

Co-combustion

of BUILDING INSULATION Foams

with municipal solid waste

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1 INTRODUCTION



Insulation foams in the building and construction industry can be manufactured from different polymers including polyurethane (PUR) and extruded as well as expanded polystyrene (XPS and EPS). The disposal of such low density foam through co-combustion in a state-of-the-art Municipal Solid Waste Combustor is the preferred option of the industry based on a total eco-impact approach assessment. This report focusses on PUR and XPS. Results are also valid for EPS, because of the close chemical similarity to XPS.

Until recently, these rigid foams for thermal insulation were blown with chlorofluorocarbons (CFC's). CFC 11 was the most commonly used blowing agent for PUR since it stayed trapped in the closed cells of the foam. It served at the same time as a thermal insulating gas. Over the last 2-3 years voluntary reductions have taken place and ozone depleting CFC's have been replaced by partially halogenated compounds (HCFC's, HFC's), hydrocarbons (pentanes) or carbon dioxide.

Prior to 1988, XPS foams contained approx. 6 wt. % of CFC 12 (dichlorodifluoromethane), an extremely stable compound known for its destruction of stratospheric ozone. Its ozone depleting potential (ODP) is as high as that of the trichlorofluoromethane (CFC 11). For this reason, it has been replaced in foams produced today by partially halogenated compounds, such as chlorodifluoromethane (HCFC 22) and 1-chloro-1,1-difluoroethane (HCFC 142b). These are both far less stable and thus contribute less to the depletion of the ozone layer (ODP 0.055(22), ODP 0.065(142b)) [German Bundestag 1989].

However, waste foams still contain substantial amounts of CFC's. Disposal by landfill is not advisable because of the large volume occupied by a low density foam (approximately 30 kg/m³). Crushing or compressing the foam, to reduce its density is a problem due to the ozone depleting blowing agents released during the process. Also, several countries in Western Europe have already limited or are about to limit landfill to "earth like" mineral substances, i.e. those having a very low content of organic material.

In order to comply with fire safety standards these foams contain flame retardants. Hexabromocyclododecane (HBCD) was used for XPS. PUR foams are usually flame retarded on the basis of phosphorous and chlorine, but may contain bromine as well. Therefore, the PUR foams tested were formulated with P, Cl and Br (from a brominated polyol).

This summary has been written to cover both of these very important insulation foam types. For the sake of brevity, certain chapters cover only the results for one of the foams as the data are very similar.

Objectives:

Although at present there is no major problem with the final disposal of these foams due to the small quantities in question, in the future, larger amounts of foams will appear in demolition debris which will have to be dealt with. The objectives of the PUR & XPS foam tests were to study:

- * efficiency of destruction of CFC-12 versus CFC-11
- * changes occurring to HCl, HF and HBr in the flue gas and their neutralisation efficiency in a two stage wet scrubbing system
- * the volatilisation of heavy metals caused by the increased levels of chlorine in the feed and
- * the potential additional formation of brominated and/or mixed halogenated dibenzo-p-dioxins and dibenzofurans.

This last effect has already been reported in the co-combustion of electronic waste where increased levels of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) are said to have been found [Lahl 1991].

For the XPS trials more emphasis was placed on (H)CFC destruction. Whereas, for the PUR tests in-depth analytical interlab uniformity testing on mixed halogenated dioxins/furans was a major aspect.

Organisation:

In order to obtain sound information on the real effects of foam co-combustion APME, EXIBA, ISOPA, and the Forschungszentrum Karlsruhe (FZK) launched two test campaigns in the test incinerator TAMARA in 1993 and 1994 for XPS and PUR respectively.

The test matrix was somewhat different for the XPS and the PUR materials. This was due to the knowledge gained from the first series of tests on XPS, which looked at the effect of temperature. A 'high' temperature, 950 °C, was chosen to represent the typical higher combustion temperature in a modern MSW incinerator. A low temperature, 850 °C, was chosen, because many regulations, such as the German emission directive for MSW incineration [Bundesministerium 1990] defines 850 °C as the minimum temperature for waste being burnt in a combustion chamber.

The XPS foam and granulate was supplied by EXIBA member companies in a form compatible with their market specifications. The PUR rigid foams were supplied by a BING (The Federation of European Rigid Polyurethane Foam Associations) member company. These were formulated to represent the expected "European average composition" of PUR insulating foam and contained the CFC11 blowing agent and a mix of flame retardants based on phosphorous, chlorine and bromine.

Sampling and analysis of the dioxin and furan-like compounds during the EXIBA test campaign was performed by Dr. Brenner, BASF, and are described in a separate report [Brenner 1995]. Sampling and analysis of the same compounds during the ISOPA test campaign have been performed by the certified laboratories: GfA in Münster, as well as MPU in Saarbrücken (sampling) and ITU in Berlin (analysis).

2 THE TEST INCINERATOR TAMARA

2 THE TEST INCINERATOR TAMARA

The test incinerator TAMARA, built for FZK during 1985/87, is a mass burner with a nominal throughput of 250 kg/h of preconditioned waste [Merz 1989]. A schematic drawing of this incinerator is given in Fig. 1.

The design of the raw gas ducts upstream from the boiler causes the separation of a substantial amount of particulate matter at high temperatures. This material will hereafter be referred to as coarse fly ash. Flue gas can pass once or twice through the horizontal tube boiler thus allowing the boiler outlet temperature to be adjusted. During these trials the outlet gas temperature was in the order of 220 °C.

The de-dusting was performed using a fabric filter (PTFE fabric tubes coated by a GORETEX® membrane). TAMARA is also equipped with a two-stage wet air pollution control (APC) system.

3 TEST PERFORMANCE AND MATERIALS

3.1 TEST PROGRAMME

The test programme for XPS and PUR was organised to last a total of three complete weeks of TAMARA operation. The respective test conditions were always established a number of hours before the sampling of all input and residue streams, in order to achieve stable conditions for testing. This was of particular importance for the factors controlling the formation of micro organics in the flue gas system.

The foam, which was delivered as cubes of 5 cm lateral length, was added manually directly into the feeding hopper of TAMARA. The exact test sequence of the campaigns and all other data can be found in the detailed reports from FZK on XPS and PUR (Vehlow 1994 and 1995) and is shown in Tables 1a and 1b.

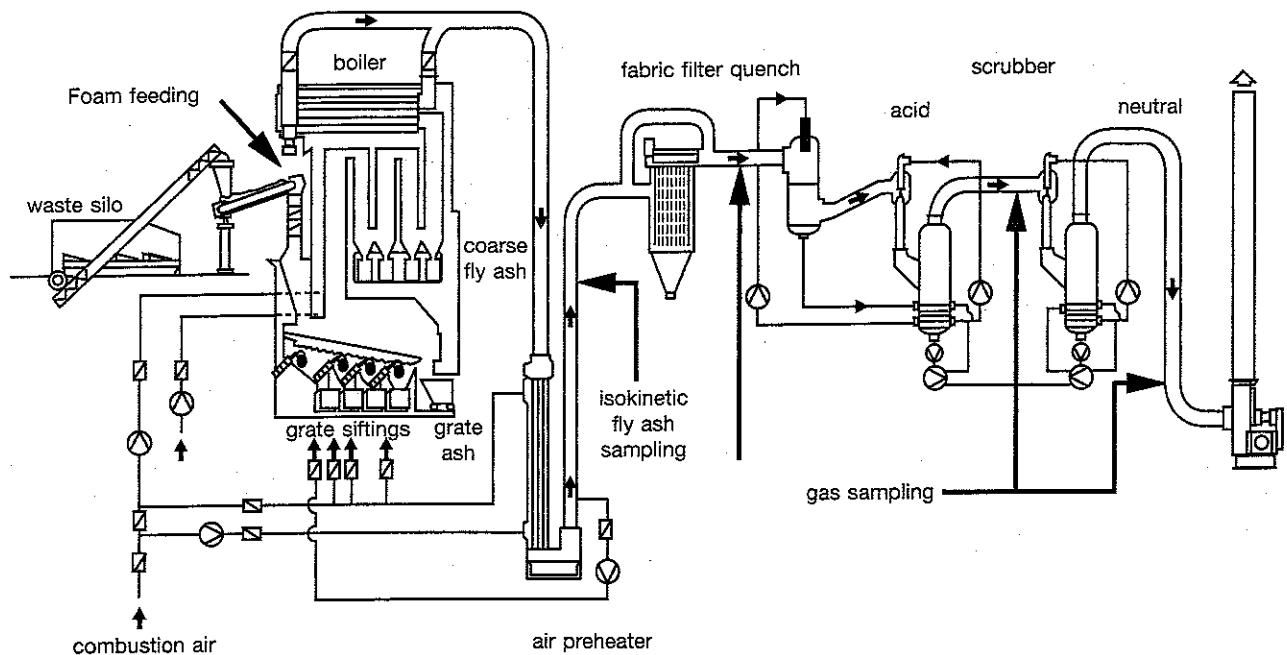


Fig. 1: Schematic drawing of the test incinerator TAMARA

2 TEST PERFORMANCE AND MATERIALS

test runs with XPS	feed	plastic addition	T
	kg/h	kg/h	°C
ref. 1	215 ± 6	0	872 ± 5
ref. 2	203 ± 23	0	845 ± 15
granulate	170 ± 27	4.9 ± 0.1	849 ± 25
CFC 12	179 ± 1	5.2 ± 0.1	849 ± 4
HCFC 22/142b	169 ± 5	4.9 ± 0.1	841 ± 6
ref. 1	246 ± 1	0	950 ± 7
ref. 2	241 ± 16	0	939 ± 12
granulate	211 ± 1	6.1 ± 0.1	952 ± 6
CFC 12	201 ± 34	5.9 ± 0.1	949 ± 26
HCFC 22/142b	216 ± 1	6.3 ± 0.1	978 ± 6

Table 1a: Table of TAMARA test campaign for XPS Foam Combustion

test runs with PUR	basic feed	PUR	T
	kg/h	kg/h	°C
ref. 1.1	217 ± 46	0	857 ± 29
ref. 1.2	225 ± 2	0	885 ± 12
PUR A.1.1.	212 ± 3	2.1 ± 0.1	906 ± 10
PUR A.1.2.	209 ± 3	2.1 ± 0.1	901 ± 8
ref.2.1.	215 ± 12	0	899 ± 12
ref.2.2.	217 ± 1	0	907 ± 13
ref.3.1.	222 ± 3	0	887 ± 11
ref.3.2.	218 ± 6	0	904 ± 11
PUR A.2.1.	198 ± 2	3.9 ± 0.1	901 ± 10
PUR A.2.2.	196 ± 4	3.9 ± 0.1	902 ± 15
PUR B.1.1.	202 ± 1	2.1 ± 0.1	914 ± 10
PUR B.1.2.	197 ± 1	2.1 ± 0.1	904 ± 15
ref.4.1.	197 ± 1	0	899 ± 10
ref.4.2.	197 ± 1	0	899 ± 8

Table 1b: Table of TAMARA test campaign for PUR Foam Combustion

3.2 BASIC FUEL QUALITY

The fuel burnt in TAMARA is a homogenised mixture of the fine fraction of household waste. This is mainly organic matter from a kind of raw compost, enriched with 25 % Refuse Derived Fuel (RDF). The mean chlorine and heavy metal contents of this mix is slightly lower than that of standard European MSW. During the TAMARA experiments representative samples of the compostable waste fraction and the RDF were analysed. The results from the XPS trials are shown in Table 2.

element	compostable fraction	RDF	basic fuel
F	410 ± 70	275 ± 30	390 ± 30
S	6 970 ± 820	3 150 ± 500	6 070 ± 500
Cl	5 570 ± 300	6 700 ± 800	5 960 ± 350
K	6 500 ± 2 600	3 870 ± 1 300	5 850 ± 2 000
Ca	40 000 ± 4 000	20 900 ± 6 200	35 200 ± 3 500
Ti	1 320 ± 80	790 ± 200	1 160 ± 60
Cr	235 ± 30	133 ± 29	215 ± 30
Mn	339 ± 65	136 ± 30	297 ± 35
Fe	7 870 ± 440	4 860 ± 520	6 870 ± 450
Ni	155 ± 43	60 ± 3	112 ± 7
Cu	180 ± 17	173 ± 5	178 ± 15
Zn	641 ± 26	591 ± 20	613 ± 25
As	15 ± 2	12 ± 4	13 ± 3
Br	247 ± 44	256 ± 7	250 ± 40
Cd	5.0 ± 2.5	2.5 ± 2	4.5 ± 2
Sn	44 ± 3	41 ± 5	42 ± 4
Sb	14 ± 2	18 ± 5	16 ± 4
Ba	490 ± 130	384 ± 10	470 ± 100
Pb	406 ± 35	490 ± 130	445 ± 25

Table 2: Analysis of 19 elements in the organic and RDF fraction of the TAMARA fuel (calculated from the actual data per run and averaged, all data in mg/kg)

The table contains the mean values of all samples. On the basis of these data the respective concentrations of the basic fuel can be calculated.

3.3 COMPOSITION OF THE FOAM MATERIALS

Table 3 shows concentrations of the same 19 elements analysed in the components of the basic fuel for the three different XPS types : the granulate and the two foams. The F and Cl concentrations in the foams could not be analysed directly due to losses during the dissolution of the foam. In these cases the (H)CFC content was measured and the respective concentrations of the pure elements were calculated on the basis of these data. The CFC 12 blown foam contained 6 wt. % of CFC 12 and 0.3 wt. % of C₂H₅Cl. The second foam contained 6.3 wt.-% of HCFC 142b and 3.3 wt.-% of HCFC 22

Table 4 summarizes the analysis of the two PUR foams, containing CFC 11.

3 TEST PERFORMANCE AND MATERIALS

element	granulate	XPS (CFC 12 blown)	XPS (HCFC 22/142 blown)
F	100 ± 10	18 960 *	38 330 *
S	< 100	< 100	< 100
Cl	43 ± 10	37 900 *	36 750 *
K	355 ± 25	< 300	361 ± 11
Ca	277 ± 95	229 ± 71	215 ± 110
Ti	140 ± 120	340 ± 150	< 150
Cr	76 ± 10	85 ± 18	69 ± 15
Mn	29 ± 10	< 20	43 ± 20
Fe	142 ± 15	173 ± 10	183 ± 33
Ni	58 ± 22	103 ± 15	88 ± 13
Cu	30 ± 4	49 ± 11	53 ± 7
Zn	62 ± 6	45 ± 11	41 ± 13
As	< 10	< 10	< 10
Br	7 800 ± 430	25 050 ± 260	25 560 ± 430
Cd	< 5	< 5	< 5
Sn	< 10	< 10	< 10
Sb	< 10	< 10	< 10
Ba	< 100	750 ± 450	450 ± 100
Pb	< 10	< 10	< 10

Table 3 : Analysis of 19 elements of the different XPS types used as co-fuel during the combustion tests (all data in mg/kg * = calculated using (H)CFC concentrations in the foams)

Tables 2, 3 and 4 give an indication of high additional inputs of F, Cl, and Br if these materials are added to the basic waste stream. The foam in all cases was of a better fuel quality than the base waste fuel.

Table 4 compiles the data of the PUR foams as analysed during the experiments in Karlsruhe. It was found that the data on F and Cl did not totally comply with that provided by the raw material supplier. For example, the F figures found in the Karlsruhe analysis are approx. 0.3 wt.-% lower and for Cl approx. 1 wt.-% lower. This may be an indication of a loss of blowing agent with time, but a more likely reason for these differences is loss occurring during sampling and dissolution of the foams in Karlsruhe. The main components of PUR foams co-combusted in TAMARA, analysed by BASF/Elastogran (before PUR foam delivery), were as follows for PUR A (2 wt% Br): N - 6wt%, F - 1.1wt%, P - 0.7wt%, Cl - 8.7wt% and Br - 2.0wt%. This was compatible with FZK data. The PUR B (4 wt% Br) differs from PUR A in that it has a content of Cl - 8.0wt% and Br - 4.0wt%.

element	PUR A (2 wt% Br)	PUR B (4 wt% Br)
F	7 700 ± 1 000	6 850 ± 1 000
P	7 120 ± 1 000	6 820 ± 1 000
Cl	76 000 ± 5 000	72 000 ± 5 000
K	6 820 ± 600	7 650 ± 600
Ca	375 ± 50	300 ± 60
Ti	8 ± 2	7 ± 2
Fe	30 ± 5	37 ± 5
Ni	2.5 ± 1	2.3 ± 1
Cu	1.5 ± 0.5	1.5 ± 0.5
Zn	8.5 ± 3	9 ± 3
Br	22 200 ± 2 000	41 700 ± 4 000
Pb	2 ± 1	1.9 ± 1

Table 4 : Analysis of 12 elements of the PUR foam used as co-fuel during the combustion tests (all data in mg/kg)

3.4 FEEDING SYSTEMS AND INPUT DATA

The organic fraction of the fuel was stored in a bunker and fed into TAMARA by means of a conveyor belt and belt scale. This allows for a high degree of accuracy to be achieved. The RDF is supplied in big bags and fed directly into the feeding chute by a special weighing system. Each of the foam materials were put into the feeding hopper. The desired mass stream could be set digitally and was accurate to within 1 - 3 %.

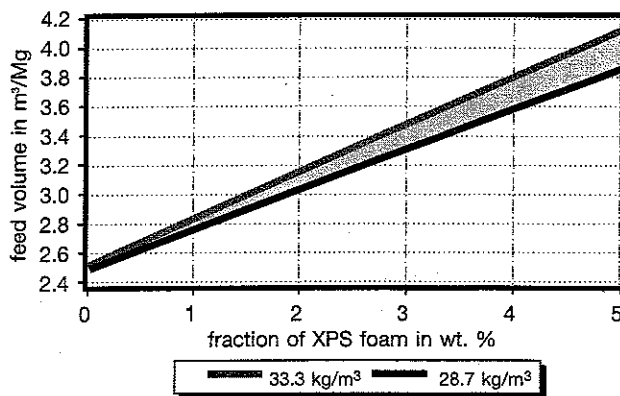


Fig. 2: Increase in feed volume by addition of low density foams

Fig. 2 demonstrates the influence that increasing the proportion of foams has on the volume of the total feed. The upper line represents the addition of the lighter weight material, the lower line that of the slightly heavier

one. Feeding of 3 wt. % of foam increased the volume by approx. 35 %. It is obvious that the technical limit for the co-combustion of foams in a MSWC will be close to this fraction.

3.5 SAMPLING AND ANALYSIS OF THE RESIDUE STREAMS

TAMARA is noted for its variety of control devices and special on-line analytical equipment. Separate collections were made from each residue stream at selected time intervals, in order to achieve a complete mass balance, flue gas samples of O₂, CO₂, CO, H₂O, HCl, SO₂, NO, and N₂O were taken for on-line monitoring.

Isokinetic sampling systems were installed at strategic locations in the flue gas ducts [Vogg 1991]. During each test run a raw gas sample of about 4 - 5 m³ was taken. The sampling time was at least 4 h during all test runs. The treatment and analysis of the sample is described in separate, detailed reports.

For analysis of (H)CFC, gas samples were taken from the raw gas of TAMARA downstream of the fabric filter. Only some control samples were taken from the treated gas as the CFC concentrations are not influenced by the installed wet APC system. So, analysis was done either directly (for CFC 12) or after enrichment (for HCFC 22, HCFC 142b) on activated carbon and following thermo-desorption by GC/ECD or GC/MSD [Rittmeyer 1993]. The detection limit for CFC 12 was approximately 0.5 micro g/m³. For both of the HCFC's a detection limit of 3 micro g/m³ was found.

Sampling for HF, HCl, and HBr was performed on the raw gas after the acid scrubber and in the clean gas using a water cooled condensation step and two gas impingers filled with 100 ml H₂O₂ each. Raw gas samples were taken directly upstream of the flue gas scrubbing system. The clean gas was sampled between APC system and stack. The analysis was performed out of the aqueous solution by means of ion chromatography for HF and HCl and by means of TRXF for HBr. The detection limit for all species was 0.05 - 0.15 micro g/m³.

4 COMBUSTION CONDITIONS AND RAW GAS DATA

4.1 GENERAL REMARKS

TAMARA achieved a stable operation in most runs. But several runs with XPS had severe combustion control problems. During four of the trials the feeding system of the compostable fraction failed due to blocking caused by oversize ingredients. In these cases the total feeding system was automatically shut down by the operation control system. To some extent this blocking was responsible for a temporary temperature decrease and for a fairly pronounced formation of CO. All volume data in this report are based on standardised conditions (0 °C, 1 013 HPa) at the actual O₂ concentration. Thus, the effect of events such as the feeding system breakdown on the production of different gas components can be evaluated more easily.

4.2 RAW GAS DATA DURING SINGLE TEST RUNS

TAMARA is equipped with a number of on-line detectors monitoring the most significant gas types in the raw gas directly upstream from the fabric filter. The following graph depicts the typical total feed, temperature measured at the end of the first vertical flue gas duct in the combustion chamber, and a number of major as well as minor gas components for one single test run. In all cases the sampling of the mixed halogenated dioxins and furans was performed during the first four hours of the shown time interval.

4 COMBUSTION
CONDITIONS AND
RAW GAS DATA

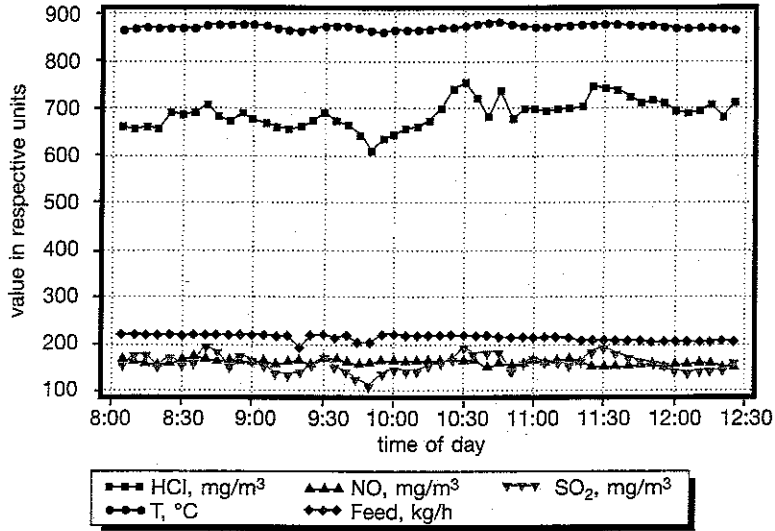


Fig. 3: Feed, temperature and major gases of the 2nd reference test run at low temperature

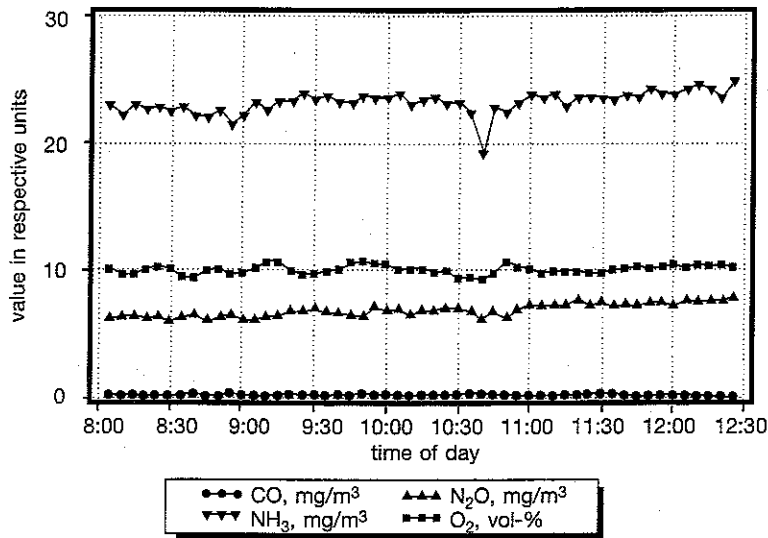


Fig. 4: Minor gases of the 2nd reference test run at low temperature

Stable feed and temperature conditions were able to be established as seen in Fig. 3.

4.3 MEAN VALUES

A more quantitative comparison of the foam results from the single trials can be obtained by comparing the mean values of parameters and their variation. This is shown in Tables 5 a and b and Tables 6 a and b but has only been done during the time span used for gas sampling for PCDD/PCDF analysis.

From the XPS data compiled in these tables it can be seen that the scattering of O₂ and CO concentrations are

most indicative of unstable combustion conditions. Thus three tests: reference 2, the XPS granulate co-combustion trials at low temperature and the XPS/CFC 12 test run at high temperature in particular have to be looked at critically for their parameter settings. In all of these trials a substantial amount of CO formation may have encouraged an increase in the formation of micro organic compounds.

Temperature and HCl levels were less influenced by the failure of the feeding system which implies that the thermal behaviour and the distribution of heavy metals remained largely unaffected.

4 COMBUSTION CONDITIONS

test run	T °C	feed (dry) kg/h	V (dry) m ³ /h	O ₂ vol.-%
ref. 1	872 ± 5	147 ± 5	1 041 ± 10	10.0 ± 0.3
ref. 2	845 ± 15	140 ± 18	1 048 ± 12	10.8 ± 1.0
granulate	849 ± 25	116 ± 19	1 044 ± 11	11.6 ± 1.3
CFC 12	849 ± 4	124 ± 1	1 058 ± 10	11.3 ± 0.3
HCFC 22/142b	841 ± 6	116 ± 3	1 080 ± 18	12.1 ± 0.2
	CO	HCl	SO ₂	NO
	mg/m ³	mg/m ³	mg/m ³	mg/m ³
ref. 1	0.2 ± 0.1	688 ± 32	159 ± 17	165 ± 5
ref. 2	10 ± 46	663 ± 52	158 ± 42	154 ± 14
granulate	48 ± 173	580 ± 57	111 ± 33	120 ± 13
CFC 12	2.9 ± 1.1	754 ± 20	107 ± 14	123 ± 4
HCFC 22/142b	6.7 ± 3.2	644 ± 21	68 ± 11	100 ± 5

Table 5a: Mean data for TAMARA XPS test runs at low temperature

The stability of the combustion process indicated by the results of the on-line monitoring in TAMARA is confirmed by the mean data shown in both of the two tables for the PUR tests.

On the first day of operation the first reference test run (ref.1) - and to a certain extent the second one (ref.2) - suffered from a comparatively low combustion temperature of only (857 ± 29) °C compared to approx. 900 °C established during the other test runs. This may

test run	T °C	V (dry) m ³ /h	O ₂ vol.-%	CO mg/m ³	HCl mg/m ³
ref.1.1	857 ± 29	1 045 ± 29	10.0 ± 1.1	0.8 ± 1.0	745 ± 51
ref.1.2	885 ± 12	1 042 ± 27	9.6 ± 0.4	0.5 ± 0.1	713 ± 22
PUR A.1.1	906 ± 10	1 020 ± 17	9.7 ± 0.4	0.1 ± 0.1	834 ± 28
PUR A.1.2	901 ± 8	1 015 ± 17	9.8 ± 0.3	0 ± 0	786 ± 25
ref.2.1	899 ± 12	1 025 ± 23	9.8 ± 0.4	0.1 ± 0.1	665 ± 29
ref.2.2	907 ± 13	1 030 ± 21	9.6 ± 0.4	0 ± 0	653 ± 24
ref.3.1	887 ± 11	1 074 ± 28	9.3 ± 0.3	1.7 ± 0.1	658 ± 20
ref.3.2	904 ± 11	1 072 ± 28	9.5 ± 0.4	1.6 ± 0.1	606 ± 52
PUR A.2.1	901 ± 10	1 061 ± 27	10.1 ± 0.4	1.5 ± 0.1	683 ± 34
PUR A.2.2	902 ± 15	1 055 ± 26	10.2 ± 0.5	1.7 ± 0.2	703 ± 80
PUR B.1.1	914 ± 10	1 044 ± 35	9.8 ± 0.3	0.2 ± 0.2	1038 ± 20
PUR B.1.2	904 ± 15	1 063 ± 51	10.3 ± 0.6	0.5 ± 0.2	999 ± 49
ref.4.1	899 ± 10	1 050 ± 24	10.0 ± 0.3	0.1 ± 0.2	668 ± 73
ref.4.2	899 ± 8	1 016 ± 29	10.1 ± 0.3	0.7 ± 0.1	722 ± 30

Table 6a: Mean data of PUR combustion temperature, flue gas volume, O₂, CO, and HCl in the raw gas

test run	T °C	feed (dry) kg/h	V (dry) m ³ /h	O ₂ vol.-%
ref. 1	950 ± 7	167 ± 1	1 041 ± 6	9.6 ± 0.9
ref. 2	939 ± 12	170 ± 3	1 059 ± 15	9.5 ± 0.5
granulate	952 ± 6	146 ± 1	1 029 ± 6	9.8 ± 0.3
CFC 12	949 ± 26	131 ± 33	1 042 ± 21	10.7 ± 1.6
HCFC 22/142b	978 ± 6	149 ± 1	1 093 ± 3	9.7 ± 0.4
	CO	HCl	SO ₂	NO
	mg/m ³	mg/m ³	mg/m ³	mg/m ³
ref. 1	2.5 ± 0.2	875 ± 53	173 ± 40	161 ± 8
ref. 2	2.3 ± 0.1	825 ± 36	138 ± 21	157 ± 5
granulate	1.9 ± 0.1	691 ± 27	133 ± 15	125 ± 4
CFC 12	33 ± 160	755 ± 142	87 ± 44	114 ± 19
HCFC 22/142b	1.6 ± 0.1	833 ± 40	100 ± 18	111 ± 3

Table 5b: Mean data for TAMARA XPS test runs at high temperature

have caused the production of low-volatile organic micro pollutants such as PCDD/PCDF and will be discussed later in more detail.

Other parameters which are indicative of the quality of combustion - such as O₂, CO, and CO₂ levels - showed very constant values in all test runs.

The nitrogen content of PUR is approx. 6 wt.-%. This adds approx. 10 % to the original N level of the basic feed and should cause no major changes in the NO

test run	CO ₂ g/m ³	SO ₂ mg/m ³	NO mg/m ³	N ₂ O mg/m ³	NH ₃ mg/m ³
ref.1.1	141 ± 14	229 ± 36	96 ± 14	1.4 ± 0.7	21 ± 7
ref.1.2	138 ± 6	216 ± 19	99 ± 7	1.2 ± 0.3	22 ± 1
PUR A.1.1	158 ± 6	204 ± 26	121 ± 9	1.6 ± 0.3	24 ± 1
PUR A.1.2	155 ± 5	171 ± 16	119 ± 7	1.2 ± 0.3	23 ± 1
ref.2.1	149 ± 7	162 ± 20	114 ± 10	1.6 ± 0.4	24 ± 1
ref.2.2	150 ± 7	167 ± 19	119 ± 10	1.3 ± 0.4	24 ± 2
ref.3.1	162 ± 5	176 ± 17	130 ± 8	1.6 ± 1.0	23 ± 8
ref.3.2	159 ± 7	261 ± 24	128 ± 9	0.9 ± 0.3	24 ± 2
PUR A.2.1	146 ± 6	242 ± 29	123 ± 10	1.8 ± 0.4	25 ± 2
PUR A.2.2	144 ± 8	315 ± 38	119 ± 13	1.2 ± 0.4	24 ± 1
PUR B.1.1	144 ± 4	222 ± 15	133 ± 9	2.1 ± 0.8	27 ± 2
PUR B.1.2	133 ± 9	186 ± 27	135 ± 10	0.9 ± 0.5	24 ± 2
ref.4.1	164 ± 5	172 ± 24	124 ± 8	1.1 ± 1.2	27 ± 2
ref.4.2	162 ± 6	168 ± 12	119 ± 8	1.5 ± 0.5	25 ± 2

Table 6b: Mean gas concentrations of CO₂, SO₂, NO, N₂O, and NH₃ in the raw gas during the PUR campaign

**5 ACID GAS
REMOVAL IN
THE TWO-STAGE
WET SCRUBBER
SYSTEM**

production or in the formation of other nitrogen containing gases. The N_2O and the NH_3 concentrations were monitored on-line during the tests. There seemed to be an increase in the NO level between the first two reference tests and the co-combustion tests feeding 1 wt.-% of PUR A. All the following experiments, however, regardless of whether PUR was fed in or not, stayed at about the same level (120 - 130 mg/m^3). The other nitrogen components also didn't discriminate between the reference test runs and the PUR co-combustion. This finding confirms the results of earlier tests in TAMARA which showed no increase in NO production with PUR feeding [Rittmeyer 1994].

The HCl levels in the reference test runs were in the concentration range of 600 - 750 mg/m^3 . The scattering of the results of each test run is within the typical range of TAMARA experiments. Feeding 1 wt.-% of PUR A and PUR B increased this level, which was expected as both materials contain chlorine from CFC 11 as well as from a flame retardant. However, if the dosage of PUR A was doubled the HCl concentration detected by the on-line monitor did not increase. This was due to measuring difficulties.

**5 ACID GAS REMOVAL IN THE TWO-STAGE
WET SCRUBBER SYSTEM**

5.1 GENERAL REMARKS

TAMARA is equipped with a separate quench followed by an acid (pH = 1) and a neutral scrubber (pH = 7), both of which are modified Venturi scrubbers. Between both scrubbers and downstream from the neutral scrubber, special sampling trains were installed. Test results from these were combined with those from raw gas concentrations derived from the isokinetic sampling system upstream of the fabric filter. The efficiency of the wet system for the different acid gases could then be calculated.

During the entire PUR test campaign the scrubber system was operated in a routine way. No optimisation for the removal of special gas components such as HBr or Br_2 took place. Due to temporary storage problems

the discharge of scrubbing solution of the first scrubber was set very low and had to be changed slightly in order to avoid salt precipitation. Despite this, for all three of the acid gases : HCl, HF, and HBr, the emission standards required by Germany could easily be met. No scrubber performance was monitored during the XPS test runs.

5.2 HCl ABATEMENT

The change in concentrations of HCl while the flue gas passed through the scrubbing system is shown in Fig. 5. Here, all data of the reference runs and the different co-combustion conditions have been averaged. The graph reveals that the installation of just an acid scrubber does not guarantee the observance of the emission limit of 10 mg/m^3 set by the German 17.BImSchV. However, after passing the second scrubber, measurements far below 1 mg/m^3 were easily achieved.

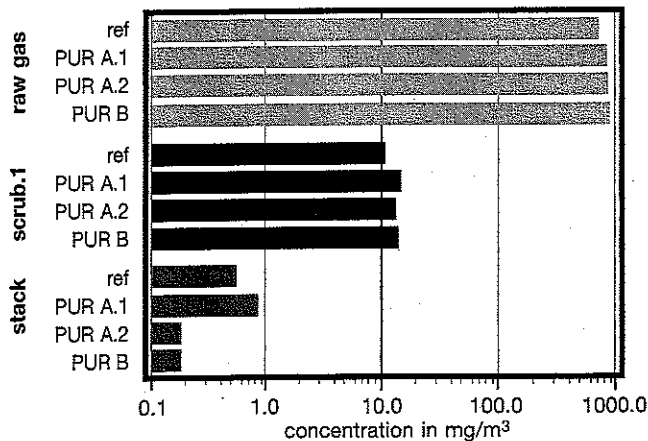


Fig. 5: Concentrations of HCl in the raw gas, downstream of the acid scrubber and in the clean gas

HF Abatement

Measurements of concentrations of HF were performed the same way as for HCl and the results are shown in Fig. 6. It is obvious that the efficiency of the first scrubber was much lower for HF than it was for HCl. Nevertheless, in the clean gas, levels of < 0.2 mg/m^3 were measured, which is well below the 17.BImSchV limit of 1 mg/m^3 .

5 ACID GAS REMOVAL IN THE TWO-STAGE WET SCRUBBER SYSTEM

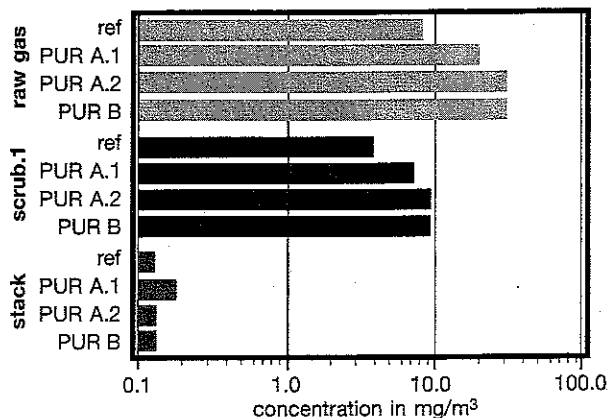


Fig. 6: Concentrations of HF in the raw gas, downstream of the acid scrubber and in the clean gas

HBr Abatement

Fig. 7 reveals that, in the same test, removal of HBr in the first scrubber was better than that of HF but did not reach the quality of that of HCl. The 17.BImSchV contains no emission limit for HBr but the German emission regulation issued in 1986, the 'TA Luft 86', sets a limit of 5 mg/m³. The respective data found in the clean gas of TAMARA were well below 0.2 mg/m³.

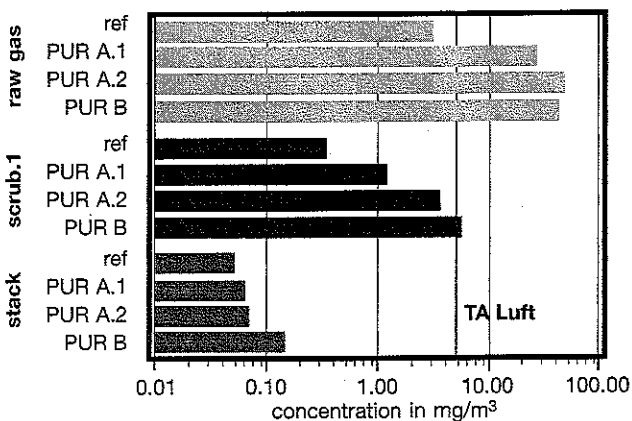


Fig. 7: Concentrations of HBr in the raw gas, downstream of the acid scrubber and in the clean gas

5.3 SCRUBBER EFFICIENCY

The scrubber efficiency is defined as the fraction of a component removed by the scrubber, divided by the input. Fig. 8 compiles the removal efficiencies of the first and second scrubber for HCl, HF, and HBr. The values are averaged for the different combustion conditions.

Approx. 98 % of the raw gas HCl was removed in the first scrubber. After having passed the neutral scrubber almost 100 % of the HCl was absorbed. For HF, the removal efficiency in the first scrubber was relatively poor, reaching only 50 % in the case of the test runs where the input concentration was low. During the co-combustion trials, when the F feed was increased, approx. 70 % removal was calculated. The overall efficiency was at least 98 %. For HBr, an efficiency in the order of 90 % could be achieved in the first scrubber. With the exception of the reference tests, with their low input, almost 100 % could be removed by the entire system.

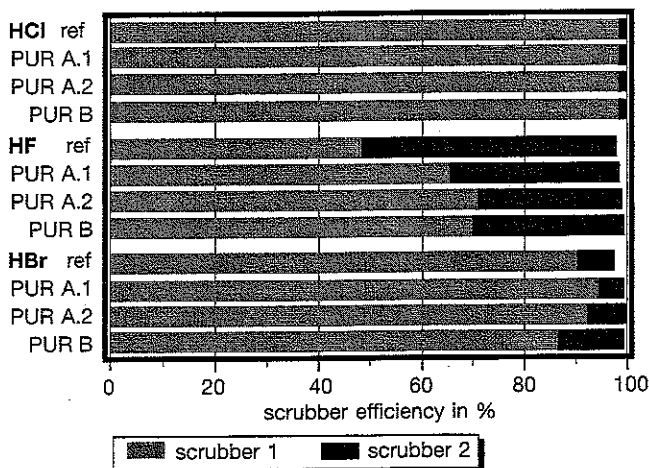


Fig. 8: Scrubber efficiency for HCl, HF, and HBr

6 RESIDUE
MASS
STREAMS

6 RESIDUE MASS STREAMS

In this section mass balances of some of the more interesting elements are discussed in more detail. There were similar findings for both PUR and XPS so only XPS findings will be shown. The generic mass stream data used for these calculations can be found in Table 7 and Table 8.

test run	feed (dry)	bottom ash	grate sift.	coarse fly ash	fly ash
	kg/h	kg/h	kg/h	kg/h	mg/m ³
ref. 1	147 ± 5	41.8	5.9	1.4	669
ref. 2	140 ± 18	39.4	5.7	2.2	635
granulate	116 ± 19	30.5	4.2	0.8	579
CFC 12	124 ± 1	32.6	4.3	0.7	639
HCFC 22/142b	116 ± 3	38.8	5.1	0.8	628

Table 7: Mass streams of residues for the XPS campaign at low temperature

test run	feed (dry)	bottom ash	grate sift.	coarse fly ash	fly ash
	kg/h	kg/h	kg/h	kg/h	mg/m ³
ref. 1	167 ± 1	58.9	6.0	1.2	630
ref. 2	170 ± 3	56.3	9.7	2.2	640
granulate	146 ± 1	56.6	6.0	1.3	539
CFC 12	131 ± 33	48	6.2	2.0	711
HCFC 22/142b	149 ± 1	52	5.5	2.6	646

Table 8: Mass streams of residues for the XPS campaign at high temperature

In the low temperature test runs, the fraction of waste leaving the MSW incinerator along with the bottom ashes was (28 ± 3) wt.-% and for the high temperature test runs, (36 ± 2) wt.-%. The difference in weight percent reflects a change in waste quality.

During the second XPS test run, performed about 5 weeks after the first, the amount of inert ingredients in the compostable waste fraction was higher, however, the mean concentrations of major and minor elements did not show significant differences.

It must be noted that the recorded masses of the coarse fly ash are characterised by a marked variation between the different test runs. This may be caused by

material falling into the sampling bins which had been accumulated in the raw gas ducts. There are two factors that prevent these variations in weight from influencing the mass balance of most elements. First, the amount of coarse fly ash is relatively small. Secondly, the material was separated from the flue gas at high temperatures meaning that it contained only small amounts of thermally mobile metals. Mass streams for the PUR campaign runs were similar to the XPS tests. Therefore the same conclusions can be drawn for these tests.

7 TOTAL BURNOUT

The parameter "burnout" can be defined in several ways. In combustion engineering the ratio between CO and CO₂ concentrations in the flue gas is used as a measure of burnout. However, when evaluating the entire waste combustion process, including residue quality, a much better parameter is the total amount of residual or incompletely burnt carbon types (TOC).

In Fig. 9 averages of TOC found in the grate ashes are given for each PUR test. The graph indicates that the burnout is improved in cases where plastic material is added to the basic feed. This was confirmed in other tests where up to 15 wt.-% of post-consumer plastic waste was burnt together with the basic feed in TAMARA [Vehlow 1994]. Similar results were achieved with the XPS foam.

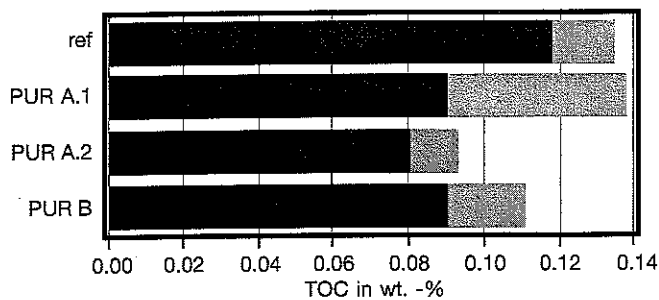


Fig. 9: TOC in the grate ashes (respective test types have been averaged, cross-hatched area = reproducibility)

8 THERMAL BEHAVIOUR OF INORGANIC SPECIES

8.1 GENERAL REMARKS

In order to get information on the behaviour of single elements, all residue streams of TAMARA were sampled and analysed. The resulting distribution of the element between the different compartments means that the fraction present in the respective residue streams was always clearly defined in relation to the amount being burnt. The completion of the mass balance is a reflection of the accuracy of the total sampling and analysis programme.

8.2 HALOGENS

Chlorine

The most abundant halogen was Cl with a typical concentration of 0.7 wt % in municipal solid waste. Fig. 10 depicts the average proportion of Cl in the respective XPS test runs. All calculations of elements were based on comparing the total input of the respective element with that found in the waste feed. The accuracy of the Cl data seemed very satisfying.

The fraction of Cl staying in the bottom ash in both the high and low temperature tests was always in the order of 20 % or below. About the same amount left the combustion chamber along with the fly ash. Between 60 and 70 % was found as HCl in the gas phase. The HCl emission measured upstream of the stack was less than 2 mg/m³ during all test trials and thus was well below the German emission limit of 10 mg/m³ [Bundesministerium 1990].

The de-novo formation of organochlorine compounds is due to the Cl concentration in the fly ash. The level of PCDD/PCDF in full scale MSWC filter ash correlates with the particulate carbon, Cl and Cu concentrations in these materials [Vogg 1986, Stieglitz 1987, Hagenmaier 1987]. Based on these findings it is often argued that an increase in Cl input, creates a risk of enhanced PCDD/PCDF production in the municipal solid waste incinerator.

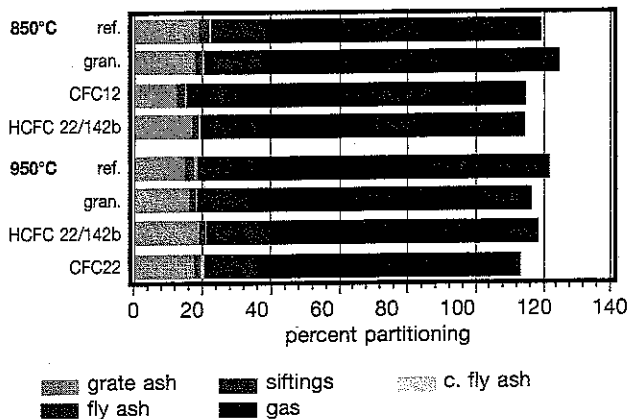


Fig. 10: Balance of Cl for all different test conditions with XPS foams (reference tests have been averaged)

It has been well documented that at elevated combustion temperatures the volatility of thermally mobile element types increases [Dalager 1993, Vehlow 1993]. These elements can exist as pure elements, their oxides or chlorides. This should imply a more distinctive presence of volatile elements in flue gas and fly ash at higher combustion temperatures. Also, in the case of acid components like halogen anions, the alkalinity of the fly ash influences the respective concentration of the species in this residue. Since the basic fuel was not changed during the experiments this value should be about the same in all those tests that were feeding XPS and PUR foam. Indeed the pH value of all fly ash measured under the conditions of the DEV S4 leaching test procedure [DIN 38 414] - meaning at a liquid-solid ratio of 10 - was in a narrow range of between 6.4 and 6.7.

Fluorine

The fluorine concentration in the basic fuel of TAMARA compares to that of typical municipal solid waste. When (H)CFC blown XPS foams were added into the system the fluorine (F) concentration increased.

From former experiments in TAMARA as well as in full scale incinerators it is known that F mass balances cannot be adequately completed [Rittmeyer 1993, Rittmeyer 1994]. The most appropriate explanation for this is that F is lost due to reactions between HF in the flue gas and the wall material in the combustion chamber or the claddings and ash shells in the hot part of a waste incinerator.

8 THERMAL BEHAVIOUR OF INORGANIC SPECIES

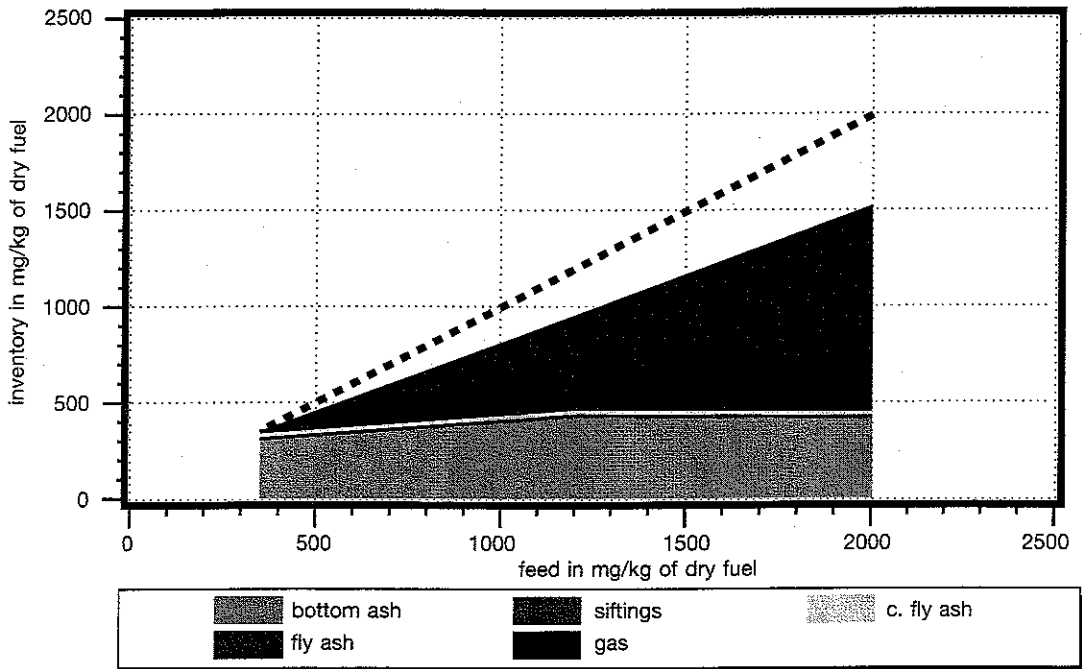


Fig. 11 : Balance of F for all different XPS foam test conditions (reference tests have been averaged)

Fig. 11 depicts the additional F masses in the different residue streams as a function of the F input per kg of dry feed. The straight line shows the limit for a completed mass balance. It is apparent that the F staying in the bottom ash originated from the basic fuel. Even when the F content of the fuel was increased by a factor of 5, only a small increase in F was detected in the bottom ash.

The additional F is originally bound to the (H)CFC. The thermal destruction of the (H)CFC and the formation of HF largely takes place in the gas phase. This means that the probability of the (H)CFC borne HF being trapped in the bottom ash is limited. This was confirmed by the results of the experiments at low temperature.

A strong correlation was found between the HF levels in the gas phase and the F containing fuel feed. The HF concentration in the raw gas was typically in the range of 5 - 10 mg/m³ for the reference test runs. At high temperature this number went up to 120 mg/m³. The emission of HF is regulated in most countries. In Germany this value is 1 mg/m³ [Bundesministerium 1990]. TAMARA is equipped with a two-stage wet scrub-

bing system. During all test trials the clean gas in front of the stack was sampled and analysed for F. All emission concentrations found were below 0.2 micro g/m³.

Bromine

According to the literature [Schneider 1986] the Br content in waste is in the order of 10 mg/kg of the waste. In the TAMARA basic fuel, however, approx. 250 mg/kg (XPS) and 170 mg/kg (PUR) was detected. Schneider's underestimation of Br levels may be due to problems of both combustion and analysis.

A recently published paper refers to raw gas concentrations of up to 4.6 mg/m³ found in a German full-scale MSWC [Kürzinger 1994]. This is the same order of magnitude as found during the reference test runs.

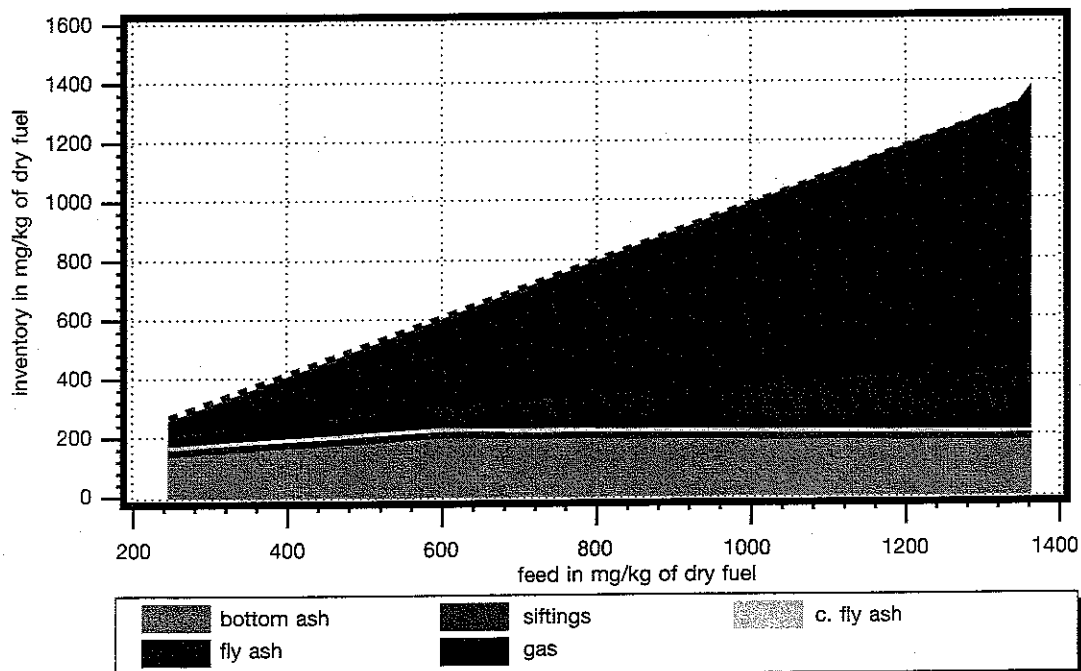


Fig. 12: Distribution of Br for all different XPS foam test conditions (reference tests have been averaged)

Fig. 12 gives the distribution of Br for all test conditions. Apart from the reference and granulate tests runs at low temperature, where certain losses were observed, the Br mass balance completed very well.

As already found for F, the amount of Br staying in the bottom ash remained fairly constant as can be seen in Fig. 12. This shows the absolute distribution between the different compartments as a function of the Br input. The reason for this is the same as for F: the Br is bound to the flame retardant which is thermally degraded in the gas phase of combustion. Again, the straight line in Fig. 12 symbolises the total input.

As in the case of F, there is a strong correlation between the production of HBr and the Br fed into the system. Although the raw gas concentration was increased up to a factor of about 20 the absolute concentration stayed moderate. Thus no emission problems are expected.

The Br distribution was also measured during the PUR tests and a similar distribution to XPS can be seen.

The 1986 German air emission ordinance, the 'TA

Luft', contains an emission limit for HBr of 5 mg/m^3 . The emission surveillance of the reference test runs resulted in $< 0.2 \text{ mg/m}^3$. During the foam co-combustion the maximum emission level found was 0.8 mg/m^3 .

The graph in Fig. 12 demonstrates increasing concentrations of Br in both the gas phase and in the fly ashes. The latter is relevant for the formation of brominated or mixed halogenated organics.

8 THERMAL BEHAVIOUR OF INORGANIC SPECIES

8.3 HEAVY METALS

Copper (Cu)

Of major interest here is the catalytic activity of copper in terms of its production of organohalogen compounds and its corresponding thermal behaviour. The component balance calculated for the XPS foam test runs at 850 °C is satisfying. However, at the higher temperature a significant surplus of Cu is found in the outlets.

Fig. 13 shows the amount of Cu transported with the fly ash out of the combustion chamber as a function of chlorine input with the fuel. As the graph demonstrates, there is no detectable influence at a combustion temperature of 850 °C whereas at about 950 °C a slight increase of Cu transfer was noted with increasing Cl input. This is in accordance with data found in earlier experiments in TAMARA [Vehlow 1994]

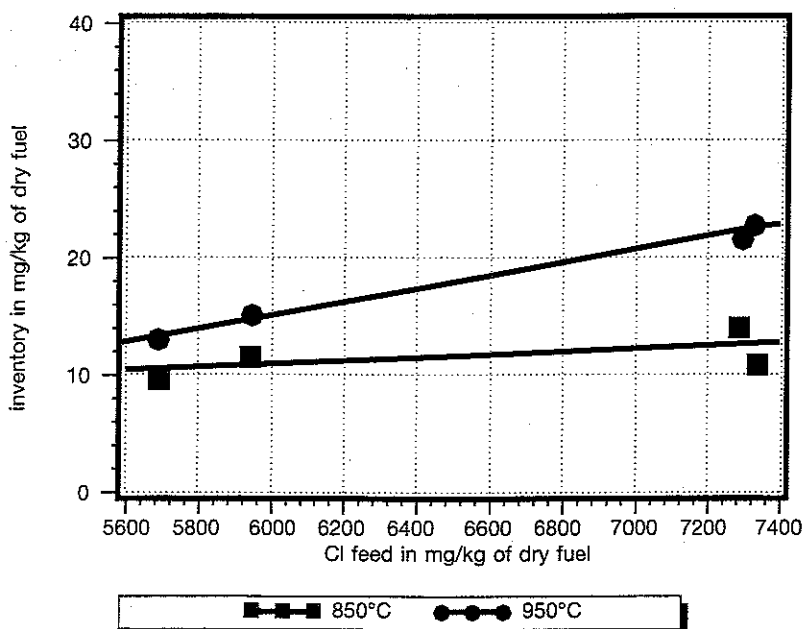


Fig. 13: Cu in fly ashes versus Cl input

A more thorough analysis points to the fact that the bottom ash - and to a lesser extent the grate siftings - were characterised by a substantial scattering of Cu. This finding is typical for more noble heavy metals such as Cu or Pb which appeared in their metallic state in both residue streams. If a certain amount of metal is present in a sample this metal is not necessarily homogeneously distributed in all sub samples by grinding.

Only the concentration of Cu in the particulate matter found in the offgases is of concern. Although Cu ranks among the more lithophilic metals, a certain fraction is volatilised as chlorides. Two stable chlorides of Cu exist: CuCl (or Cu_2Cl_2) with a boiling point of 1367 °C and CuCl_2 with a boiling point of 993 °C.

8.4 HEAVY METAL VOLATILITY

The volatilisation of heavy metals during waste combustion is controlled by the presence of Cl because metallic chlorides characteristically exhibit higher vapour pressures. This is why the mass transfer of a selected number of potentially thermally mobile elements such as Cu, As, Cd, and Sb were calculated and correlated with the Cl feed. In all cases these data were standardised with the amount of dry waste burnt in TAMARA.

From calculations of the XPS foam low combustion temperature runs it is evident that at this temperature no correlation between the metal transfer and the Cl being fed with the fuel can be found. It is likely that the main reason for this finding is that the effects are too small to

9 THERMAL DESTRUCTION OF (H)CFC

be significant. There is only a small difference in the Cl feed of approx. 6 g/kg in the basic fuel and 7.4 g/kg in the foam experiments. However, in earlier TAMARA experiments at 950 °C, a clear correlation with the Cl input has been revealed and documented.

In conclusion it can be stated that all findings concerning the mass balances and volatility of metals during the XPS co-combustion tests compare well with data already published. [Brunner 1986, Schneider 1986, Angenend 1990, Dalager 1993]. Similar conclusions can be made for the PUR co-combustion. It is well known from experimental results and corroborated theoretical considerations that the temperature in the fuel bed and the Cl input in the fuel are the generic controlling factors of volatilisation of elements in waste incineration [Vogg 1984, Borchers 1989, Vehlow 1993].

9 THERMAL DESTRUCTION OF (H)CFC

9.1 INPUT DATA

Three different (H)CFC's were fed into the incinerator along with the XPS foam. Table 9 gives an overview of the expected levels of (H)CFC with no thermal destruction taking place. For CFC 12 blown foams a separate experiment of 2 h was performed at a medium temperature in a later TAMARA test run.

temperature °C	CFC 12 mg/m ³	HCFC 22 mg/m ³	HCFC 142b mg/m ³
850	312 ± 10	150 ± 8	290 ± 10
880 - 900	350 ± 10		
950	340 ± 10	190 ± 10	360 ± 10

Table 9: Theoretical (H)CFC concentrations in the flue gas calculated on the assumption that no thermal destruction took place

9.2 DESTRUCTION OF CFC 11 AND OF CFC 12

In earlier extended experiments in TAMARA, as well as in a full scale MSW combustor, an almost complete thermal destruction of CFC 11 (in PUR foams) was confirmed. At temperatures above 800 °C no temperature influence could be detected.

Due to its higher chemical stability a different behaviour in the incinerator could be expected for the CFC 12.

During the reference test runs the concentration of CFC 12 was approx. constant at both combustion temperatures as can be seen in Fig. 14. An average CFC 12 level of (2.6 ± 1.3) micro g/m³ was analysed. The actual values scatter in a range of between 0.8 and 8 micro g/m³. During the co-combustion experiments a certain influence of the combustion temperature was found in CFC 12 destruction. At the low temperature of approx. 850 °C residual concentrations of up to 1 000 micro g/m³ were analysed. At 950 °C remaining CFC levels of 10 - 20 micro g/m³ were found. In order to verify these experimental findings an additional TAMARA test campaign was used to run some more experiments at temperatures between 870 and 900 °C. The results from these experiments fit nicely into the original results. Nevertheless, the destruction efficiency calculated from the above given concentrations is more than 99.9 % at 900 °C.

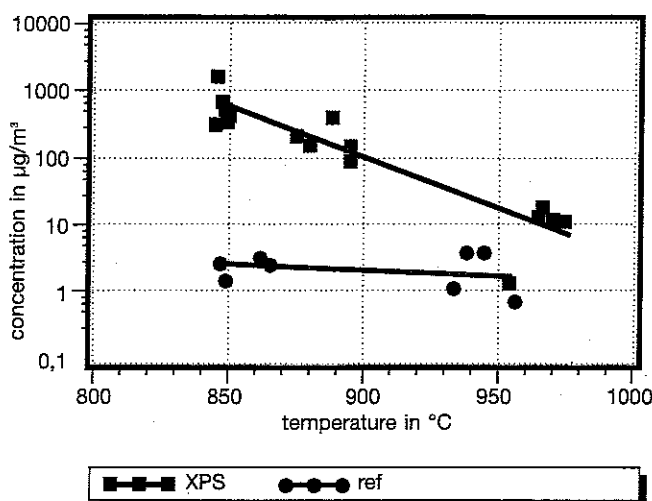


Fig. 14: CFC 12 concentrations in the flue gas versus combustion temperature for the XPS foam.

10 HALOGENATED DIBENZO-P- DIOXINS

9.3 DESTRUCTION OF HCFC 22 AND HCFC 142B

In contrast to CFC 12, the partially halogenated HCFC 22 and HCFC 142b were below the detection limit of 3 micro g/m³ in the flue gas of TAMARA during all test trials. On the basis of the amounts of respective HCFC fed into the incinerator (compare Tables 1^a and 3) minimum destruction yields can be calculated for HCFC 22 of 99.9 % and for HCFC 142b of 99.9 %. As a consequence, the HCFC blown foams used today can be incinerated in a MSW combustor in an ecologically beneficial way.

10. HALOGENATED DIBENZO-P-DIOXINS AND DIBENZOFURANS

10.1. GENERAL REMARKS

If flame retardant foams are incinerated in a MSWC the possibility of the formation of chlorinated, brominated, and mixed halogenated - Cl and Br substituted - dibenzo-p-dioxins and dibenzofurans has to be considered. There is evidence that under 'de-novo' conditions the Br : Cl ratio may control the actual amount and distribution of the different elements [Funcke 1993]. It is also well known that bromine compounds can promote the effect of chlorination reactions.

Uncontrolled combustion of flame retarded TV sets with polybrominated diphenylethers [Zelinski 1993] and the pyrolysis and mono-combustion of flame retardants in a laboratory setup [Dumler, 1989] have been identified as sources of Br containing dibenzo-p-dioxins and dibenzofurans. Sampling in the Swedish full scale MSWI resulted in only small amounts of brominated aromatic compounds being found. Brominated and mixed halogenated dioxins and furans were always below the detection limit [Öberg 1990]. The authors conclude that during normal operation of a MSWI, organobromine compounds do not create an environmental risk through uncontrolled air emissions.

The total concentrations of brominated and mixed halogenated compounds in the raw gas and in the fly ashes of a MSWI comprise only a small percentage of

the PCDD/PCDF levels [Öberg 1989, Donnelly 1990].

Investigations during the co-combustion of electronic waste (circuit boards), flame retarded with polybrominated diphenylethers, in a full scale facility are reported to have shown a significant increase in PCDD/PCDF levels in the flue gas [Lahl 1991]. A critical review of this paper, however, leaves some question as to whether this increase is significant when the data are compared with the variation of PCDD/PCDF production during normal operation.

Time Dependent Variation of PCDD/PCDF levels in TAMARA

TAMARA is a small test facility which needs several days to reach a stable condition for the production of halogenated organic compounds, particularly PCDD/PCDF. During one week of operation PCDD/PCDF concentrations are higher at the beginning of the week than they are after a couple of days. The decrease is striking during the first week where a quadratic regression equation can be used to describe the time dependent variations in concentrations. In the second week of operation the time influence is less pronounced and can be approximated by a linear regression.

The time dependency of PCDD/PCDF raw gas levels found in TAMARA in the first week of operation is illustrated in Fig. 15 which compiles data analysed during the last test series. All tests were conducted burning basic feed (reference tests) under similar operation conditions, the combustion temperature was (900 ± 50) °C. The time scale starts with the first feed of waste into the combustion chamber. These data can be interpolated using the following quadratic regression equations:

$$^{\circ}\text{PCDD} = 101 - 1.67 \text{ time} + 0.0078 \text{ time}^2 \text{ (equ. 1)}$$

$$^{\circ}\text{PCDF} = 125 - 2.15 \text{ time} + 0.0092 \text{ time}^2 \text{ (equ. 2)}$$

For approaching the respective data during the second week of operation the following linear regressions are used:

$$^{\circ}\text{PCDD} = 27 - 0.212 \text{ time (equ. 3)}$$

$$^{\circ}\text{PCDF} = 31 - 0.218 \text{ time (equ. 4)}$$

**10 HALOGENATED
DIBENZO-P-
DIOXINS**

Concentrations calculated from these equations are estimated to be inaccurate by at least $\pm 30\%$. In the following chapters (10.2 and 10.3) an evaluation of the potential influence of XPS and PUR co-combustion is done. Respective PCDD/PCDF concentrations are compared with a theoretical reference value calculated by using the above given equation over exactly the same time period as for the co-combustion tests.

For evaluating the practical relevance of the results, the PCDD/PCDF raw gas levels were compared with the respective values from modern full scale waste incineration plants. (See Table 10). Such data are rarely found in literature. The TAMARA results found in the first day are not taken into consideration.

Facility	PCDD ng/m ³	PCDF ng/m ³	I-TEQ ng/m ³	source
TAMARA	8 - 50	10 - 60	< 0.3 - 2	
MSWC, recipr. grate	55	110		Vogg 1990
MSWC, roller grate, par. flow	9 - 60	8 - 47	0.2 - 1.5	Horch 1991
MSWC, roller grate			4.7 - 24	Kempin 1994
MSWC, reverse acting grate	21.2 - 70.0	96.6 - 155.6	2.7 - 4.3	Kerber 1994

Table 10: PCDD/PCDF levels in TAMARA and full scale MSWI

The table demonstrates that the PCDD/PCDF raw gas concentrations in modern MSW may vary substantially. The levels monitored in TAMARA correspond to the best data reported for full scale facilities. This confirms the technical relevance of the TAMARA test results.

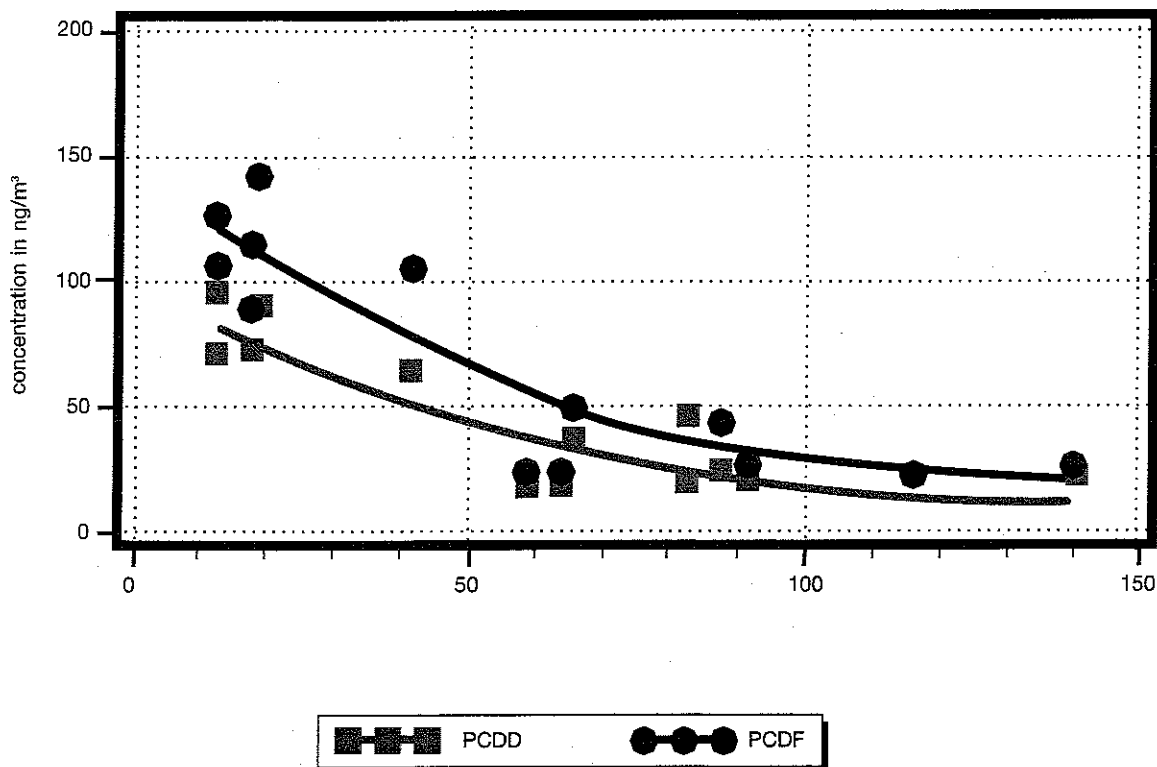


Fig. 15: Time dependent PCDD/PCDF levels in TAMARA during the first week of operation at combustion temperatures of $(900 \pm 50)^\circ\text{C}$ for reference test conditions

10 HALOGENATED DIBENZO-P- DIOXINS

Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans : Gas Sampling, Method Comparison

The sampling of low volatile organic compounds during the XPS trials was performed in raw gas, using two different sampling trains. One being the 'long-term sampler' LPS, developed by FZK [Vogg 1991] and the other, the BASF 'PU/Impinger-Hi-Vol' sampling train [Brenner 1994]. The FZK set-up includes a heated PTFE plane filter, a condenser-scrubber combination, and an XAD 2 adsorber. The BASF train consisted of an intensive tube-bundle cooler, PU foam plugs and multi-jet-Hi-Vol-impingers. Both trains were installed close to each other in the raw gas duct upstream from the fabric filter in TAMARA (see Fig. 1.). The sampling methods, clean-up, and GC/MS analysis will be described in detail in a separate EXIBA report [Brenner 1995]. In this report only a summary of the main results will be included.

The sampling during the PUR foam campaign for low volatile organic compounds was also performed in raw gas, and by two different analytical laboratories: the GfA (Gesellschaft für Arbeitsplatz- und Umweltanalytik mbH, Münster) and the MPU (Mess- und Prüfstelle Technischer Umweltschutz GmbH, Saarbrücken). Again, two different sampling trains were installed at two locations close to each other in the raw gas duct directly upstream from the fabric filter in TAMARA (compare Fig. 1).

The GfA train was specially designed to absorb low-volatile organic compounds in one single sampling phase. This was done with a combination of quartz wool and XAD-2 resin [Funcke 1993a]. The method is limited to particulate loads $< 1 \text{ g/m}^3$. Clean-up and analysis were performed according to GfA's own protocols [Funcke 1994]. The GfA sampled all test runs and analysed all samples for chlorinated, brominated, and mixed halogenated dibenzo-p-dioxins and dibenzofurans, for polychlorinated biphenyls (PCB), - benzenes (PCBz), and - phenols (PCP), and for polyaromatic hydrocarbons (PAH). The analytical results for PCB, PCBz, PCP, and PAH were, in almost all samples, below detection limit and will not be discussed in detail.

The MPU used a sampling train in accordance with

German pre-standard VDI 3499. This comprises a dedusting with quartz wool, a high-intensity condensation followed by a demister, and an absorption on XAD-2 [VDI 3499]. This method allowed a separate analysis of compounds present in the gas phase or absorbed in the fly ash. MPU sampled all test runs. Only samples from two reference test runs (ref.3.1 and ref.4.1) and from two co-combustion tests (PUR A.2.1 and PUR B.1.1) were analysed by ITU (Ingenieurgesellschaft Technischer Umweltschutz, Berlin) for halogenated dibenzo-p-dioxins and dibenzofurans.

Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans : Gas Sampling Results

The data for PCDD/PCDF obtained through the different sampling strategies during the XPS foam test described above were consistent and satisfactory. This is demonstrated by the following graphs which compare the respective raw gas concentrations obtained by both sampling and analysis procedures.

Fig. 16 and 17 display the PCDD results at a combustion temperature of 850 °C. The total concentrations are well within an error range of $\pm 30 \%$ of the mean. This is to be expected for two laboratories using totally different methods. The homologue pattern also shows good conformity and similar conformity is found for the furans. Taking the total deviation of the mean values into account, all PCDD raw gas levels at a given temperature overlap each other in the tests. The distribution of the different homologue groups also stayed almost constant during all experiments.

10 HALOGENATED
DIBENZO-P-
DIOXINS

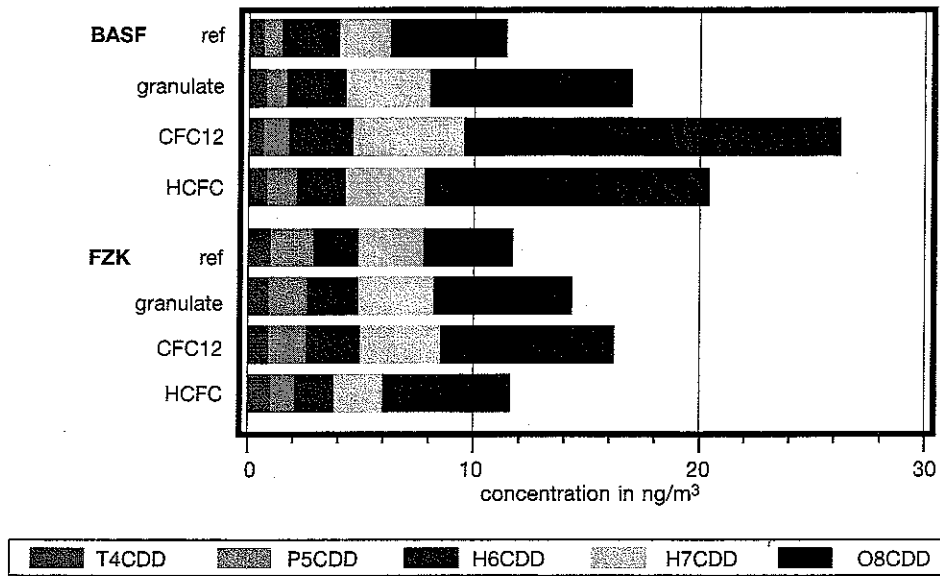


Fig. 16 Comparison of PCDD concentrations in the raw gas of TAMARA at 850 °C XPS Runs

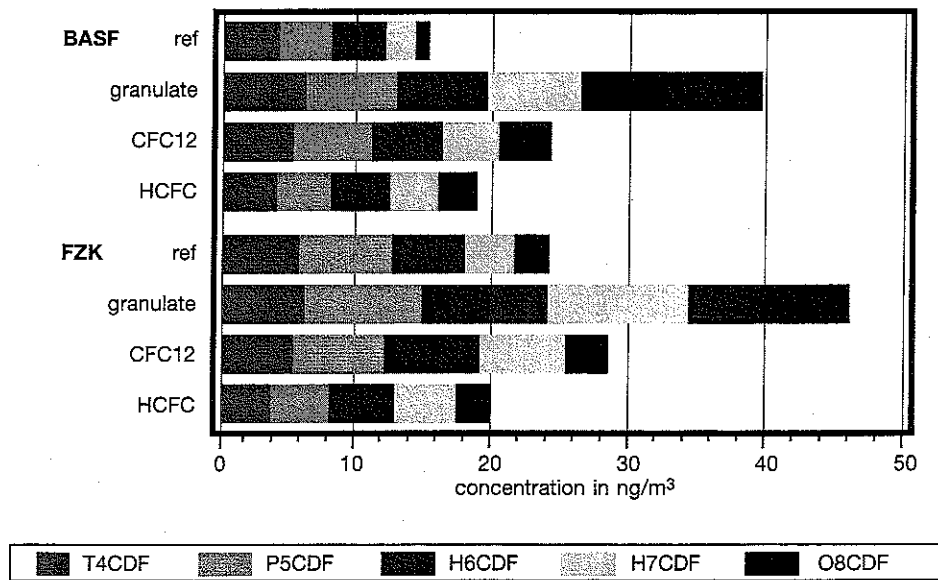


Fig. 17 Comparison of PCDF concentrations in the raw gas of TAMARA at 850 °C XPS Runs

Polybrominated and Mixed Halogenated Dibenzop-Dioxins and Dibenzofurans

Inter-Laboratory Comparison of Analytical Results

Whereas the analytical data obtained by GfA and ITU showed excellent conformity for PCDD and PCDF, the

same was not expected for materials containing bromine. The limited separation of different chromatographic peaks and the shortage of certified standards had already caused less consistent results in the preliminary inter-laboratory analysis of a dust sample.

**10 HALOGENATED
DIBENZO-P-
DIOXINS**

Figs. 18 and 19 compare the analytical results of gas samples during the PUR campaign obtained by both laboratories. While ITU detected approx. 3 ng/m³ of monobrominated and less than 0.4 ng/m³ of dibrominated dibenzo-p-dioxins in reference tests, GfA found no dioxins others than purely chlorinated ones. Congeners

containing three bromine atoms together with chlorine could not be detected by either laboratories.

The ITU value of the reference tests revealed 15 - 20 % of the PCDD levels. This seems high compared to data found in former test campaigns [Vehlow 1995] or in

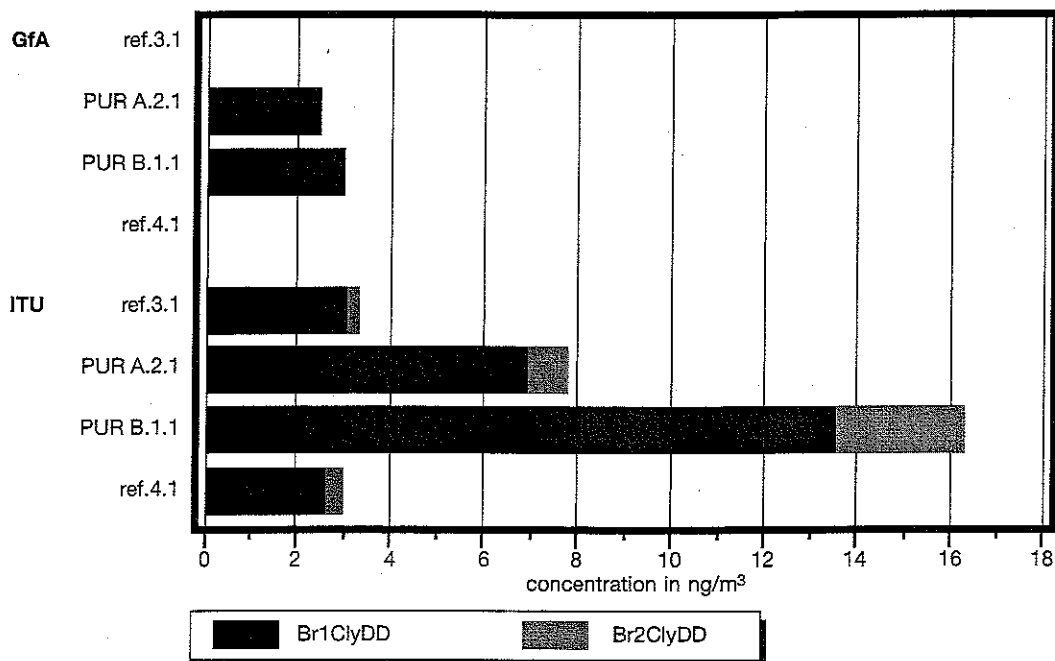


Fig. 18: Comparison of results of monobromo-polychlorinated, dibromo-polychlorinated and polybrominated dibenzo-p-dioxins analysed by GfA and ITU

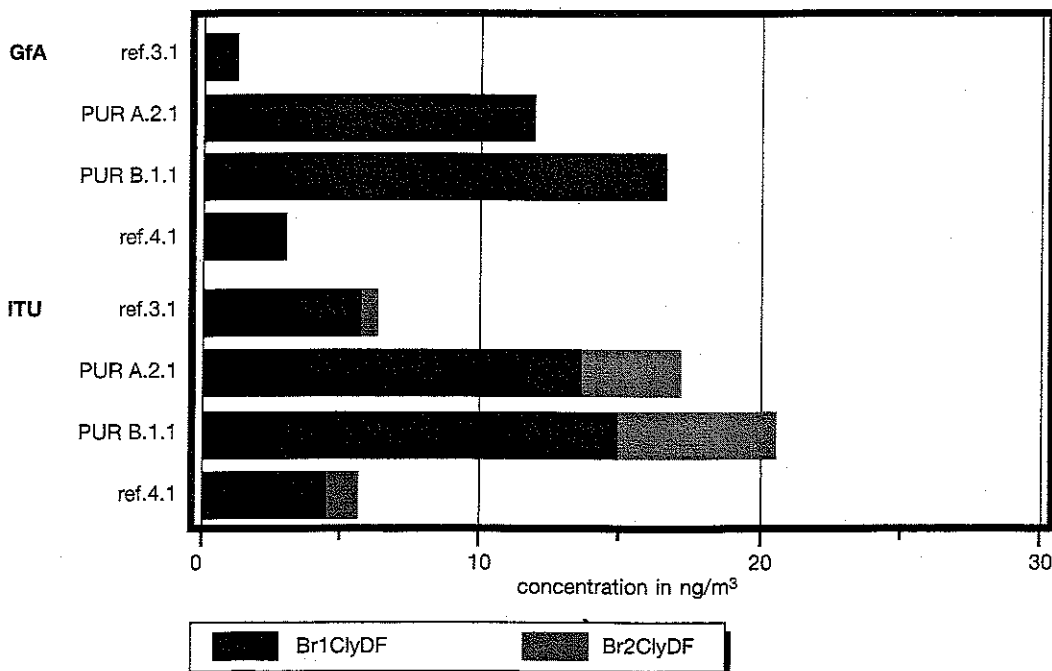


Fig. 19: Comparison of results of monobromo-polychlorinated, dibromo-polychlorinated and polybrominated dibenzofurans analysed by GfA and ITU

literature [Öberg 1989, Donnelly 1990] which were in the order of only a few percent. In both of the PUR test runs the bromine feed concentration was almost identical. This is reflected in the GfA data. However, the ITU data are a factor of two higher in the PUR B test than in the PUR A.2 test, almost reaching the PCDD level.

The results of the bromine containing dibenzofurans show better consistency than those of the dibenzo-p-dioxins, as can be seen in Fig. 19. The sum of polybrominated dibenzofurans is the same. Again, ITU found higher amounts than GfA. All other PBDF's were below detection limits.

These results are a good indicator of the order of magnitude of analytical errors in an advanced field of investigations.

Taking into account the different sampling and analytical protocols, the lack of certified standards and the low concentrations found, the results are satisfactory.

10.2 POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS

Results

The homologue pattern for PCDD/F is shown in Fig. 20 for the PUR campaign.

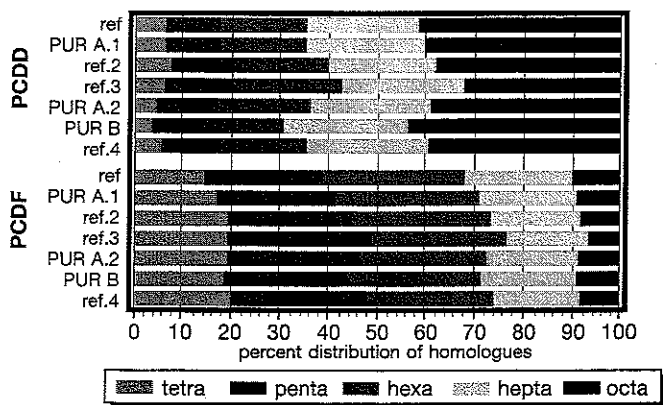
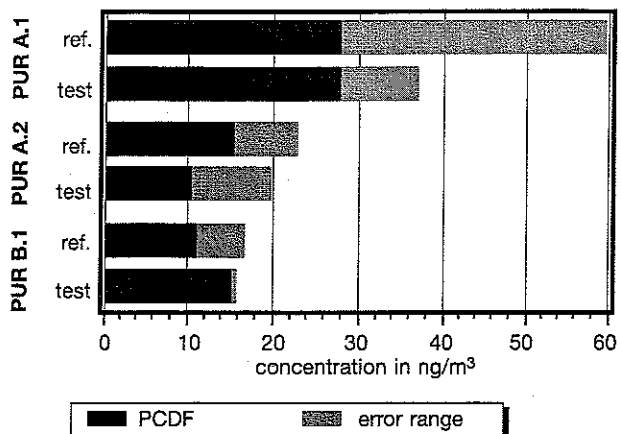
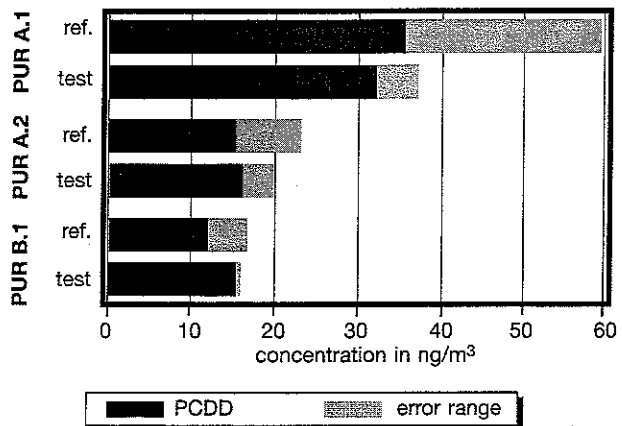


Fig. 20. Homologue pattern of PCDD and PCDF from the PUR campaign.

Addition of bromine containing PUR foam did not change the distribution between the tetra and the octa dioxins and furans when plotted in a normalized form.

The same statement can be made for the addition of XPS. The final corrected concentrations for the addition of PUR foam are shown in Figs. 21 and 22. The values have been calculated on the basis of regression equations, using the average time of operation as a base. The cross hatched areas symbolize the mean error range which was estimated at $\pm 30\%$.



Figs. Nr. 21 and 22: Averaged PCDD and PCDF levels for the co-combustion with PUR foams.

**10 HALOGENATED
DIBENZO-P-
DIOXINS**

For all tests the error range of the reference tests overlap with the values of the co-combustion tests. From the results it can be concluded that there is no correlation between the addition of foam and the formation of chlorinated dioxins and furans.

**10.3 POLYBROMINATED & MIXED HALOGENATED
DIBENZO-P-DIOXINS AND DIBENZOFURANS
Results**

Effects of the PUR Co-Combustion

The raw gas concentrations of chlorinated, brominated and mixed halogenated dibenzo-p-dioxins are shown in Fig. 23. During the reference tests no mixed halogenated substances were found. However, the graph reveals the formation of (mono-) brominated-chlorinated dibenzo-p-dioxins as the flame retarded foams were added. The total concentrations were approx. 1ng/m³ for the 'low-bromine' and 2 - 3 ng/m³ for the 'high-bromine' experiments. During the latter experiments approx. 15 - 20 % of the PCDD levels were reached.

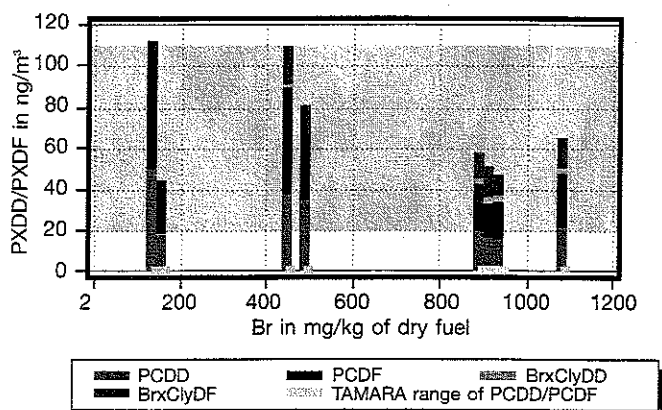


Fig. 23: Chlorinated and Brominated and mixed halogenated dibenzo-p-dioxins in all PUR test trials

Fig. 23 also displays Br containing dibenzofurans. Small amounts of these compounds had already been found during the reference test runs. Again, an increase in the concentrations could be detected with the increase in Br feed during the co-combustion tests. Given an analytical uncertainty of at least ± 30 %, all data obtained during the co-combustion trials stayed around this range.

Effects of the XPS Co-Combustion

Similar results are shown below for XPS foam co-combustion. Brominated congeners are present in extremely low concentrations of approx. 1-5 pg/m³ for the PBDD and 0.1 - 2 ng/m³ for the PBDF. Out of the large number of mixed brominated and chlorinated elements only those containing 1 or 2 Br atoms were analysed.

The bar plots in Fig. 24 and Fig. 25 compile the sum concentrations of dibenzo-p-dioxins and dibenzofurans broken down into pure chlorinated, pure brominated, and mixed halogenated compounds. For the reference test runs modelling the typical 'low-Br' residential waste, the graphs confirm the above cited low share that Br containing homologues, which are present in the order of 1 % [dibenzo-p-dioxins] or 5 - 10 % [dibenzofurans], add to the levels of the respective chlorinated compounds.

An additional input of Br into the incinerator promotes the specific formation of mixed halogenated congeners significantly. In order to evaluate the relevance of these increases, the total concentration of all halogenated substances of both compound classes needs to be compared with the typical range of PCDD/PCDF concentrations in TAMARA (see Table 10). This is presented as a grey area in each graph.

10 HALOGENATED DIBENZO-P- DIOXINS

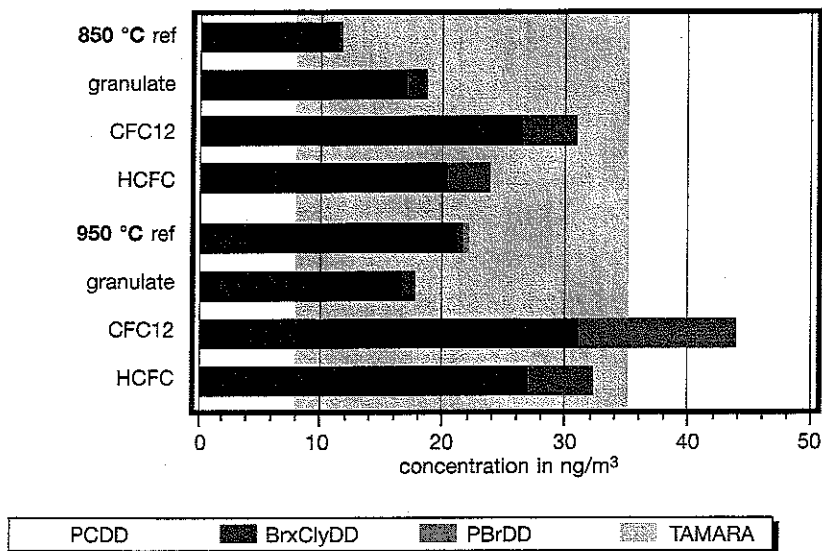


Fig. 24: Chlorinated, brominated, and mixed halogenated dibenzo-p-dioxins (XPS)

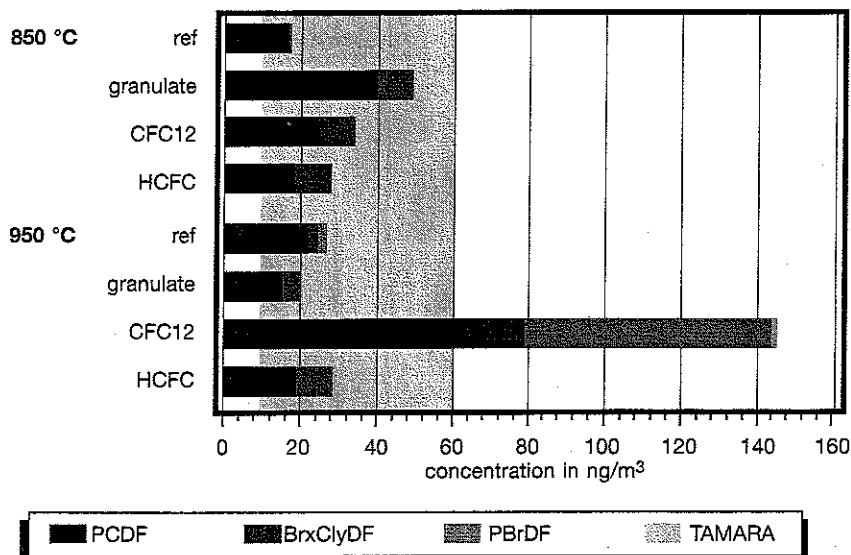


Fig. 25: Chlorinated, brominated, and mixed halogenated dibenzo-p-furans

This visualisation indicates that, in general, the levels of all halogenated dibenzo-p-dioxins and dibenzofurans for both foams stayed well within the band width of PCDD and PCDF concentrations found in TAMARA. Outstanding results are noted for the test run of CFC 12 blown XPS foam as the co-fuel at 950 °C. This test has already been discussed with respect to its poor

combustion conditions and the consequences for the PCDF concentrations in the flue gas. Whilst the lack of combustion control in the case of chlorinated compounds only promoted the formation of PCDF, for materials containing Br, both the levels of dibenzo-p-dioxins and dibenzofurans were affected. The furans, however, responded more sensitively.

10 HALOGENATED
DIBENZO-P-
DIOXINS

Effects of Bromine on PXDD/F

In Fig. 26 the totals of all Br containing dibenzo-p-dioxins and dibenzofurans are plotted against the Br input into the combustor. This is calculated as the sum of Br analysed in all residue streams. The dioxins seem to correlate with the increase in Br feed whereas the furans tend to plateau at concentrations exceeding 400 mg/kg Br in the feed. To obtain more detailed information further experiments, particularly those covering the feed range below 500 mg/kg, would need to be considered.

The correlation of dioxins at low Br levels and the plateau of furans at higher Br levels may be explained by the view that the same de novo synthesis found for the PCDD/PCDF [Vogg 1986, Stieglitz 1987, Hagenmaier 1987, Schwarz 1990] is responsible for the formation of the brominated and mixed halogenated compounds. In this case the bromide concentration in the fly ash could play a major role in this formation. The concentration of Br in the fly ash correlates with the Br feed. The reference test runs resulted in bromide concentrations below 2 wt.-%. This is far less than the typical concentration range of chlorides in fly ash from European full scale MSWC which covers approx. 3 - 6 wt.-% or even more in modern facilities. The Cl loads in the fly ash of the TAMARA were in most cases above 20

wt.-%. During co-combustion, the Br concentration in the fly ash was pushed up to more than 12 wt.-%.

It is considered that the concentration range for Cl typically found in fly ash from modern mass burn systems reaches a state of 'saturation' where the Cl is no longer able to control the formation of PCDD/PCDF. This is the reason why almost all attempts to verify the popular hypothesis of the dioxin promoting potential of PVC in waste combustion have failed. It has been proven that a relatively small addition of chlorides on top of high levels already present in the fly ash does not increase the formation of PCDD and PCDF significantly [Kerber 1994, Vehlow 1994, Chandler 1995].

However, from zero to the concentration at which this level of saturation is reached there is some kind of correlation between the concentration of the respective halogen in the fly ash and the PCDD/PCDF levels in the raw gas. Recently published results from small scale experiments modelling the influence of PVC on PCDD/PCDF formation in the raw gas of a fluidised bed combustor, seem to support this hypothesis [Wikstrom 1995].

The same type of influences as those outlined for Cl can be expected between the bromine level and the formation of Br containing dibenzo-p-dioxins and dibenzofurans.

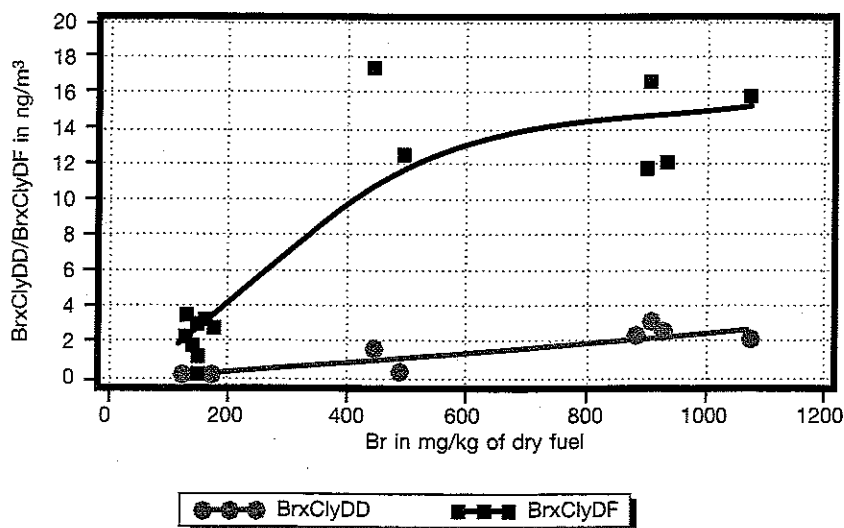


Fig. 26: Sum of brominated and mixed halogenated dibenzo-p-dioxins and dibenzofurans versus Br feed

In Fig. 27 the total concentrations of all Br containing dibenzofurans are depicted as a function of the Br concentration in the filter ash.

For comparative reasons results achieved during the co-combustion of flame retarded XPS foams have been included into this graph. It should be noted that the sampling and analysis during the XPS co-combustion was performed by BASF using a different sampling and clean-up method [Brenner 1995].

For the XPS co-combustion, the Br concentrations in the fly ash were increased from 0.5 to 5 wt.-%. The PUR tests resulted in higher Br levels, reaching almost 13 wt.-% in the fly ash. These differences may be attributed to operating conditions as well as to sampling and analytical error ranges. Nevertheless, both test results support the same conclusions. The results seemed to be more consistent for the furans than they were for the dioxins.

In both cases the Br presence in the fly ash did slightly influence the amount of bromine containing dibenzo-p-dioxins, whereas the impact on the formation of dibenzofurans was more pronounced. The combination of results for both XPS and PUR supports the reasoning for the potential influences of halogens on the formation of halogenated dibenzo-p-dioxins and dibenzofurans discussed above.

With low concentrations of Br in the fly ash there appeared to be a good correlation with the raw gas concentration of Br containing dibenzo-p-dioxins and dibenzofurans. At levels between 4 and 8 wt.-% of Br in the fly ash a plateau was reached and a further increase in Br feed no longer increased the level of these compounds.

The maximum addition of foam during the TAMARA experiments (3 wt.-%) reflects more or less the limits of technical feasibility. The low density of PUR and XPS foams prevents a higher fraction of these materials being added to a full scale MSWC.

For that reason it can be concluded that flame retarded XPS or PUR foams which are combusted together with residential waste in a full scale MSWC will not enhance the total level of halogenated dibenzo-p-dioxins and dibenzofurans in the raw gas to a greater extent than that found in TAMARA.

If we assume that the toxicity of brominated or mixed halogenated dibenzo-p-dioxin and dibenzofuran congeners is close to that of the respective PCDD/PCDF then we can conclude that the raw gas is not significantly altered by the addition of bromine containing XPS or PUR foams. This implies that there is no risk at all in the emission of these compounds as long as an effective air pollution control system is installed.

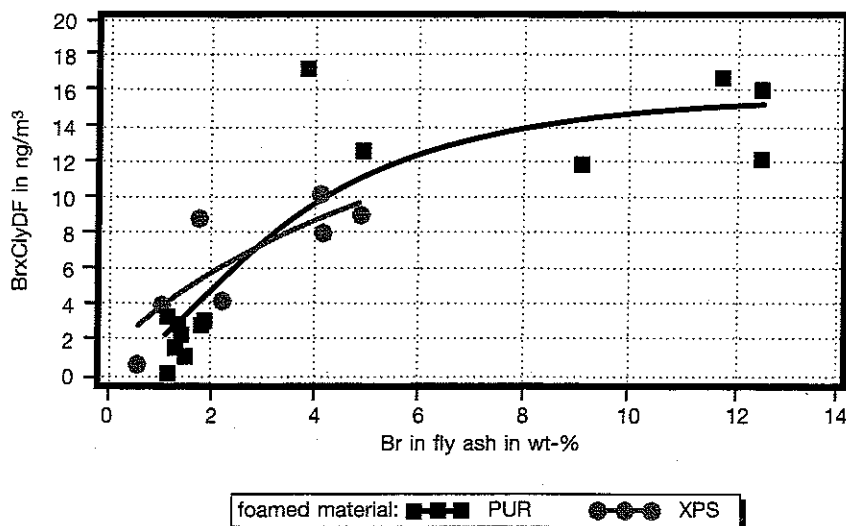


Fig. 27: Brominated and mixed halogenated dibenzo-p-dioxins in the flue gas versus Br in the fly ashes

11 CONCLUSIONS

11 CONCLUSIONS

The main objectives of these foam combustion trials were to establish information on :

- the thermal destruction of the blowing agents CFC 12 and HCFC 22, 142b
- the thermal destruction of flame retardants and
- the distribution of additional F and Br fed with the foam.

In addition, the in-depth review of the potential influence of co-combustion on the formation of chlorinated, brominated, and mixed halogenated dibenzo-p dioxins and dibenzofurans lead to these most important results :

The overall burnout, particularly in the bottom ash and fly ash, was excellent during all test trials. The burnout correlated with the combustion temperature and the calorific heat value of the waste fuel. It was not negatively influenced by the addition of XPS granulates or PUR and XPS foam.

The tested foam materials added substantially to the Br content in the incinerator. An increase by a maximum factor of 6 was attained. The Br levels in the bottom ash stayed almost constant during all experiments and the additional Br load was more or less totally released into the flue gas. This indicates that the bromine containing flame retardant is first released from the foam and then burnt in the gas phase. The formation of HBr and Br concentrations in the fly ash thus show a strong correlation with the Br in the feed.

During the foam experiments considerable amounts of F were also introduced into the combustor which caused an increase in the F content by a factor of about 6 for XPS and 1.5 for PUR. The fluorine balance suffered losses, presumably due to reactions with silicate matter. Most of the additional F in the feed was found as HF in the flue gas. This fraction increased with increasing combustion temperature. The fly ash transported only a small percentage of F even though its concentration in this sample correlated with the F input. F concentration in the bottom ash was little affected.

The Cl level in the feed was only increased by about

20 to 25 % when the CFC 11 blown PUR and the (H)CFC blown XPS foams were added. The Cl, nevertheless, promoted the volatilisation of some thermally mobile elements such as K, Cu, Zn, As, Cd, Sn, and Pb at the higher combustion temperature. At 850 °C only minor effects could be observed. The mobilisation of such metals prevents them from forming water soluble compounds in the bottom ashes which is beneficial to co-combustion in terms of bottom ash quality.

The enhanced levels of acid gases do not challenge a state-of-the-art air pollution control system such as a two-stage wet scrubber. The HCl does not exceed typical raw gas concentrations excessively and the HCl emissions were always < 2 mg/m³. HBr was present in low concentrations as was HF. The emission values measured for HF were < 0.2 and those for HBr < 0.8 mg/m³. All these values comply well with the most stringent air emission regulations and create no pollution problem at all.

The CFC 12 used in former years as a blowing agent for foams is quite a stable compound. At a combustion temperature of around 900 °C over 99.9 % thermal destruction is achieved for CFC 12. CFC 11 is already destroyed at lower temperatures. The partly halogenated HCFC 22 and 142b were never detected in the flue gas of TAMARA. The calculated destruction efficiency is far better than 99.99 % even at 850 °C.

The sampling and analysis of chlorinated, brominated and mixed halogenated dibenzo-p-dioxins and dibenzofurans was performed by different experienced analytical laboratories for each campaign. The compatibility of results for the PUR campaign concerning the chlorinated elements were excellent. The inter-laboratory results for the brominated and mixed halogenated species were not in such close agreement but in view of the complex spectra, lack of standards and frequently low concentrations, they must be considered satisfactory.

No significant increase in PCDD and PCDF raw gas levels in connection with the co-combustion of PUR or XPS could be detected.

The brominated compounds PBDD and PBDF were

11 CONCLUSIONS

generated at very low levels of some pg/m^3 in the case of PBDD and typically $< 1 \text{ ng}/\text{m}^3$ for PBDF. These concentrations are close to the detection limit and allow no clear-cut information on whether there is a correlation with the Br input. The production of mono- and dibrominated mixed halogenated dibenzo-p-dioxins, and dibenzofurans could also be detected, at very low concentrations.

There is an apparent linear correlation between the specific formation of mixed brominated congeners in the raw gas and Br input. The increase, however, is moderate and amounts to a concentration level of approx. 20 % of PCDD or 50 % of PCDF if the Br input is increased by a factor of 6 as in the case of XPS foam. A saturation effect can be seen in excess of 5-10 wt% Br in the fly ash. Although rigid polystyrene foams ($15\text{-}30 \text{ kg} / \text{m}^3$) produced from expandable polystyrene (EPS) beads were not included in these studies, it could be generally assumed

that such a study with flame retarded EPS foams would have resulted in similar emissions of HBr and halogenated dibenzodioxins and dibenzofurans, as supported by the results from the XPS granulate.

Recommendations :

Assuming that Br containing congeners exhibit the same degree of toxicity as chlorinated ones and that abatement technologies work at a comparable efficiency. It can be concluded that the brominated and mixed halogenated dibenzo-p-dioxins and dibenzofurans neither add substantially to the overall hazard of the raw gas of a MSWC, nor to that of air emission.

An assessment of all the results clearly states that co-combustion in a modern MSWC is an environmentally recommended option for the disposal of foams. The disposal strategy is simple, makes full use of the energy of the plastic material, and offers an overall environmental benefit compared with other disposal options.

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12 REFERENCES

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