raw gas level. The same conclusion can be drawn from the PSF results, since the slight increase in PCDD/F concentration between A1 and B1/C1 is well inside the typical concentration range found in the plant.

It is known that increased levels of bromine in waste promote the formation of bromine containing dioxins (Dumler et al., 1989; Öberg et al., 1990). Detailed investigations on WEEE co-incineration in the Karlsruhe TAMARA test facility for waste incineration revealed indeed an increase in mixed halogenated PXDD/F with increasing bromine input, which levelled off when

a certain bromine content was reached. The formation was limited by the availability of organic precursors rather than that of halogens (Vehlow et al., 2000, 2003).

The raw gas concentrations of bromine containing dioxins are included in Table 9. PBDD/F were not detected. This finding is in line with the TAMARA results, where only traces of such compounds were analysed at extremely high bromine concentrations of up to 1000 mg m^{-3} in the raw gas.

The total sum of PXDD/F increased from 11.6 ng m^{-3} in the base test to 110.8 ng m^{-3} with increasing PSF addition. The level of these congeners was by a factor of five higher than found in the WEEE co-incineration tests in 2004, although this time the bromine inventory was by at least one order of magnitude lower (Mark et al., 2006). The finding is, at first glance, surprising since the PCDD/F concentrations were in the same order of magnitude in both tests. Furthermore, HBCD disintegrates in the hot zone of the combustor and its molecular structure shows no similarity to any dioxin precursor such as PCB or PBDE. However, the concentrations resembled those found in the TAMARA tests on WEEE co-incineration and can thus be looked upon as not out of range, the more so since no influence on the emission could be detected.

In the Würzburg plant the calcium hydroxide based dry scrubbing system uses activated charcoal for the abatement of semi-volatile micro-organic compounds. The emission concentrations of the halogenated dioxins are compiled in Table 10. During the tests A1 and C1 the sum of PCB has also been analysed. The concentration was below the LOQ during the two tests. For comparative reasons, data obtained during the above-cited co-incineration tests of ASR in 1997 and of WEEE in 2004 have also been listed.

The table documents the excellent abatement efficiency of the MSWI plant. All analysed emission concentrations are extremely low. PXDD/F concentrations were below the LOQ and the values of PCDD/F are much more than one order of magnitude lower than the emission limit of 0.1 ng m^{-3}. The air emission quality is more or less the same as during former tests executed in the plant.

HBCD destruction

When calculating the destruction efficiency of HBCD, all mass flows throughout the incineration plant and the HBCD

Table 10. Emission concentrations of PCDD/F, PBCD/F, PXDD/F, and PCB.

	Unit	A1	B1	C1	ASR tests	WEEE tests
PCDD/F	ng(ITEQ) m^{-3}	0.0021 ± 0.0009	0.0004[a]	0.0002[a]	0.002–0.005	0.002–0.013
PBDD/F	ng m^{-3}	<0.5[a]	<0.5[a]	<0.5[a]	n.a.	n.a.
PXDD/F	ng m^{-3}	<1.1[a]	<1.0[a]	<1.0[a]	n.a.	0.55
PCB	ng m^{-3}	<0.0002[a]	n.a.	<0.0002[a]	n.a.	0.78

[a]Below LOQ.
ASR: automotive shredder residues; ITEQ: international toxic equivalents; n.a.: not available; WEEE: waste from electrical and electronic equipment.
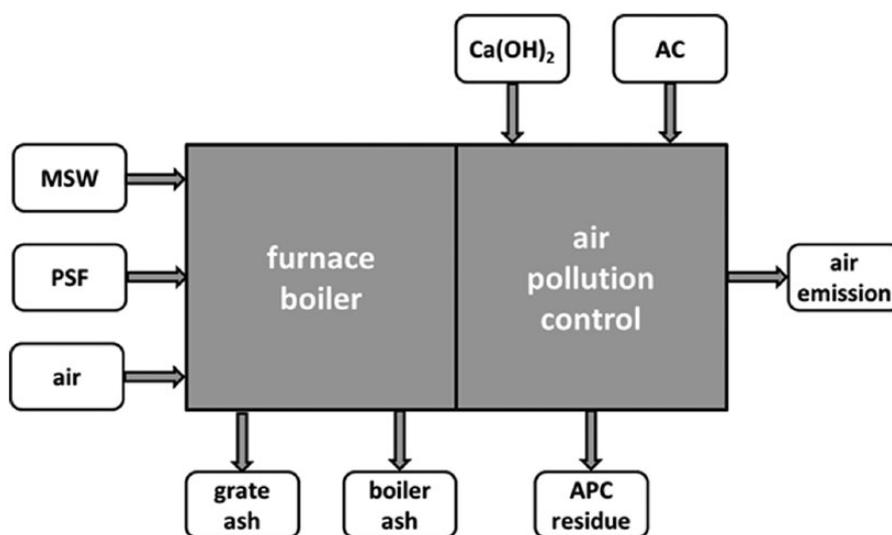
Figure 2. Scheme of mass flows in the waste incinerator.
AC: activated carbon: APC: air pollution control; MSW: municipal solid waste; PSF: polystyrene foam.

concentrations in all of these streams have to be known as precisely as possible. The respective mass flows are depicted in Figure 2.

The input streams are MSW, PSF, and combustion air. The MSW feed was recorded by the crane load scale, its accuracy is expected to be ± 5%. The respective PSF amount was taken according to a prepared list as described above. These input mass flows are also expected to have an error range of ± 5%. For the destruction calculation only the test runs A1, B1, and C1 have been used.

The combustion air during the co-incineration tests was in the order of 40,000 m^3 h^{-1}. Would the highest previously cited HBCD concentration of 610 pg m^{-3} (Remberger et al., 2004) be assumed, the input of HBCD would result in approximately 25 mg h^{-1}, a figure that can be neglected for the destruction calculation. The same conclusion applies for the additives to the APC system, Ca(OH)$_2$, and activated carbon, which did not contain any HBCD.

The mass flows of grate ash, boiler ash, as well as APC residue, are average values taken from the annual statistics of the plant in 2013. For these streams, a standard deviation of ± 20% is estimated. In previous test runs, 1993/1994, the mass streams were measured during the 8 h measuring period and showed a good approximation to these averages. The mass flows used for the destruction calculations are compiled in Table 11.

As outlined, the HBCD concentrations in the input streams were averaged from four sources. For the analysis of the HBCD concentration in the residue streams, extended investigations concerning the analytical LOQ in the various matrices were conducted. The respective figures were 1 ng m^{-3} for the flue gas and 1.4 µg kg^{-1} for the solid residues. The analytical error in these low concentration ranges has to be estimated to ± 10%.

Table 12 compiles the concentrations in all input and output streams. Given the technical requirements in this report, no differentiation regarding separate HBCD isomer distributions in the PSF, in the residues, as well as in the flue gas, has been considered; all HBCD concentrations are given as the sum of all isomers.

The concentrations in all solid residues were almost the same and all close to the LOQ. A correlation with the HBCD input could be seen for the flue gas concentration, but also on a very low level. With these data the HBCD substance flows have been calculated. The results are compiled in Table 13. In case of findings below the LOQ, the LOQ values have been used for the calculation.

From the above data, virtually identical destruction efficiencies (DE) of >99.999% for the B1 as well as for the C1 test have been calculated. The table points out that not only the DE values, but also the accumulated HBCD output mass flows, were

Table 11. Mass flows used for the HBCD destruction calculation.

	Unit	A1	B1	C1
MSW	kg h^{-1}	8,800 ± 440	9,100 ± 455	9,900 ± 495
EPS	kg h^{-1}	0	60 ± 3	110 ± 5.5
XPS1	kg h^{-1}	0	30 ± 1.5	55 ± 2.8
XPS2	kg h^{-1}	0	30 ± 1.5	55 ± 2.8
Grate ash	kg h^{-1}	2,200 ± 440	2,275 ± 460	2,480 ± 500
Boiler + cooler ash	kg h^{-1}	315 ± 63	359 ± 72	390. ± 78
APC residue	kg h^{-1}	125 ± 25	129 ± 26	141 ± 28
Flue gas	m^3 h^{-1}	62,400 ± 6,200	67,400 ± 6,700	63,500 ± 6,400

APC: air pollution control; EPS: expanded polystyrene; MSW: municipal solid waste; XPS: extruded polystyrene.

Table 12. HBCD concentrations in the input and output streams used for balance calculation.

	Unit	A1	B1	C1
EPS	g kg^{-1}	0	6.1 ± 0.7	6.1 ± 0.7
XPS1	g kg^{-1}	0	11.1 ± 1.5	11.1 ± 1.5
XPS2	g kg^{-1}	0	21.6 ± 1.8	21.6 ± 1.8
Grate ash	µg kg^{-1}	1.40[a] ± 0.14	1.40[a] ± 0.14	2.40 ± 0.24
Boiler + cooler ash	µg kg^{-1}	1.40[a] ± 0.14	2.30 ± 0.23	1.40[a] ± 0.14
APC residue	µg kg^{-1}	1.40[a] ± 0.14	1.40[a] ± 0.14	1.40[a] ± 0.14
Flue gas	ng m^{-3}	0.50[a] ± 0.05	2.60 ± 0.26	5.60 ± 0.56

[a]Measured concentrations below LOQ.
APC: air pollution control; EPS: expanded polystyrene; XPS: extruded polystyrene.

Table 13. Substance flows of HBCD and its destruction efficiency.

	Unit	A1	B1	C1
EPS	g h^{-1}	0	366 ± 46	671 ± 84
XPS1	g h^{-1}	0	333 ± 48	610.5 ± 88
XPS2	g h^{-1}	0	648 ± 63	1,188 ± 115
Accumulated inputs	g h^{-1}	0	1,347 ± 96	2,470 ± 145
Grate ash	mg h^{-1}	3.08 ± 0.70	3.18 ± 0.75	5.94 ± 1.32
Boiler + cooler ash	mg h^{-1}	0.44 ± 0.10	0.82 ± 0.18	0.55 ± 0.11
APC residue	mg h^{-1}	0.18 ± 0.04	0.18 ± 0.04	0.20 ± 0.04
Flue gas	mg h^{-1}	0.031 ± 0.006	0.18 ± 0.04	0.36 ± 0.07
Accumulated outputs	mg h^{-1}	3.80 ± 0.70	4.36 ± 0.82	7.04 ± 1.33
Destruction efficiency	%	–	99.999	99.999

APC: air pollution control; EPS: expanded polystyrene; XPS: extruded polystyrene.

similar, regardless of whether HBCD containing foams were added or not. Even doubling the HBCD input did not considerably change the results. Such findings indicate a virtually total destruction.

Conclusions and recommendations

The disposal of end-of-life PSF by co-incineration with MSW has been investigated in the state-of-the-art MSWI in Würzburg, Germany. The main objective was the destruction efficiency of HBCD. Even assuming that the MSW did not contain any HBCD, the analysed DE in all tests was well above 99.999%, independent of the amount of HBCD fed into the system.

The co-incineration had neither an influence on the operation of the plant nor on the air emission of all regulated components including PCDD/F. The concentration of PXDD/F in the raw gas was higher than analysed in previous tests on co-incineration of bromine containing plastic materials (ASR and WEEE), however, the emission concentrations were in the same order of magnitude as measured during the former tests.

The results from these tests indicate that co-treatment of PSF in MSWI plants is a safe disposal route for any PSF end-of-life foams. The typical combustion temperature of 900–1000 °C guarantees the virtually total combustion of HBCD and the foam matrix, a combustion at higher temperature levels as in a HWI is not needed.

PSF can be handled in a large scale MSWI if certain provisions are met.

- Mixed or single boards could be delivered with other construction waste.
- Delivery of complete board packages in plastic wrapping should be minimised as the crane has to break down these parcels.
- Typical market size boards as delivered for the tests can be handled.
- Good mixing of MSW and PSF boards is essential to achieve a good combustion control.

MSW incineration is widely applied in many industrialised countries. The plants offer short transport distances for the lightweight foams. State-of-the-art MSWI are highly energy efficient and allow the recovery of high shares of the energy inventory of the PSF.

Based on the results of these full-scale test trials it is recommended to include MSW incineration technology into the official list of recognised destruction technologies for specific POPs.

The results lead also to the recommendation to base the performance requirements for the destruction of compounds, at least of those that disintegrate easily, on air emission and residue quality standards rather than on fixed destruction or reduction efficiencies.

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