

# ENERGY AND MATERIAL RECOVERY BY CO-COMBUSTION OF WEEE AND MSW

**J. Vehlow<sup>1</sup>, B. Bergfeldt<sup>1</sup>, H. Hunsinger<sup>1</sup>, K. Jay<sup>1</sup>, H. Seifert<sup>1</sup>, F.E. Mark<sup>2</sup>, L. Tange<sup>3</sup>, D. Drohmann<sup>4</sup>**

<sup>1</sup> Forschungszentrum Karlsruhe GmbH, ITC-TAB, POB 3640, D-76021 Karlsruhe, Germany

<sup>2</sup> Dow Europe, Horgen, Switzerland, <sup>3</sup> Eurobrom B.V. DSBG, Rijswijk, The Netherlands, <sup>4</sup>Great Lakes Chemical, Bergisch Gladbach, Germany

Co-combustion tests of high Br WEEE polymers showed that 60 – 80 % of Br enter the gas phase. At high Br loads Br<sub>2</sub> was formed and a reducing agent had to be added to the alkaline scrubber for good removal efficiency. From the effluents of the wet scrubbers up to > 99 % of the Br in the raw gas can be recovered. Br promoted the volatilisation of heavy metals during fuel bed burnout. The halogen inventory did not influence the PXDD/F level in the raw gas. The share of Br containing congeners increased with increasing Br/Cl ratio.

## Introduction

Waste from electrical and electronic equipment (WEEE) is rapidly growing and becoming more and more complex with a large number of different polymer materials. Most of these plastics are flame retarded by means of brominated organic compounds. Recovery and recycling of this material mix with various types of plastics, metals and composites is difficult. In former test programs of Forschungszentrum Karlsruhe (FZK) and APME (Association of Plastic Manufacturers in Europe) it has been demonstrated, that co-combustion together with municipal solid waste is an ecologically sound and economically viable waste management route for limited amounts of WEEE polymers [Vehlow et al. 2000]. This strategy implies the chance to combine the inertisation of organic matter with the recovery not only of energy but also of bromine and eventually heavy metals. A recent research program, co-sponsored by FZK, APME, and EBFRIP (European Brominated Flame Retardants Industry Panel), extended the co-feeding to higher amounts of various types of WEEE polymers and focussed mainly on the potential of Br recovery from the effluents of a wet scrubbing system. An important aspect in this respect are the limits for the formation of elementary bromine, its eventual influence on the formation of halogenated organic compounds in the flue gas, and the Br effects on the volatilisation of heavy metals.

## Material Characterisation and Experiment Design

The co-combustion experiments have been conducted in 2 one week campaigns at the Karlsruhe TAMARA pilot plant for waste incineration. The performance followed the strategies applied in the former test programs [Vehlow et al. 2000].

TAMARA has 3 feeding systems for waste and other fuel fractions. The reference fuel was a mix of pre-treated municipal solid waste (MSW), enriched by 30 % of a pelletised refuse derived fuel (RDF). The lower calorific value was thus adjusted to approx. 10 MJ/kg. During the co-combustion tests the RDF was replaced by WEEE polymers in a way, that the total energy input into the furnace was kept constant at approx. 0.5 MW<sub>therm</sub>. Table 1 compiles the actual feeding conditions.

**Table 1** Mean data of the input of MSW, RDF and the WEEE polymer materials in kg/h

	test	1		2		3		4		5	
		fuel	kg/h	fuel	kg/h	fuel	kg/h	fuel	kg/h	fuel	kg/h
camp.1	fuel 1	MSW	138	MSW	138	MSW	138	MSW	138	MSW	138
	fuel 2	RDF	59	MIX2	40						
	fuel 3					MIX1	40	TV/BP1	25	TV/BP2	25
camp.2	fuel 1	MSW	138	MSW	138	MSW	138	MSW	138		
	fuel 2	RDF	54					RDF	9.5		
	fuel 3			TV/BP2	25	TV/BP2	27	PWB	50		

The WEEE polymers used in the tests came from different sources. Their major properties are shown in Table 2.

**Table 2** Characteristics of the WEEE materials (LHV : lower heating value)

co-fuel		LHV MJ/kg	ash wt %	C wt %	H wt %	Br wt %	Cl wt %	S wt %
MIX1	mixed WEEE shredder residue	31	10.6	67.4	6.84	1.30	3.15	0.11
MIX2	mixed WEEE shredder residue	25.4	18.9	56.6	5.97	1.75	5.65	0.10
TV/BP1	shredded television back plates	38	1.2	82.2	7.21	3.50	1.90	0.03
TV/BP2	shredded television back plates	35.7	1.2	81.5	7.09	2.65	0.39	0.02
PWB	shredded printed wiring boards	16	48	53.7	5.59	1.85	2.30	0.08

All input and output mass flows have been recorded, sampled and analysed in order to calculate balances of single elements. Great efforts were made to analyse the different Br (HBr and Br<sub>2</sub>) and S species (SO<sub>2</sub> and SO<sub>3</sub>) in the gas phase.

### Burnout of all Residues

As experienced in former tests in TAMARA, the addition of high calorific waste fractions did not deteriorate the combustion control and the burnout of the solid residues and the off gas.

Fig. 1 documents that > 99 % of the total C fed into the incinerator were transformed into CO<sub>2</sub> with no significant difference between the reference tests (MSW.1 and MSW.2) and the co-combustion tests. The grate ashes contributed most to the products of incomplete combustion with 0.3 – 0.6 wt-% of TOC, again with no significant difference between the single test runs. The contribution of the other residues was much lower. The gas phase contained very low CO (<2 mg/m<sup>3</sup>) and TOC (<1 mg/m<sup>3</sup>) levels.

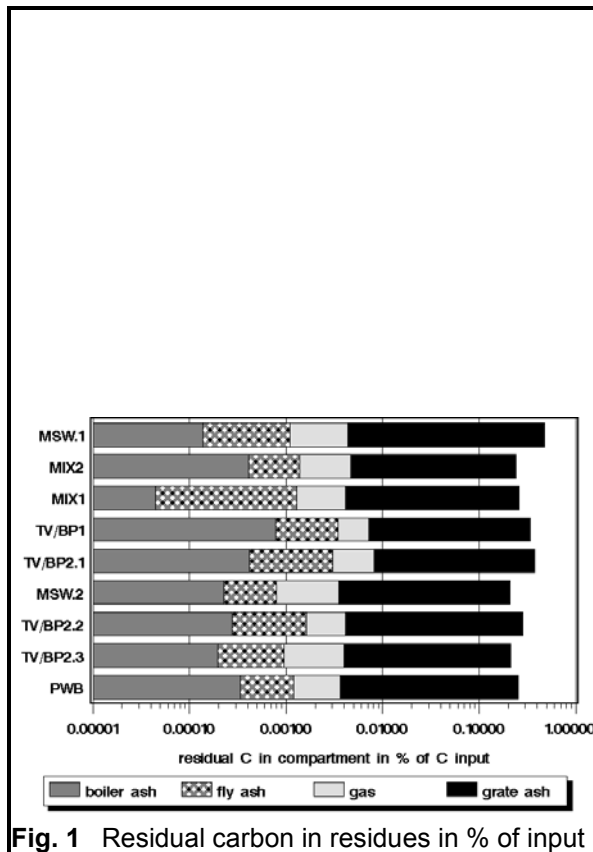


Fig. 1 Residual carbon in residues in % of input

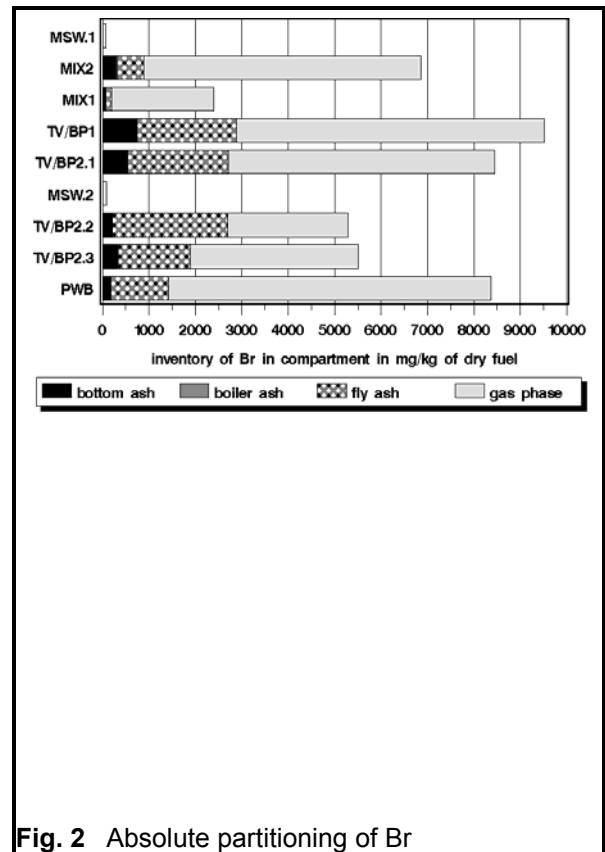


Fig. 2 Absolute partitioning of Br

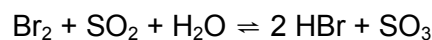
### Partitioning of Br and its Speciation in the Gas Phase

The input of Br into the system along with the WEEE materials reached almost 1 wt-% in the dry fuel. Fig. 2 visualises the absolute partitioning of Br between the residue compartments. The major fraction is always found in the gas phase. Recent data available in literature document a typical share of 80 – 90 % of the Br entering the raw gas [Belevi & Mönch 2000] in MSW combustion which is in line with our findings during the reference tests. The TV back plates only are showing a rather high fraction of Br staying in the fly ashes.

The maximum Br concentration established in former tests was almost 250 mg/m<sup>3</sup>. Up to this concentration only traces (< 0.1 mg/m<sup>3</sup>) of Br<sub>2</sub> could be present and all Br showed up as HBr.

These tests, however, revealed at higher Br loads of the raw gas the formation of Br<sub>2</sub>. The speciation of the gaseous Br analysed in all tests is plotted as a function of the total Br concentration of the raw gas in Fig. 3.

It is well known that Br<sub>2</sub> oxidises SO<sub>2</sub> to SO<sub>3</sub> according to



Hence as soon as Br<sub>2</sub> was analysed in the raw gas, also SO<sub>3</sub> could be found (Fig. 4).

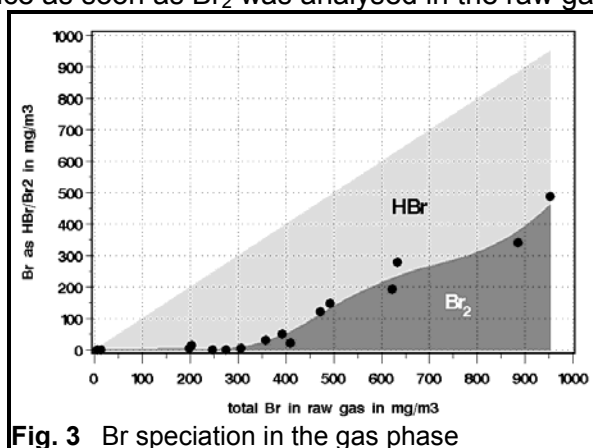


Fig. 3 Br speciation in the gas phase

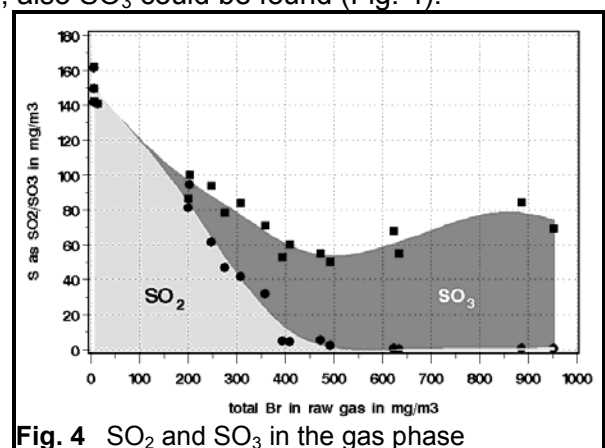


Fig. 4 SO<sub>2</sub> and SO<sub>3</sub> in the gas phase

## Recovery of Br

It has been demonstrated in former TAMARA campaigns that the implemented two-stage wet scrubbing system enables a very efficient removal of HBr in the acid scrubber [Vehlow & Mark 1995]. Br<sub>2</sub> present in the flue gas, however, is not absorbed in an acid solution and also in an alkaline scrubber its removal is rather limited. The measure of choice is the addition of a (cheap) reducing agent to the alkaline scrubber. Industrial hazardous waste incinerators use in most cases Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> or Na<sub>2</sub>SO<sub>3</sub>. After having experienced that Br<sub>2</sub> is formed, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> has been added to the second scrubber of TAMARA. This strategy resulted in a very high Br removal efficiency over the total air pollution control system.

**Table 3** Br in raw gas, scrubber effluents, and total removal efficiency  $\eta$  (\*: without Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>)

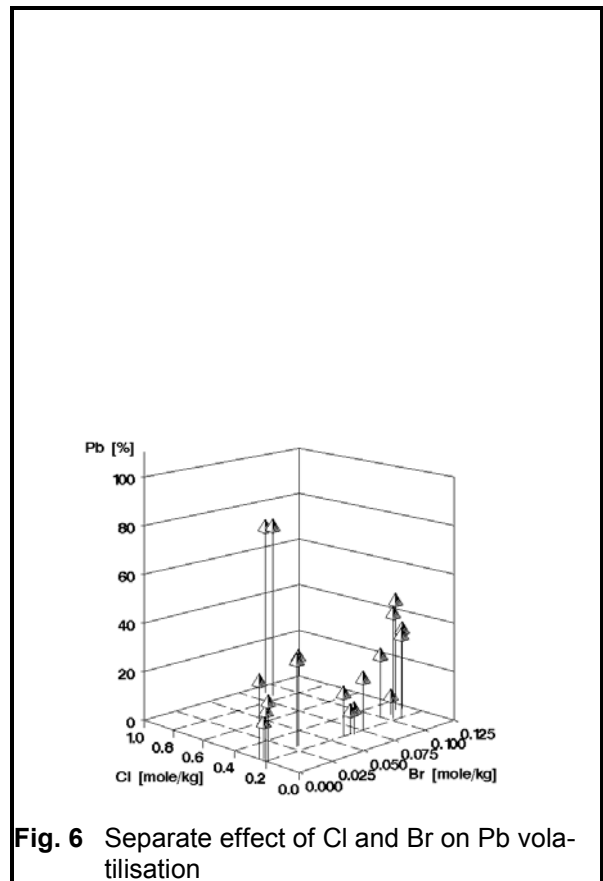
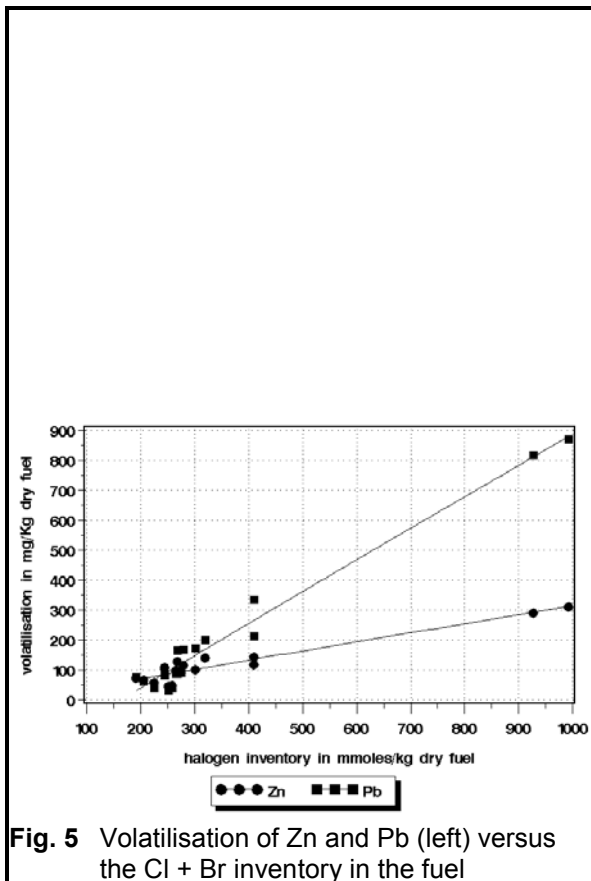
test	HBr mg/m <sup>3</sup>	Br <sub>2</sub> mg/m <sup>3</sup>	scrub. 1 g/l	scrub. 2 g/l	$\eta$ %
MIX1	190	9	2.5	3.2	99.18
MIX2	340	240	3.7	7.7	68.78*
TV/BP1	400	135	6.4	14.3	93.18
TV/BP2.1	415	35	7.3	11.3	95.77
TV/BP2.2	225	0.2	4.5	4.2	99.33
TV/BP2.3	280	3.8	7.6	8.7	99.22
PWB	405	415	9.6	20.4	96.79

The HBr and Br<sub>2</sub> concentrations in the raw gas, the resulting Br concentrations of the co-combustion tests in both scrubbers, and the total removal efficiency are compiled in Table 3 for all co-combustion tests. With the exception of one test, where no Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> had been added, the overall removal efficiency is exceeding 93 and in some cases reaching even > 99 %. That means that 60 – 70 % of the total Br input into the system have been accumulated in the scrubber solutions.

In the acid scrubber effluents concentrations of up to 10 g/l were obtained. In a special counter-current bypass scrubber for concentration of HBr in the acid scrubbing stage maximum Br concentrations up to 18 g/l could be reached. The most convenient Br recovery method from acid solutions should be distillation. In the alkaline scrubber with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> addition up to 20 g/l of Br<sup>-</sup> were found. This bromide can be recovered by crystallisation processes. At the moment activities are on the way to reveal the most suitable scheme for Br recovery from waste incineration scrubber effluents.

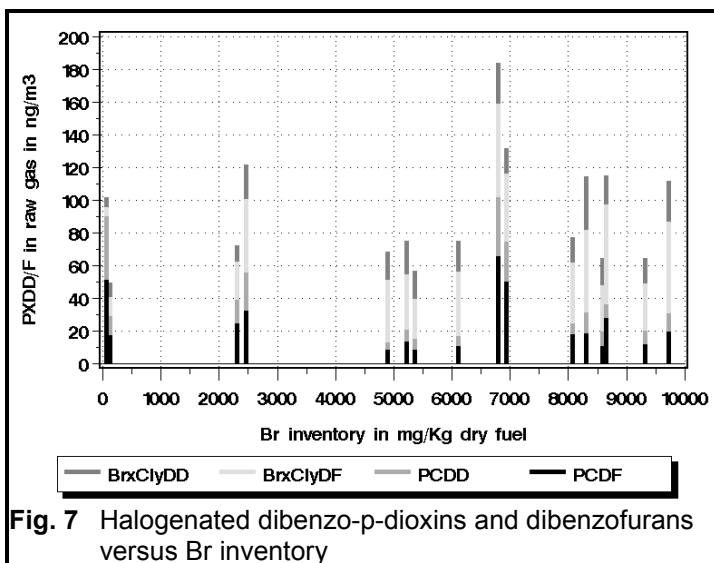
## Heavy Metal Volatilisation

It is well known that Cl in a fuel promotes the volatilisation of heavy metals out of the fuel bed by the formation of metal chlorides [International Ash Working Group 1997]. The same effect should theoretically be seen for Br, since many bromides have similar low boiling points as the chlorides of the respective metals. In MSW incineration the Br effect is not recognised due to the low concentration of Br compared to Cl in waste. Furthermore, the molar concentration of the halogens is controlling the volatilisation and that again, the much higher molar weight of Br compared to that of Cl prevents a separation of the influence of both elements. However, if the Br inventory is increased, the specific activity of Br becomes evident. This could be demonstrated in former TAMARA campaigns [Vehlow 2000]. Fig. 5 documents that there is a correlation of the accumulated molar inventory of Cl and Br on the volatilisation of the heavy metals Zn and Pb out of the fuel bed. The fuel bed temperature showed no major changes during the tests. The three-dimensional plot in Fig. 6 on the dependency of Pb volatilisation of Cl and Br shows, that the effect of Br is rather high (compare concentration ranges).



### Effect of Br on the Formation of Halogenated Dibenzo-p-dioxins and Dibenzofurans

The former tests on the co-combustion of various plastic waste streams in TAMARA have already made sure, that neither high amounts of Cl [Vehlow et al. 1996], nor those of Br [Vehlow & Mark 1995, Vehlow et al. 2000] do influence the level of halogenated dioxins in the raw gas of waste incineration plants, provided a good combustion control is taken care of.



These results could more or less be confirmed by the tests described in this report. The majority of the obtained mixed halogenated congeners contained one Br atom per molecule. The contribution of compounds with two Br atoms could reach the same order of magnitude for high Br levels in the fuel. Species with three Br atoms were very rare. Purely brominated compounds of this class could hardly be detected. The bar plot in Fig. 7 shows again that there is no correlation between the Br inventory in the waste fuel and the total concentration of all halogenated dioxins and furans in the raw gas.

However, as experienced before [Funcke et al. 1997, Vehlow et al. 2000] and described

theoretically already [Funcke et al. 1993], there is a correlation between the molar Cl/Br ratio in the waste and the ratio of chlorinated and Br containing homologues in the flue gas. The graph shows clearly that the amount of PCDD/F is decreasing with increasing Br inventory and that at the same

time the amount of mixed halogenated homologues is increasing. At high Br level more Br containing dioxins and furans are found than PCDD/F.

### Energy Recovery in Waste Incineration

All German and most European waste incineration plants are equipped with energy recovery systems. The boiler of a modern waste incinerator has a primary energy efficiency of > 80 % which is almost as high as that in a coal fired power plant. If electric power is generated the efficiency is typically 20 – 24 %. In this case the efficiency of power plants is not reached due to lower steam parameters. These are set to reduce corrosion in waste boilers.

In many modern waste incineration plants combined heat and power strategies are followed and that means that a high share of the energy inventory of any waste fraction – including plastic materials – can be recovered in such facilities.

Since the co-combustion tests revealed no negative influence of neither the high amount of polymers nor the high level of halogens on the combustion process, this degree of energy recovery will also be reached if WEEE polymers are disposed of in municipal solid waste incineration plants.

### Conclusions

Co-combustion tests of up to 22 wt-% of flame-retarded WEEE polymer fractions together with a pre-treated municipal solid waste in the Karlsruhe TAMARA pilot plant for waste incineration extended the range of Br inventory in the waste to an approx. 100 times higher level than in MSW incineration plants. The major findings were:

- The addition of high loads of plastic material with high loads of Br had no negative influence upon the combustion performance in the waste incinerator and allows an efficient energy recovery.
- 60 – 80 % of the Br inventory were released into the raw gas. As soon as the total Br concentration in the gas phase exceeded 300 mg/m<sup>3</sup> the appearance of elementary Br<sub>2</sub> could be observed. The appearance of Br<sub>2</sub> went along with the disappearance of SO<sub>2</sub> and the finding, that all S in the gas phase was present as SO<sub>3</sub>.
- If a reducing agent is added to the neutral scrubber, high abatement efficiencies of even > 99 % can be obtained in wet scrubbing systems.
- In the effluents from the acid scrubber of TAMARA a Br concentration of up to 10 g/l could be reached. This concentration could be increased to 18 g/l to a maximum in the first stage of a counter-current two stage acid scrubbing system. In the second scrubber of TAMARA Br concentrations up to 20 g/l were obtained.
- This enables the recovery of 60 – 80 % of the Br inventory from the effluents of the gas scrubbers.
- As experienced in earlier co-combustion tests the volatilisation of heavy metals was promoted by the Br as well as by Cl.
- The elevation of the Br inventory did not increase the formation of chlorinated dibenzo-p-dioxins and dibenzofurans. Like in former tests an increased Br concentration correlated with an increase in Br containing congeners with the preference on the formation of dibenzofurans. The summation of all halogen containing dibenzo-p-dioxins and dibenzofurans resulted in an almost constant total concentration.

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