

Recycling of bromine from plastics containing brominated flame retardants in state-of-the-art combustion facilities

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SUMMARY

Implementation of the EU Directive on the management of waste electrical and electronic equipment (WEEE) will require diversion from landfill and the achievement of specific recycling and recovery targets. In many instances, mechanical recycling of WEEE is not eco-efficient due to local market circumstances and environmental requirements.

Trials conducted at the TAMARA pilot scale municipal solid waste combustion (MSWC) facility in the Forschungszentrum Karlsruhe (Karlsruhe Research Centre) have demonstrated that in modern MSWC plants equipped with suitable wet scrubbing systems, recycling of the bromine in plastics waste containing brominated flame retardants is technically feasible. Different types of commercial bromine-based finished products can be produced, including bromine itself, hydrogen bromide or sodium bromide.

With the separate collection of WEEE, full-scale commercial operations can be assured a regular raw material supply. Given suitable adaptation, sufficient MSWC capacity already exists in Europe to recycle all of the bromine available in WEEE plastics. Thus recycling of bromine adds an important new dimension to the existing range of eco-efficient waste management options available for end-of-life WEEE plastics.

1 INTRODUCTION

Plastics have become key to innovation in the electrical and electronic (E&E) industry, making information, communication and convenience accessible and affordable for increasing numbers of people. Initially used for E&E equipment housing, plastics now play an important part in the equipment's entire construction and functionality, enabling reduced weight, miniaturisation and reduced production costs. The rapid pace of technology change is increasing the quantity of waste electrical and electronic equipment (WEEE) faster than the growth of average municipal waste. A second consequence of innovation is that the composition of WEEE will become increasingly complex.

Depending on their specific application, plastics in some E&E equipment must incorporate flame retardants, both to meet public demands for fire safety and to comply with fire safety regulations. The presence of flame retardants in E&E plastics waste must therefore be taken into account in waste management decision making, influencing both the choice and design of recycling processes. End-of-life E&E equipment needs to be viewed as a valuable resource rather than as a problem, but it is important that the route chosen to recover this resource is eco-efficient, combining maximum environmental protection with sound economics.

Trials involving WEEE plastics [1] and insulation foams [2] containing brominated flame retardants have demonstrated that energy recovery is an eco-efficient waste management option, satisfying the most stringent emission regulations. This can be a preferable recovery route either where recycling is deemed to be impractical or, in a decreasing number of cases, where historic waste fails to meet legislative requirements for product quality.

The trials described in this report have evaluated the impact of introducing significantly higher levels of plastics containing brominated flame retardants into an energy recovery facility's feed. This could be expected to provide specific benefits in terms of the volatilisation of heavy metals from the bottom ashes, opening the technical possibility of recycling both these and the bromine, and increasing the potential for safe use of grate ashes in applications such as building and construction.

The report outlines the role of brominated flame retardants in E&E plastics, describes a pilot scale demonstration of bromine recycling, and discusses the outlook for commercial bromine recycling when secure supplies of WEEE become available. The technical information provided will be of help to decision makers seeking optimum solutions to divert E&E plastics waste from landfill.

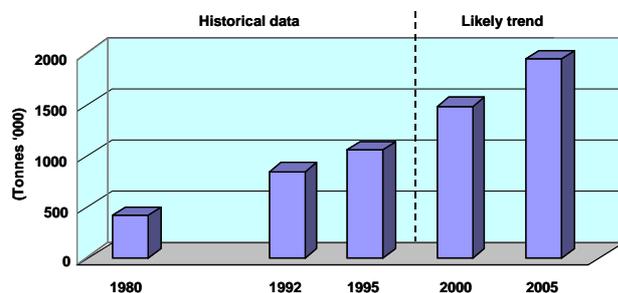
PLASTICS IN WEEE

2 PLASTICS IN ELECTRICAL AND ELECTRONIC EQUIPMENT

The definition of electrical and electronic (E&E) equipment used in this report is the same as that used in the proposal for an EU Directive on waste E&E equipment [3]. In the proposal, E&E equipment is defined as all appliances dependent on electric currents or electromagnetic fields in order to work, and which use AC voltages up to 1000 V or DC voltages up to 1500 V. The definition includes wiring and cable that is part of E&E equipment, but not transmission cables, for example those that are under the sea or embedded within structures such as buildings and roads.

2.1 Consumption of plastics in the E&E sector

The production of E&E equipment is growing rapidly as markets expand, as new applications are developed and as new technology replaces old. Plastics have become an increasingly important part of E&E equipment; the average proportion has increased from 12% to 20% by weight during the last 10 years. The total quantity of plastics used in E&E equipment has therefore increased significantly and is projected to continue to rise.



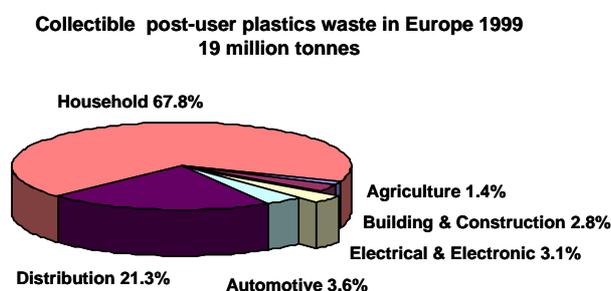
Source: TN Sofres Consulting for APME

Figure 1. Consumption of plastics in the E&E sector

The largest increases are occurring in the most innovative sectors. IT and telecommunications are bigger users of plastics than any other type of E&E equipment.

2.2 Plastics in E&E equipment waste

E&E products can have a relatively long lifetime, so the quantity of E&E waste generated today is a function of the production levels of many years ago, longevity of the equipment and the rate of replacement through technical obsolescence. The weight of plastics in E&E waste in 1999 was 733,000 tonnes in Western Europe and represented 3.1% of total collectable post-consumer plastics waste.



Source: TN SOFRES Consulting for APME

Figure 2. Plastics waste in Europe, by sector

Today's E&E equipment waste includes a range of end-of-life products, each of which can incorporate one or more different polymer types - see Table 1.

Table 1. Typical major plastic types used in E&E equipment

Product category	PE	PP	PVC	PS	ABS	PC	PA	PET	Other
Large domestic appliances	•		•	•	•	•	•	•	PU
Small domestic appliances	•	•	•	•	•	•	•		Epoxy
Data processing equipment	•	•	•	•	•		•	•	Epoxy, PU
Brown goods		•	•	•	•	•	•	•	PET
Telecommunications equipment					•	•			
Electrical equipment						•	•	•	Thermosets
Office equipment	•	•	•	•	•	•	•	•	Epoxy, PU
Medical equipment			•		•		•		
Cables	•		•						

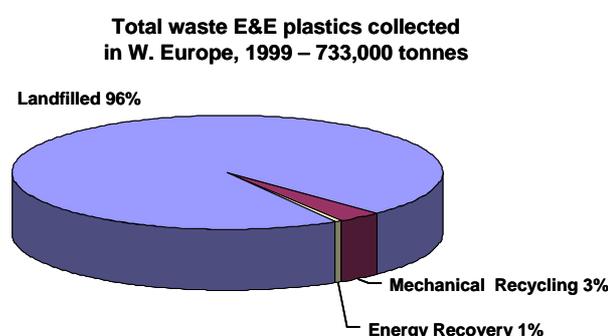
Some examples of the types of products included in these categories are as follows:

- Large domestic appliances: refrigerators, washing machines
- Small domestic appliances: vacuum cleaners, toasters
- Data processing equipment: mainframe and personal computers, peripherals
- Brown goods: televisions, radios
- Telecommunications equipment: telephones, fax machines
- Electrical equipment: drills, sewing machines
- Office equipment: photocopiers, electric typewriters
- Medical equipment: radiotherapy equipment, dialysis machines

The plastics fraction of waste electrical and electronic equipment, referred to in this report as WEEE plastics, typically becomes available for recovery after one of two mechanical treatment processes. These can be either manual dismantling and separation or mechanical shredding and refining. There is also a thermal separation route using pyrolysis.

2.3 Management of E&E plastics waste

The majority of WEEE plastics, as much as 96%, is currently landfilled.



Source: TN Sofres Consulting for APME

Figure 3. Management of post-consumer E&E plastics waste

APME considers the most important waste management objective to be the diversion of this waste from landfill, and in its place eco-efficient recovery. A constructive debate is required on the optimal solutions for E&E waste recovery, one based on experience and high quality technical and statistical studies. APME sponsors research and large-scale trials to determine the most eco-efficient recovery methods for the plastics fraction.

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2.4 Metals in WEEE

As reported previously [1], plastics are not the main source of metals in E&E waste. In addition to its plastics content, E&E equipment consists of a combination of many materials, including several ferrous and non-ferrous metals. The quantity of these which remain with the waste plastics fraction will depend on the type of separation process used. A significant number of the heavy metals, especially Cu, Zn, Sn and Pb, are present as pure metal (e.g. Cu wire) or alloy (e.g. solder). Before any recovery of the plastics content of waste electrical and electronic equipment (WEEE), for example by mechanical recycling or energy recovery, the metals fraction must be efficiently separated out.

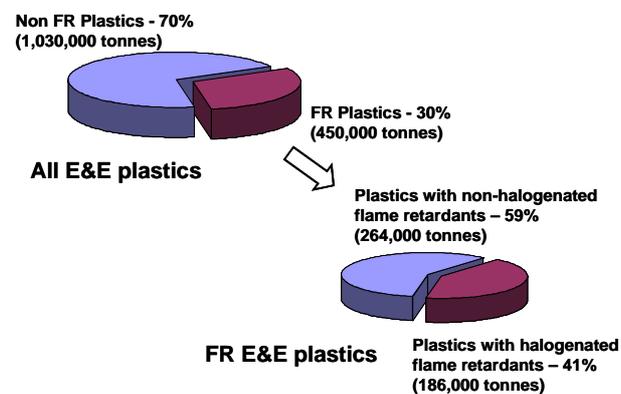
The levels of metals and heavy metals in the plastics content of WEEE depends on several factors. In particular they are influenced by the type of equipment and when it was produced. Data comparing plastics from different sectors, and comparing WEEE plastics with E&E plastics produced today have been published by APME [1]. The data show that the level of heavy metals in today's WEEE plastics is similar to that of typical municipal solid waste. Over the years since the products that are today's waste were produced, there have been many changes in materials, colorants and additives. The E&E plastics being produced now, which will become waste in the future, contain a significantly lower total level of heavy metals than the plastics in today's WEEE.

2.5 Flame retardants in WEEE plastics

The use of flame retardants in certain E&E plastic components is essential to ensure safety and comply with relevant safety regulations. There are several families of flame retardants which can be based on bromine, chlorine, phosphorus or nitrogen. In addition there are inorganic flame retardants. On average, 30% of the plastics used in E&E equipment contains either halogenated or non-halogenated flame retardants.

Figure 4 shows the consumption data for the year 2000,

and the proportion of the two types of flame retardants used.

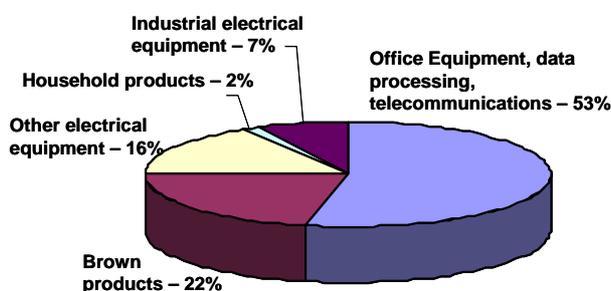


Source: TN SOFRES Consulting for APME

Figure 4. Use of flame retarded plastics in E&E equipment – 2000 data

Halogenated flame retardants have traditionally been used in plastics because of their efficiency and suitability with various types of plastics. Bromine and chlorine have been prevalent, with bromine typically preferred because it requires the lowest quantity of flame retardant for the highest level of fire safety. In addition to this resource efficiency advantage, bromine minimises the impact of the flame retardant additive on the polymer's performance.

Brominated flame retardants (BFRs) are used in several E&E components, the major applications being in equipment housings and printed circuit boards.



Source: TN Sofres Consulting for APME

Figure 5. E&E equipment using brominated flame retardants

Different types of brominated flame retardant have been used in E&E plastics:

- Tetrabromobisphenol – A (TBBPA)
- Octabromodiphenyl ether (Octa-BDE)
- Decabromodiphenyl ether (Deca-BDE)
- Oligomeric brominated flame retardants

Of these, TBBPA represents over 50% by weight of the BFR market. The first three are undergoing an EU risk assessment process which is expected to be finalised in 2002 for Octa-BDE and Deca-BDE and in 2003 for TBBPA.

2.6 Proposed EU WEEE Directive

Ten of the current fifteen member states of the European Union have either implemented, or intend to implement in the very near future, separate collection and recycling schemes for WEEE. The proposal for an EU Directive on waste electrical and electronic equipment [3] will harmonise requirements for its management. The draft Directive calls for separate collection of WEEE and lays down targets for its recovery and reuse/recycling. It sets an initial target for collection of 1.5 million tonnes per year in 2006. Assuming an average E&E equipment plastics content of 20 wt%, this equates to 300,000 tonnes of WEEE plastics and represents about half of the annual generation of WEEE plastics estimated by APME (see Figure 2).

A separate but parallel proposal for another Directive will impose restrictions on the use of certain substances in the production of new E&E equipment with effect from 1st January 2008 [5]. Included in the substances listed for phase-out are polybrominated biphenyls (PBBs) and the three polybrominated diphenyl ethers (PBDEs). However, specific provision is made in the draft Directive for a final decision on the suitability of using deca-BDE and octa-BDE, the PBDEs of relevance to E&E Equipment applications, following completion of ongoing risk assessments. This final decision is expected in 2002. Manufacture of PBBs has already

stopped, and one of the PBDEs, Pentabromodiphenyl ether, is scheduled to be phased out by the EU before the end of 2003.

2.7 Trends

In recent years the bromine industry has developed a range of brominated flame retardants based on oligomers which exhibit high compatibility with various plastic matrices. This has helped achieve a combination of good fire safety and mechanical performance of plastics in increasingly complex E&E equipment. The plastics industry has made available a range of raw materials which contain these new types of brominated flame retardants. Non-halogenated flame retardants such as phosphorus or mineral based compounds are also supplied.

TRIALS AT THE TAMARA PILOT PLANT

3 TRIALS AT THE TAMARA PILOT PLANT

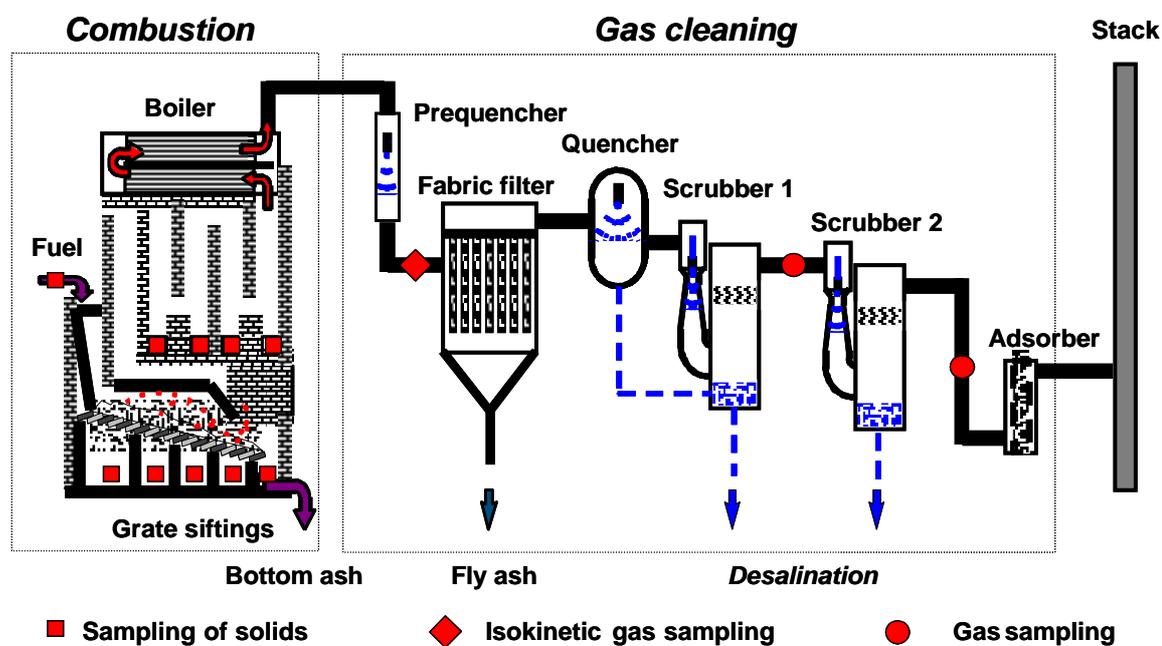


Figure 6. The TAMARA pilot plant for municipal solid waste combustion

3.1 Design and operation of the plant

The TAMARA pilot plant at Karlsruhe is a mass burning reciprocating grate type combustor with a nominal throughput of 200 – 250 kg/h of preconditioned waste [6]. A schematic drawing of the plant is shown in Figure 6. The design of the combustion chamber can be changed from the original counter-current into a parallel flow geometry by the installation of variable roof elements. For all of the trials described in this report, only two roof elements were installed, forming a middle flow configuration.

Dedusting is performed by a fabric filter consisting of PTFE fabric tubes coated with a GORETEX™ membrane. For flue gas cleaning there is a two-stage wet scrubbing system with a separate quench stage. The first scrubber is operated with a pH regime of 1 or lower to remove HCl, HBr, HF and Hg from the flue gases. The second scrubber is adjusted to a pH of approximately 7, mainly to absorb SO₂.

During all the test runs, the plant was operated with the combustion temperature in the first flue held at a constant level of approximately 1000°C. This temperature is at the upper end of the range found in full-scale plants. It was chosen in order to obtain a high release of volatile products out of the fuel bed and to achieve an optimum burnout in the gas phase.

3.2 Test program

Purpose

Building on earlier trials carried out in the TAMARA combustion plant [1,2, 6-9], the main purpose of this test program was to measure the influence of increasing levels of bromine on the combustion process and on all the outputs from the plant. This was achieved by adding specific WEEE fractions to the standard fuel mix. Of special interest was the effect of high bromine concentrations on metal volatilisation.

Standard and Test Fuels

The standard fuel used at TAMARA is a mixture of 70% organic/green waste and 30% refuse derived fuel (RDF). Addition of the RDF fraction brings the lower heat value of the mix up to a level of 9-10 MJ/kg, a level which is typical of MSW found in Western Europe. In this series of tests, the RDF fraction was replaced by a quantity of each of the test fuels that would provide an equivalent energy input.

The test material used in the trials were prepared quantities of specific plastics waste streams that would be representative of materials available in the year 2000.

The types of WEEE test materials used were as follows

- MIX 1 and MIX 2 – two types of WEEE shredder residues containing mixed polymers
- TV 1 – Shredded television housings
- TV 2 – Shredded television housings from a different source
- PWB – Shredded printed circuit boards (also known as printed wiring boards)

Tables 2 and 3 show a basic fuel analysis of these fractions.

Table 2. Fuel analysis of the WEEE fractions

	MIX 1	MIX 2	TV 1	TV 2	PWB
Lower Heat Value (MJ/kg)	31	25.4	38	35.7	16
Ash (%)	10.6	18.9	1.22	1.19	48
C (%)	67.4	56.6	82.2	81.5	53.7
H (%)	6.84	5.97	7.21	7.09	5.59
N (%)	2.94	2.81	0.99	0.66	1.90
S (%)	0.11	0.1	0.03	0.02	0.19
O (%)	8.2	8.24	1.07	3.24	8.44

Table 3. Analysis of the WEEE fractions (levels in mg/kg)

	MIX 1	MIX 2	TV 1	TV 2 1/2	TV 2 3/4	TV 2 5/6	PWB
Cl	31350	56400	19040	6850	1520	3540	23000
K	810	70	<20	540	570	750	720
Ca	9980	1260	<10	500	900	1000	17620
Cr	70	6	<1	<16	27	22	220
Mn	60	4	<1	7	<20	<12	230
Fe	1570	80	<2	145	640	225	3095
Ni	110	8	<1	16	30	35	470
Cu	2720	80	<1	20	60	140	66200
Zn	850	40	<1	210	305	220	1310
As	18	15	55	30	25	20	40
Br	13100	17400	34900	26600	26000	25000	18540
Rb	<10	.	<1	<20	50	<15	<20
Sr	70	4	<1	<7	<15	<10	160
Mo	6	95	6	5	5	5	3
Cd	70	110	70	20	22	13	40
Sb	6950	7190	23980	14540	13000	10900	5730
Sn	580	935	170	70	80	310	5550
Ba	390	<25	<20	120	290	135	770
Pb	3500	1010	220	145	170	220	4960

3.3 Bromine

Partitioning

Bromine is the major flame retardant related element in the WEEE materials. The absolute and percentile partitioning of Br are depicted in Figures 7a and 7b, which demonstrate the significant increase of the Br inventory during the co-combustion of the WEEE plastics. With the exception of MIX 1, Br inventories between 0.5 and 1 wt% were achieved in all co-combustion tests. This level is more than 100 times higher than the typical concentration in MSW.

TRIALS AT THE TAMARA PILOT PLANT

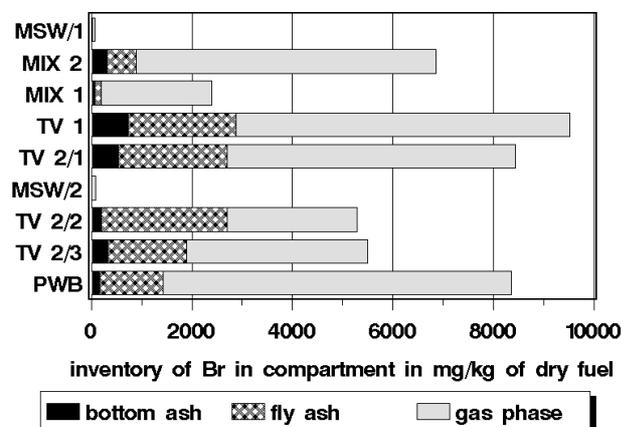


Figure 7a. Absolute partitioning of Br

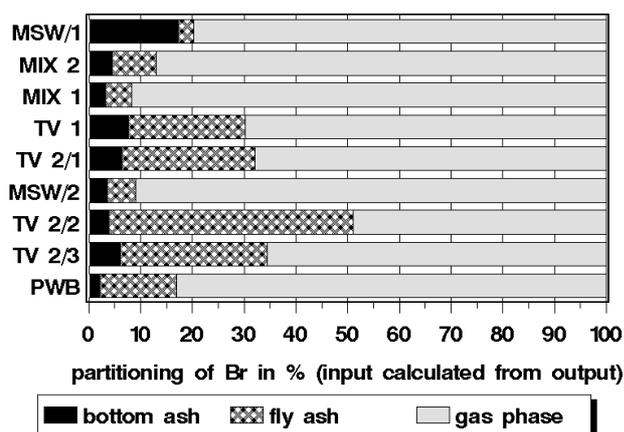


Figure 7b. Percentile partitioning of Br

Figure 7b illustrates the high fraction, up to 90%, of the Br entering the gas phase. In the case of co-combustion of TV housings - the three TV 2 tests and the TV 1 run – a significant amount, between 25% and more than 40% of the Br stays in the fly ashes.

As soon as the total Br concentration in the gas phase exceeded some 300 mg/m³ the appearance of elementary Br₂ could be observed (see Figure 8). The share between HBr and Br₂ was significantly controlled by the S content in the flue gas. The appearance of Br₂ is accompanied by disappearance of SO₂ and the finding that all S in the gas phase is present as SO₃. It can be speculated that the formation of Br₂ is suppressed as long as enough SO₂ is available.

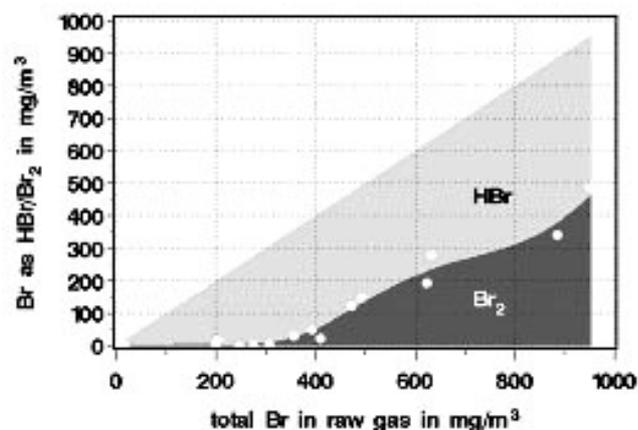


Figure 8. Partitioning of Br in the raw gas

Absorption

The TAMARA plant is equipped with a two-stage wet scrubbing system. During the co-combustion tests, flue gas was sampled in the raw gas upstream of the filter and downstream of both the first and second scrubber. The sampling positions are indicated in Figure 6.

The TAMARA scrubber system is a modified Venturi system. In its typical mode of operation it easily achieves compliance with all emission limits, even at high HCl and HBr levels. In the first co-combustion test with MIX 2, substantial concentrations of Br₂ were measured and the scrubbing system could not handle this species with the needed efficiency. Hence, to cope with high amounts of elementary Br₂, Na₂S₂O₃ was added to the neutral scrubber in all subsequent test runs.

The overall abatement efficiency of the wet scrubbing system is shown in Table 4. The data indicate that Cl is always removed at approx. 99.9%. The levels achieved for Br are not as high, but the typical efficiency is in the range 95% – 99%. The low number found in the MIX 2 trial was due to the fact that no thiosulphate had been added to the second scrubber since no elemental Br₂ was expected to be present in the raw gas.

Table 4. Cl and Br concentrations in scrubber effluent

	Scrubber 1 (g/l)		Scrubber 2 (g/l)		Overall abatement efficiency (%)	
	Cl	Br	Cl	Br	Cl	Br
MIX 2	42.1	3.7	2.4	7.7	99.98	68.78
MIX 1	30.0	2.5	1.5	3.2	99.97	99.18
TV 1	30.6	6.4	1.4	14.3	99.96	93.18
TV 2.1	26.4	7.3	8.6	11.3	99.90	95.77
TV 2.2	29.7	4.5	1.2	4.2	99.88	99.33
TV 2.3	29.6	7.6	1.2	8.7	99.87	99.22
PWB	43.9	9.6	1.7	20.4	99.94	96.79

In the effluents from the acid scrubber, a Br concentration of up to 10 g/l could be reached. This concentration could be increased to a maximum of 18 g/l in the first stage of a counter-current two-stage acid scrubbing system. In the second scrubber, Br concentrations up to 20 g/l were obtained. However, in these effluents the Br is present as bromide and is accompanied by high concentrations of sulphate (the oxidised reducing additive).

3.4 Metal volatilisation

General remarks

The volatility of metals in thermal processes depends basically on the maximum temperature achieved in the process. A further decisive factor is the chemical speciation of the metal in question. It is well known that the volatility of metals is promoted by the Cl inventory of the fuel, since the chlorides often have the lowest boiling points of all metal compounds. Like the chlorides, many metal bromides have a similar, and in some cases an even lower, boiling point. Hence Br can also be expected to promote volatility. In considering the mobilising effect of both halogens, their molar ratio needs to be taken into account. The molar weight of Br is about 2.25 times higher and its concentration in MSW is about 100 times lower than that of Cl. This is why the influence of Br is not observed in waste combustion.

Percentile volatilisation is defined as the metal fraction which is transferred out of the fuel bed and found in the boiler and fly ashes. With the exception of Hg, no gaseous metal species could be detected in the raw gas at temperatures below 200°C.

Combined influence of Cl and Br

In line with the experience of earlier TAMARA co-combustion tests with high Br input, the volatilisation of heavy metals is strongly promoted by both the Cl and Br inventory of the fuel. Especially for Cu, Zn, Sb, Sn, and Pb a significant increase of the transfer into the fly ashes could be observed.

Consequently, an almost linear correlation can be seen between the amount of some metals (for example Zn, Cd, Sn, and Pb) transferred out of the fuel bed and the molar sum of the two halogens (see Figures 9a and 9b). In the case of other metals the relationship is not as linear.

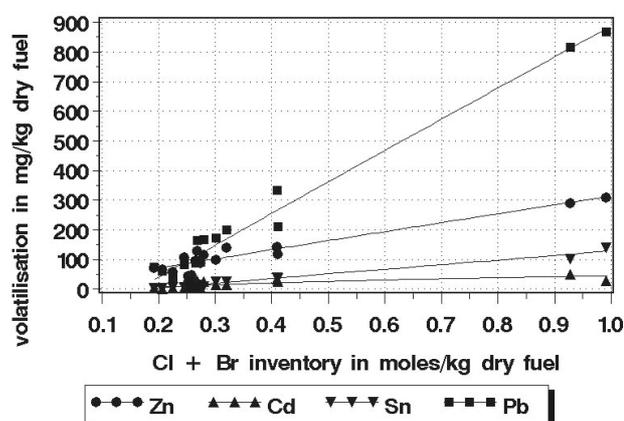


Figure 9a. Volatilisation of Zn Cd, Sn and Pb as a function of the accumulated molar Cl and Br inventory in the fuel

To highlight the separate effect of both halogens, data is presented for Zn and Pb in Figure 9b using a three-dimensional plot, with the Cl and Br inventory in the feed stream as independent variables.

TRIALS AT THE TAMARA PILOT PLANT

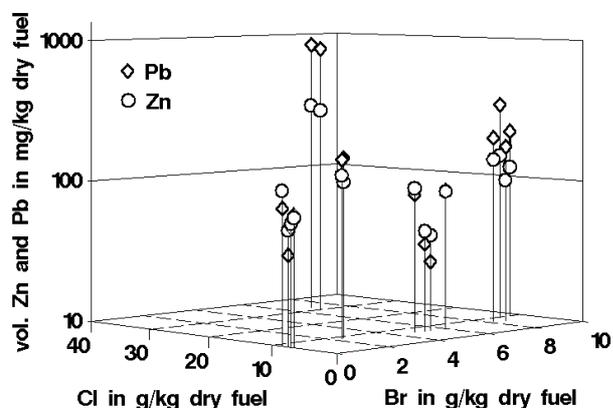


Figure 9b. Volatilisation of Zn and Pb as a function of the Cl and Br inventory of the fuel

3.5 Dioxin/Furan emissions

Previous tests in the TAMARA combustor with WEEE [1,10] and flame retarded plastic foams [2] demonstrated that the relatively high halogen levels did not cause an increase in levels of poly-halogenated dibenzo-p-dioxins and dibenzofurans in the raw gas downstream of the boiler. The stack emission was always comfortably below the most stringent regulatory limit, set by the German 17th BImSchV. From the point of view of dioxins and furans, the aim of this test program was to investigate the effect, if any, of a considerably higher Br load compared with the earlier tests.

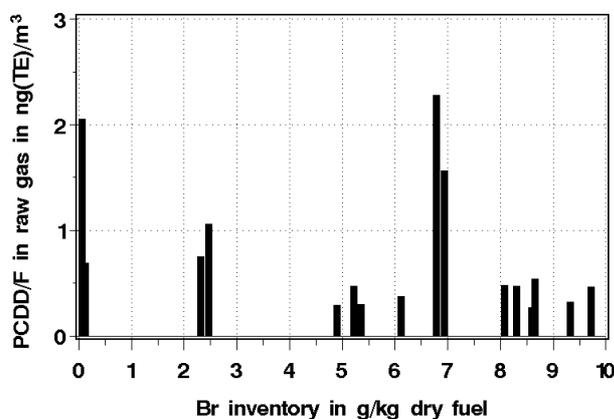


Figure 10. PCDD/F in the raw gas versus Br inventory in the fuel

The previous findings were verified: co-combustion of WEEE with the standard fuel did not increase the formation of PCDD/Fs, as can be seen in terms of toxic equivalents (I-TE) in Figure 10. The raw gas levels are of the same order of magnitude as those found in well operated full-scale plants. There is no positive correlation of the PCDD/F level in the raw gas and the Br inventory in the fuel. The high levels at a Br inventory of approximately 7 g/kg occurred in the MIX 2 trials which followed immediately the first reference test which had also been characterised by high PCDD/F levels. The absence of any correlation suggests that these two tests are influenced by other (unknown) operational parameters rather than the result of increased Cl and Br loads.

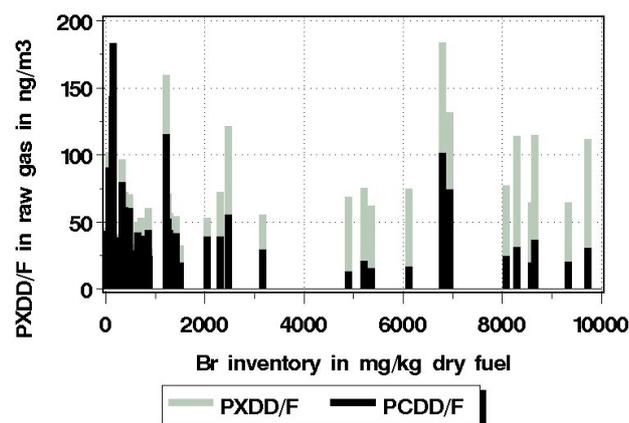


Figure 11. Halogenated dioxins and furans in the raw gas versus Br inventory in the fuel

The increase of the Br inventory of the fuel caused an increased formation of Br-containing dibenzo-p-dioxins and dibenzofurans with the furans by far predominating. Purely brominated congeners were rarely found and the majority of mixed halogenated congeners contained only 1 or 2 Br atoms. Again, as in former tests, the level of all halogenated dioxins and furans showed no significant correlation with the Br inventory. The ratio of Br content to purely chlorinated congeners, however, increased with increasing Br/Cl ratio.

For two typical tests, Mix 1 from the first and TV 2 from the second campaign, the grate ashes were analysed for brominated and mixed halogenated dioxins

and furans. Because of their low mass flow, boiler ashes were not analysed. Their dioxin and furan concentrations are typically lower than those in the grate ashes, which means that their contribution to the total PXDD/F load of the combustion residues can be ignored.

The analysed PBDD/F concentrations in the raw gas and in the grate ash allow the calculation of the reduction of the PBDD/F inventory originally present in the WEEE plastics fractions.

This reduction can be interpreted as thermal destruction. The term destruction, however, is not used since the obtained data, especially the raw gas concentrations, are a mix of thermal decomposition inside the combustion chamber and a new formation inside the boiler. The level of thermal decomposition is close to 100 %. Both effects are difficult to discern.

Figure 12 shows the PBDD and PBDF concentrations in the fuel and the accumulated concentrations of the respective compounds in the raw gas and in the grate ashes, always calculated for 1 kg of dry waste fuel. The graph documents a total reduction yield of >98 %.

The calculated balances indicate that all brominated dioxins and furans which might be present are almost totally removed by combustion in a state-of-the-art municipal solid waste combustion plant.

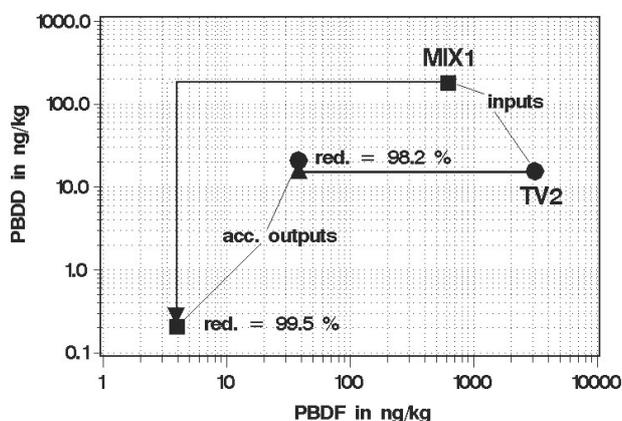


Figure 12. Concentration of PBDD vs. PBDF in the fuel and in all residues of two tests.

3.6 Recycling of bromine

A major purpose of the trial was the recovery of Br from the acid scrubber effluents. For this purpose a special packed-column bypass scrubber system comprising two acid and one neutral stage was used. The two acid stages were operated in a counter-current mode in order to concentrate HCl and HBr in the first scrubber.

The bypass scrubbing system was operated for 24 hours without any discharge. The scrubbing solution volume of the first stage was 4 l, and of the other two 5 l each. On average, a gas volume of 11.5 m³/h was passed through the system. The neutral stage was not operated with a reducing agent. The concentrations of Cl and Br in the different stages are listed in Table 5.

Table 5. Cl and Br concentrations in the different stages of the bypass scrubbing system

	Concentrations (g/l)					
	Stage 1		Stage 2		Stage 3	
	Cl	Br	Cl	Br	Cl	Br
MIX 2	151.9	18.3	10.1	0.6	0.08	0.60
MIX 1	29.3	3.3	0.6	0.02	0.02	0.09
TV 1	24.6	10.4	0.04	0.2	0.03	0.62
TV 2.1	15.8	9.8	0.03	0.2	0.02	0.50
MSW	54.8	1.6	0.36	0.01	0.02	0.01
TV 2.2	32.1	8.6	0.16	0.04	0.02	0.01
TV 2.3	31.3	14.7	0.1	0.1	0.02	0.01
PWB	50.2	18.1	0.24	0.3	0.02	0.93

It can be seen that the HCl concentrations in the first stage were, with the exception of the MIX 2 run, of a similar order of magnitude to those in the first (acid) scrubber of the standard TAMARA wet scrubbing system.

BROMINE RECYCLING POTENTIAL

However, in all tests the Br concentrations were much higher in the first bypass scrubber than they were in the corresponding standard scrubber. The second – also acid – bypass scrubber contained very low concentrations of both halogens, indicating that the concentration in the first one was very efficient. In the neutral scrubber almost no Br was absorbed. (This scrubber was operated without $\text{Na}_2\text{S}_2\text{O}_3$.)

Using the raw gas and liquid volumes as well as the respective concentrations, an evaluation of the approximate absorption yields can be made. The basis for the calculation is the quantity of Br released per kg of WEEE. The calculated releases of Br, separately depicted as HBr and Br_2 , and the total amount of Br recovered in the bypass system are presented in Figure 13.

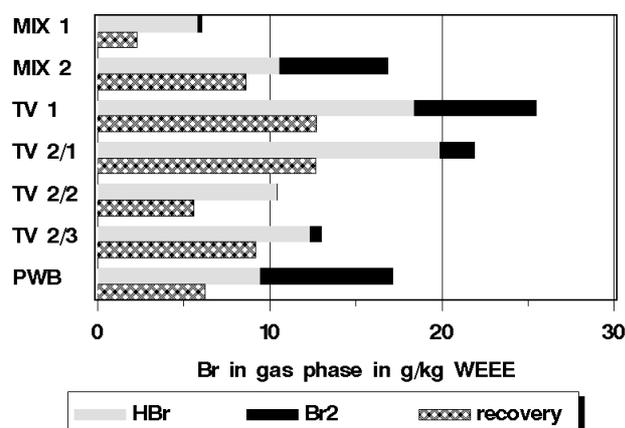


Figure 13. Br release and recovery in the bypass scrubber system

Taking the many sources of error for such an estimation into account - especially the overestimation of HBr by the sampling method - it can be assumed that the bypass system recovers the total HBr but almost no elementary Br_2 as no Br-containing bleaching agent such as bisulphite is used.

4 BROMINE RECYCLING POTENTIAL

4.1 Bromine recycling methods

The bromine present in flame retarded WEEE plastics is released during thermal processes such as incineration or pyrolysis/gasification. Under standard conditions, depending on the sulphur content and the maximum level of Br present in the feed, the Br will be released as HBr. To avoid excessive emissions, the released HBr present in the flue gas must be scrubbed in a wet flue-gas cleaning system. The first scrubber needs to operate under acidic conditions. The acids present, e.g. HF, HCl and HBr, will be quenched in the aqueous solution. Standard incinerators typically have a system of two wet scrubbers in which the second scrubber operates with a reducing agent such as sodium bisulphite or sodium formate at a pH of 7.4 – 7.8.

Three main process routes, distillation, neutralisation and peroxide are available to convert these acids into usable products. These are illustrated in Figure 14.

Distillation route

Given suitable economics, it is possible to distil the recovered aqueous solution of HBr, HCl and HF. Because of its high water content, it would not be economically feasible to transport the brine coming from the scrubber over a long distance: the distillation unit should therefore be installed at the combustor site.

Neutralisation route

The second option is to neutralise the HBr with NaOH. The formed NaBr will be dissolved in the scrubber solution. The scrubber liquid is drained to achieve a constant salt quality. This brine stream can be treated in several purification steps such as electro dialysis or membrane technology to produce a clean brine solution ready for use in certain applications.

To recover Br from the brine solution, Cl₂ is used to release the Br_2 which is then steamed out. This option is

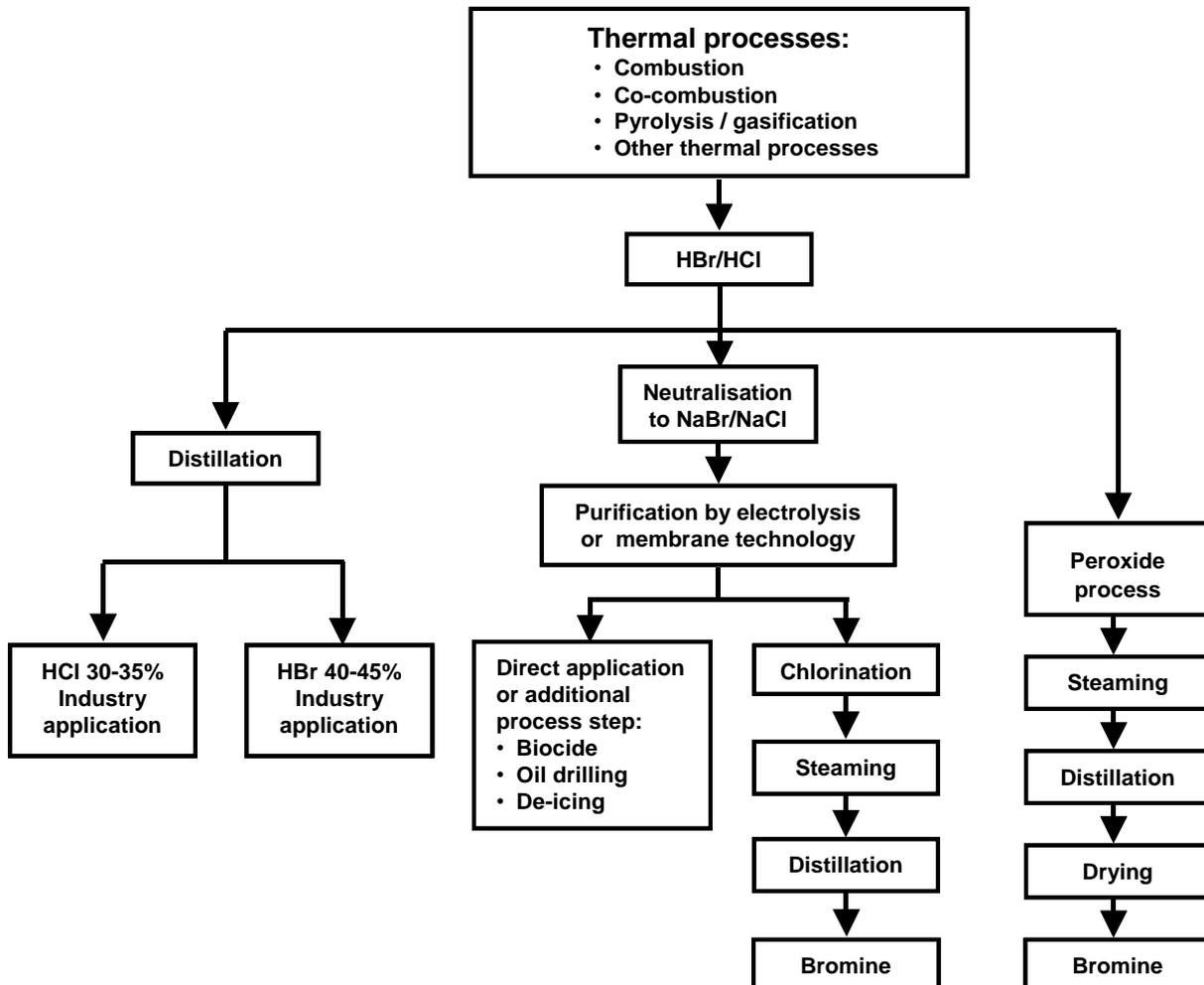


Figure 14. Potential recycling routes for Br in WEEE

only possible if a chlorine supply is available on site. Otherwise the installation would be too expensive and not economical.

Peroxide route

The third alternative is to mix the HBr-containing acidic stream with peroxide and steam out the formed Br₂. Once the Br₂ is released it must be distilled to remove the Cl₂ and other low boilers if they are present. A drying step with sulphuric acid is necessary to make the Br₂ ready for transport.

Both the neutralisation and the peroxide route are being evaluated by the bromine industry and the results are expected to be available in 2002.

4.2 MSWC capacity in Europe and WEEE plastics containing bromine

In 2000 there were 304 large MSWC plants in Europe [11]. Large plants are considered to be those with a capacity of more than 30,000 tonnes per year. Typical plants have a capacity of more than 100,000 tpa. 96% of the large plants recover energy from waste. MSWC capacity in Europe is both increasing and being modernised. There is a trend for smaller facilities to be replaced by larger installations that have better environmental performance, improved energy efficiency and lower unit operating cost. Two recent EU Directives are influencing this trend.

BROMINE RECYCLING POTENTIAL

The latest EU Directive on the landfilling of waste (1999/31/EC of 26 April 1999) has set targets to reduce the landfilling of biodegradable waste and replace it with, among other things, energy recovery. Modern MSW combustors are able to comply with the most demanding of emission regulations. The Incineration Directive (2000/76/EC of 4 December 2000) has tightened emission limits and requires new plants to have energy recovery facilities. Another trend is an increasing interest in novel processes using pyrolysis and gasification as alternatives to waste combustion.

The MSWC capacity needed to recover the bromine in collected WEEE plastics can be calculated on the basis of the available quantity of WEEE plastics containing bromine and the rate at which it can be added. The total quantity of WEEE plastics available for collection in Europe in 2000 was 777,000 tonnes [12]. Approximately 12.5% of this (95,000 tonnes) contains brominated flame retardants, with a typical bromine level of 8 - 9%. From this it can be estimated that the quantity of bromine potentially available for recycling is of the order of 8,000 tonnes per year. The level of bromine measured in the TV housings used for this demonstration was in the range 2.5—3.5% (see Table 3, page 9). The difference between this and the level in plastics containing brominated flame retardants is due to

the diluting effect of housings containing either no flame retardants or flame retardants not based on bromine.

On the basis of previous work [1] and the trials in the TAMARA facility reported here, 2-3% of WEEE FR plastics can be safely added. At this rate, the ratio of MSWC capacity to FR plastics added will range from 33:1 to 50:1.

Table 6 illustrates that, from an energy recovery point of view, sufficient capacity exists to recycle all of the bromine in WEEE FR plastics.

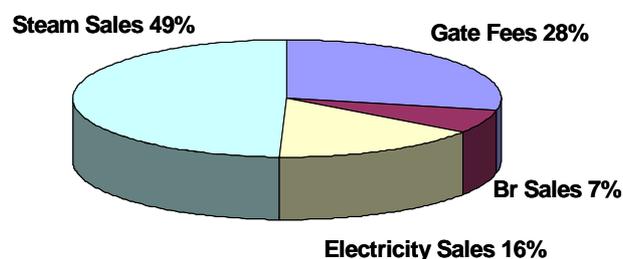
4.3 Bromine recycling economics

A typical MSW combustor line treats 20 tonnes of MSW per hour. Normally, to achieve suitable economies of scale, several lines operate alongside each other. If 3% of WEEE plastics containing 2.5 wt% bromine is added to three lines, (1800 kg/h WEEE plastics), this represents 45 kg/h of bromine in the feed. At a typical scrubber efficiency of >97% and a bromine recycling yield of >90%, such a unit could recycle 310 tonnes of bromine per year. It is possible to distil HBr as a 48% solution, in which case the recycling level would be around 660 tonnes of HBr 48% per year.

Figure 15 provides an indication of the relative income streams for an MSWC plant recycling bromine at a rate of 500 tonnes per year.

Table 6. MSWC plants able to recycle Br in WEEE FR plastics

Country	(A) WEEE FR Plastics ('000 t/year)	(B) MSWC Capacity ('000 t/year)	Ratio B:A
Germany	37	13 300	360
France	26	10 800	420
UK	26	21 000	815
Italy	19	2 150	114
Spain	12	1 200	100
Others	8	13 800	1 700



Source: Kennedy & Donkin Ltd (1999)

Figure 15: MSWC income streams

The range of incomes of MSWCs in Europe is quite wide and in many cases the contribution of the gate fee is a larger proportion than that shown in Figure 15. Another approach to recycling of bromine is pyrolysis/gasification. In the case of a dedicated or multipurpose facility using such a process, it is possible to feed 4 tonnes per hour of pure WEEE plastics with a potential of recycling 83 kg/h of bromine or about 660 tonnes of bromine or 1250 tonnes of HBr 48% annually.

5 CONCLUSIONS

The work in the TAMARA pilot scale MSWC plant described here has demonstrated that under the right circumstances, recycling of the bromine in WEEE plastics can be carried out in modern MSWC facilities equipped with suitable wet scrubbing systems while

meeting all operational and environmental requirements. Different types of finished products can be produced for sale, including Br₂, HBr or NaBr. There is therefore clear potential for establishing a bromine recycling capacity in Europe, thus providing an additional waste recovery option for WEEE plastics containing brominated flame retardants. Establishing an eco-efficient bromine recycling operation at an MSWC facility will be based on several factors including:

- Availability of suitable E&E waste streams
- Market conditions for the finished products: Br₂, HBr or NaBr
- The availability of chlorine on the site
- Choice of recycling process

These commercial and technical decisions will be further influenced by the economics of the recycling operation, and made in the context of implementation of the proposed EU Directive on WEEE.

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5 REFERENCES AND WEBSITES

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Dow Europe

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Great Lakes Chemical

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