

Guidance on best available techniques and best environmental practices for the recycling and disposal of articles containing polybrominated diphenyl ethers (PBDEs) listed under the Stockholm Convention on Persistent Organic Pollutants

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Abbreviations and acronyms

ABS	acrylonitrile-butadiene-styrene
ASR	automotive shredder residue
BAT	best available techniques
BDP	bisphenol A-bis(diphenylphosphate)
BEP	best environmental practices
BFR	brominated flame retardant
BSEF	Bromine Science and Environmental Forum
c-DecaBDE	decabromodiphenyl ether
c-OctaBDE	commercial octabromodiphenyl ether
c-PentaBDE	commercial pentabromodiphenyl ether
CFC	chlorofluorocarbon
CKD	cement kiln dust
COP	Conference of the Parties
CRT	cathode ray tube
DOPO	dihydrooxaphosphaphenanthrene
EAF	electric arc furnace
EEE	electrical and electronic equipment
ELV	end-of-life vehicle
EMS	environmental management system
ESM	environmentally sound management
FPF	flexible polyurethane foam
FR	flame retardant
GHG	greenhouse gas
HBB	hexabromobiphenyl
HBCD	hexabromocyclododecane
HFC	hydrofluorocarbon
HIPS	high impact polystyrene
MSW	municipal solid waste
NIR	near-infrared
ODS	ozone depleting substances
PBB	polybrominated biphenyl
PBDE	polybrominated diphenyl ether
PBDD/PBDF	polybrominated dibenzo-p-dioxins and polybrominated dibenzofurans
PBT	polybutylene terephthalate
PC	polycarbonate
PCB	polychlorinated biphenyl
PCDD/PCDF	polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans
PET	polyethylene terephthalate
PFR	phosphorous based flame retardant
POPs	persistent organic pollutants
POPRC	Persistent Organic Pollutants Review Committee
PP	polypropylene
PPE	polyphenyl ether PPO polyphenylenoxide
PS	polystyrene
PUR	polyurethane
PVC	polyvinylchloride
PWB	printed wiring board
PXDD/PXDF	polybrominated polychlorinated dibenzo-p-dioxins and dibenzofurans

RDP	resorcinol-bis(diphenylphosphate)
RoHS	Restriction of the use of certain hazardous substances in electrical and electronic equipment
S/F	sink and float
SVOC	semi-volatile organic compound
VOC	volatile organic compound
WEEE	waste electrical and electronic equipment
XRF	X-ray fluorescence
XRT	X-ray transmission

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1 Introduction

1.1 Purpose

In May 2009, the Stockholm Convention on Persistent Organic Pollutants (POPs) was amended by the Conference of the Parties (COP) to the Convention to include several polybrominated diphenyl ethers (PBDEs) in its Annex A:

- Hexabromodiphenyl ether and heptabromodiphenyl ether¹
- Tetrabromodiphenyl ether and pentabromodiphenyl ether²

For the purpose of this document, these chemicals are collectively referred to as POP-PBDEs. Hexabromodiphenyl ether and heptabromodiphenyl ether are contained in commercial pentabromodiphenyl ether (c-PentaBDE), and tetrabromodiphenyl ether and pentabromodiphenyl ether are contained in commercial octabromodiphenyl ether (c-OctaBDE).

The main objective of this document is to provide guidance on best available techniques (BAT) and best environmental practices (BEP) for the recycling and final disposal of products and articles containing POP-PBDEs in an environmentally sound manner, following the recommendations of the COP on the elimination of POP-PBDEs from the waste stream. BAT means the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical, which indicate the practical suitability of particular techniques. BEP describes the application of the most appropriate combination of environmental control measures and strategies. This document also aims to assist Parties reviewing and updating their NIPs with information on how to meet the obligations of the Convention on POP-PBDEs in relevant material flows as shown in the figure 1-1. It provides guidance on developing action plans for the environmentally sound management (ESM) of POP-PBDE-containing articles and materials based on the POP-PBDE inventory results. In particular, this document will be of use to national Stockholm Convention focal points, the project coordination unit implementing the NIP review and update project, and task teams responsible for conducting POP-PBDEs inventories and developing action plans for managing POP-PBDEs.

In addition, this document addresses the recycling of products and articles containing POP-PBDEs, and the elimination of these chemicals.

1.2 Structure of the guidance document

Chapter 1 outlines the purpose and structure of this document (see figure 1-1). It also explains its relationship to the Basel Convention (BC) on the control of transboundary movements of hazardous wastes and their disposal.

¹ The listing includes tetrabromodiphenyl ether and pentabromodiphenyl ether, meaning 2,2',4,4'-tetrabromodiphenyl ether (BDE-47, CAS No: 40088-47-9) and 2,2',4,4',5-pentabromodiphenyl ether (BDE-99, CAS No: 32534-81-9) and other tetrabromodiphenyl and pentabromodiphenyl ethers present in commercial pentabromodiphenyl ether.

² The listing includes hexabromodiphenyl ether and heptabromodiphenyl ether, meaning 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153, CAS No: 68631-49-2), 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154, CAS No: 207122-15-4), 2,2',3,3',4,5',6 heptabromodiphenyl ether (BDE-175, CAS No: 446255-22-7), 2,2',3,4,4',5',6-heptabromodiphenyl ether (BDE-183, CAS No: 207122-16-5) and other hexabromodiphenyl and heptabromodiphenyl ethers present in commercial octabromodiphenyl ether.

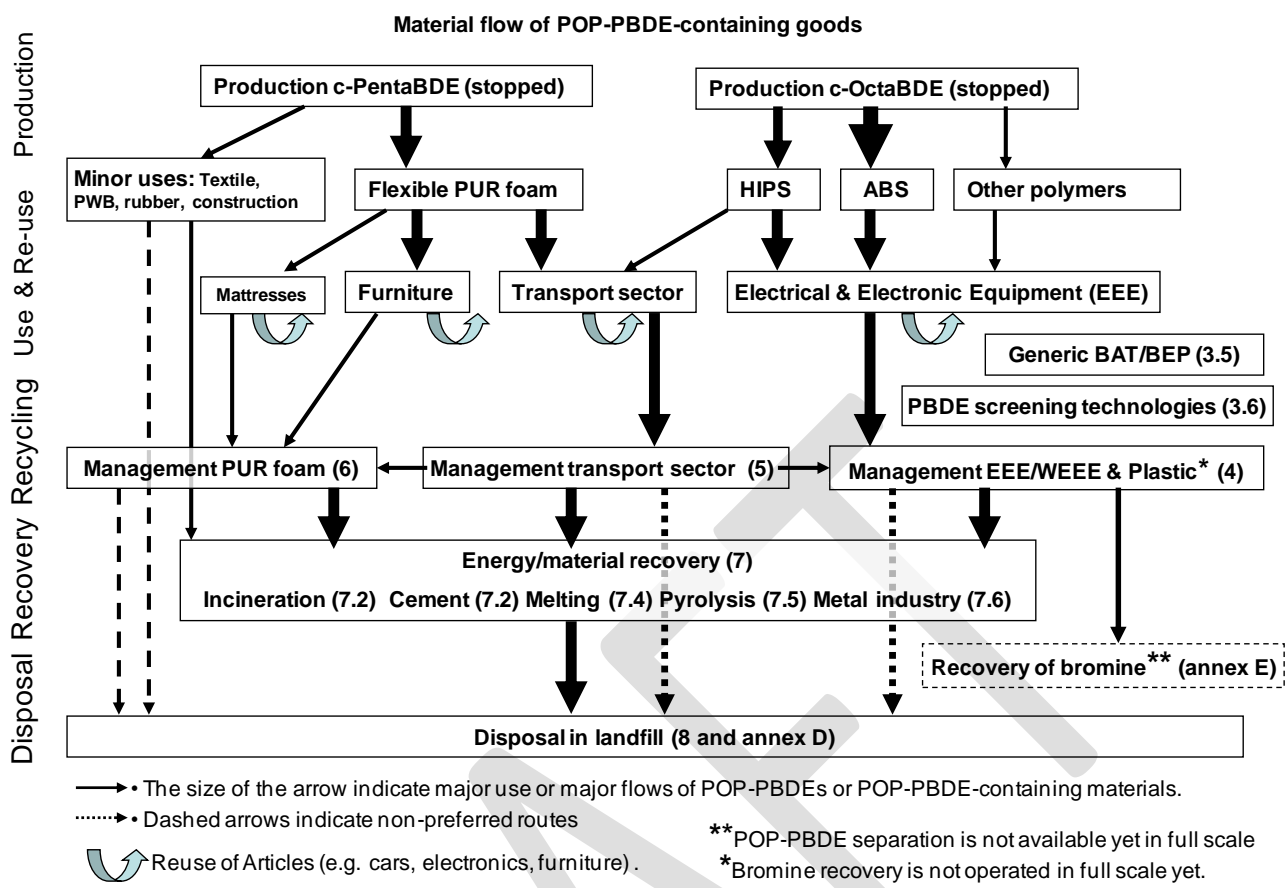


Figure 1-1: Structure of the guidance and mass flow for the relevant production and application of c-PentaBDE and c-OctaBDE and the reuse, recycling and disposal of articles containing these substances

Chapter 2 provides background information on POP-PBDEs (2.1), an estimation of the total production amount of c-PentaBDE and c-OctaBDE (2.2), the major former uses of c-PentaBDE and c-OctaBDE (2.3), risks associated with POP-PBDEs (2.4), and information on POP-PBDEs in material/recycling flows and at end-of-life.

Chapter 3 (supplemented by annexes 1 and 2) includes general principles and cross-cutting considerations for recycling and disposal of articles containing POP-PBDEs based on the waste management hierarchy (3.2), life cycle management (3.3), alternatives to POP-PBDEs (3.4), and monitoring of the bromine/POP-PBDEs in polymers (3.5).

Chapter 4 addresses BAT/BEP technologies for the reuse of electrical and electronic equipment (EEE) (4.1), material recycling of plastics from WEEE (4.2), technologies to separate POP-PBDEs-containing plastics (4.3), and end-of-life management of POP-PBDEs-containing plastics (4.4).

Chapter 5 reviews BAT/BEP options for management of POP-PBDEs-containing materials in the transport sector (cars, buses, trucks, trains, ship, and planes) for reuse (5.1), treatment and recycling of end-of-life vehicle (ELV) (5.2), and energy recovery and disposal of automobile shredder residue (ASR) and other ELV residues (5.3).

Chapter 6 describes BAT/BEP for the management and processing of POP-PBDEs-containing polyurethane foam including the reuse of furniture and mattresses (6.1), recycling/recovery of PUR foam (6.2), labelling of articles produced from recycled PUR foams (6.3), and other materials possibly impacted by POP-PBDEs (6.4).

Chapter 7 contains information about thermal treatment options for POP-PBDEs-containing materials (7.1), including waste incineration (7.2), cement kilns (7.3), melting systems (7.4), and pyrolysis technologies (7.5). The BAT/BEP considerations for different secondary metal industries processing POP-PBDEs-containing materials (for metal or energy recovery) are also described (7.6).

Chapter 8 (and annex 3) addresses concerns about the least favoured approach of disposal of POP-PBDEs-containing waste to landfill, recognizing that not all countries have access to alternative disposal technologies.

1.3 Relationship to the Basel Convention

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal was adopted in 1989 and entered into force in 1992. The Basel Convention is directly relevant to the application of BAT and BET for the management of wastes consisting of, containing or contaminated with POPs. Considering that WEEE polymers are major potential POP-PBDEs-containing material flows, synergies between the Stockholm Convention and Basel Convention are of high importance. The Basel Convention places obligations on countries that are Parties to, inter alia, minimise generation of hazardous waste, ensure that adequate disposal facilities are available, and ensure environmentally sound management of wastes.

The COP to the Basel Convention, at its eighth meeting in December 2006, adopted updated general technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with POPs. These guidelines address matters related to all three of the outstanding definitional issues raised in paragraph 2 of Article 6 of the Stockholm Convention. At its tenth meeting in October 2011, the COP to the Basel Convention adopted a work programme³ with regard to POPs listed under the Stockholm Convention in 2009, for the updating of the general guidelines and the preparation of specific technical guidelines.

1.4 Relationship to other environmental concerns

Article 3 para. 6 of the Stockholm Convention requests Parties that have a specific exemption and or acceptable purpose to take measures to ensure that any production or use under such exemption or purpose is carried out in a manner that prevents or minimizes human exposure and releases to the environment. This guidance document has been developed to guide Parties in adequately addressing the risks of perfluorooctane sulfonic acid (PFOS) and its related substances.

POP-PBDEs-containing material flows could contain other critical pollutants:

- **EEE** contains a wide range of pollutants as detailed by the Swedish Environmental Protection Agency (EPA) (Naturvardsverket, 2011). Certain EEE fractions, in particular air conditioners, contain ozone depleting substances (ODS) such as chlorofluorocarbons (CFCs) or greenhouse gases (GHGs) such as hydrofluorocarbons (HFCs).
- **ELVs** contain, in addition to a range of POPs, other pollutants including heavy metals, ODS and/or GHGs.
- **PUR foam** can contain critical blowing agents having ODS (e.g. CFCs) or GHG potential (e.g. dichloromethane).

³ Decision BC-10/9.

In recycling and disposal of these material flows these toxic chemicals can be mobilized and released, resulting in human exposure and environment contamination (Wong et al., 2007; UNEP, 2010b). Compounds of most concern during recycling and deposition of WEEE are lead, mercury and, along with PBDEs, also Annex C chemicals (in particular polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDF)) and the related brominated dioxins and furans. Extreme high levels (in some cases the highest ever measured) of these compounds have been measured in environmental and human samples collected in areas where uncontrolled WEEE recycling is taking place (UNEP 2010a, 2010b; Naturvardsverket, 2011). The release of ODS and GHG is also of high concern and could take place if BAT/BEP approaches were not adopted for final disposal of WEEE, ELV wastes, etc.

Therefore, the recycling and disposal of POP-PBDEs-containing material flows require a holistic approach that considers all these pollutants, the related releases/emissions and the associated risks. The presence of ODS, GHG, heavy metals (including lead and mercury), new POPs and unintentionally produced POPs presents an opportunity to synergize all related implementation activities of the Conventions (Stockholm, Rotterdam and Basel Conventions, Montreal Protocol, and UN Climate Change Convention) by minimizing the various pollutants with different risks. The life cycle assessment approach (described in section 3.3 as a decision tool) guarantees that all these environmental impacts are taken into consideration and adequately evaluated for knowledge-based decisions by tuning into the most appropriate recycling and disposal scheme for the individual POP-PBDEs-containing material flows. For these material flows, Parties are encouraged to take appropriate precautions to ensure that releases of all these pollutants are minimized when applying BAT/BEP as set out in the these guidelines.

2 Background information on POP-PBDEs

2.1 POP-PBDEs listed in the Convention

Polybrominated diphenyl ethers (PBDEs; see figure 2-1) are a group of industrial aromatic organobromine chemicals that have been used since the 1970s as additive flame retardants in a wide range of — mainly — consumer products. PBDEs were produced with three different degrees of bromination, and marketed as commercial PentaBDE, commercial OctaBDE and commercial DecaBDE (Alaee et al., 2003; Prevedouros, 2004a; SFT, 2009). Typical homologue distributions of the commercial mixtures are shown in table 2-1. Although c-DecaBDE⁴ has not been found to contain POP-PBDEs, it can form POP-PBDEs by debromination during its life cycle, thus representing an important reservoir of POP-PBDEs (UNEP, 2010c; Ross et al., 2009).

Commercial PentaBDE (c-PentaBDE), the homologues “tetrabromodiphenyl ether and pentabromodiphenyl ether” as well as c-OctaBDE, “hexabromodiphenyl ether and heptabromodiphenyl ether” are listed under the Stockholm Convention.

TetraBDE, pentaBDE, hexaBDE and heptaBDE are listed in Annex A of the Convention, and their production and use have to be eliminated by Parties subject to the exemptions allowed by the Convention. These listed POPs are referred to in this document as POP-PBDEs. The octaBDE, nonaBDE, and decaBDE present in the mixture are not defined as POPs because they do not meet all POP criteria. These highly brominated PBDEs, however, can degrade to POP-PBDEs by debromination (UNEP, 2010b, 2010c).

POPs-PBDEs are highly persistent in the environment, bioaccumulative and have a high potential for long-range environmental transport. These chemicals have been detected in humans and biota in all regions. There is evidence of harmful effects in humans and wildlife (Shaw et al., 2010).

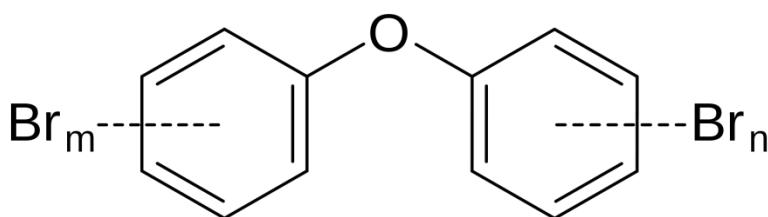


Figure 2-1: Structure of polybrominated diphenyl ethers (PBDEs)

Table 2-1: Typical PBDE homologue distribution in commercial PBDE products

Commercial product	Congener % by weight						
	tetraBDEs	pentaBDEs	hexaBDEs	heptaBDEs	octaBDEs	nonaBDEs	decaBDE
C-PentaBDE	24-38	50-60	4-8				
C-OctaBDE			10-12	44	31-35	10-11	<1
C-DecaBDE						<3	97-98

(Sellstrom et al., 2005; La Guardia et al., 2006)

⁴ DecaBDE can degrade in thermal processes, environment processes and in biota to lower brominated PBDEs including POP-PBDEs (UNEP, 2010c). Other key degradation products are polybrominated dibenzofurans and, depending on conditions, polybrominated dibenzo-*p*-dioxins (Weber and Kuch, 2003; Ebert and Bahadir, 2003; UNEP, 2010b).

2.2 Production of commercial PBDE mixtures

C-PentaBDE was produced in Israel, Japan, the United States and the European Union (EU), and possibly China (UNEP, 2006, 2010b). Production in the EU ceased in 1997. It is assumed that since the late 1990s POP-PBDEs were mainly produced in the United States and production ended in 2004.⁵

C-OctaBDE was produced in the Netherlands, France, United States, Japan, United Kingdom and Israel. Production stopped in the EU, United States and the Pacific Rim in 2004, and there is no information indicating that it is being produced in developing countries (BSEF, 2007).

The compilation of PBDE production data prepared for the POPs Reviewing Committee of the Stockholm Convention estimated the total production of all PBDE from 1970 to 2005 as between 1.3 million and 1.5 million tonnes (UNEP, 2010a). The total amounts of c-PentaBDE and c-OctaBDE used in the world were estimated at around 100,000 tonnes each. The production of c-DecaBDE,⁶ which is not listed as a POP, was estimated at over 1.1 million tonnes until 2005 (see table 2-2). While the production of POPs c-PentaBDE and c-OctaBDE ended in 2004, the production of DecaBDE continues.

Table 2-2: Estimated total production of PBDE commercial mixtures, 1970-2005

Commercial Mixture	Tonnes
c-PentaBDE	91,000 to 105,000
c-OctaBDE	102,700 to 118,500
c-DecaBDE	1,100,000 to 1,250,000

(UNEP, 2010a: derived from Schenker et al., 2008 and Li, 2010)

2.3 Former uses of POP-PBDEs

The main manufacturing sectors that have used POP-PBDEs are as follows:

- Organobromine industry
- Electrical and electronics industry
- Transport industry
- Furniture industry
- Textiles and carpet industry
- Construction industry
- Recycling industry

2.3.1 Former uses of c-PentaBDE

It is considered that between 90% and 95% of the use of c-PentaBDE was for the treatment of PUR foam. These foams were mainly used in automotive and upholstery applications. Minor uses included textiles, printed circuit boards, insulation foam, cable sheets, conveyer belts, lacquers and possibly drilling oils (UNEP, 2007). The total amount of c-PentaBDE used for these minor uses is estimated to account for 5% or less of the total usage (SFT, 2009; UNEP, 2010b). Alcock et al. (2003) estimated that 85,000 tonnes of c-PentaBDE overall was used in the United States and the remaining 15,000 tonnes in Europe. There may have been production and use in Asia but reliable data are not available.

⁵ Some uncertainty exists about c-PentaBDE production in China and when this production ended (UNEP, 2010a, 2010b).

⁶ DecaBDE is degraded over time to the lower brominated PBDEs including POP-PBDEs (UNEP, 2010b, 2010c).

An approximate distribution of c-PentaBDE use of 36% in transport, 60% in furniture and a 4% residual in other articles is considered to be reasonable and is generally consistent with the analytical data for different waste streams (UNEP, 2010b).

The average content of c-PentaBDE in PUR foam is reported to be around 3-5% for upholstery, cushions, mattresses, and carpet padding (ENVIRON, 2003; UNEP, 2010a) used in particular in countries with flammability standards for these applications (e.g. United States, United Kingdom). PUR foam in the transport sector might have used lower concentrations for applications like seats or arm/head rests at 0.5-1 wt % (Luedeka, 2011).⁷ Considering the approximately 100,000 tons of c-PentaBDE and a use of 4% in PUR foam, the historic production of c-PentaBDE treated foam can be conservatively estimated to be approximately 2.5 million tonnes. This number might have been considerably higher considering that a major application (PUR foam in transport in the United States) used c-PentaBDE at lower dosage rates. Furthermore, recycling of contaminated PUR foams by mixing them together with non-impacted PUR foams led to increased total quantities of POP-PBDEs-contaminated PUR foam materials. For more details, see chapter 2 of the *PBDE Inventory Guidance*.

2.3.2 Former uses of c-OctaBDE

The main former use of c-OctaBDE was in acrylonitrile-butadiene-styrene (ABS) polymers, accounting for about 95% of c-OctaBDE supplied in the EU. The treated ABS was mainly used for housings/casings of EEE, particularly for cathode ray tube (CRT) housings and office equipment such as copying machines and business printers.⁸ Other minor uses were high impact polystyrene (HIPS), polybutylene terephthalate (PBT), and polyamide polymers. Although the majority of these polymers were used in electronics, there was also some use in the transport sector.

Other minor uses found in literature include nylon, low density polyethylene, polycarbonate, phenolformaldehyde resins, unsaturated polyesters, adhesives and coatings (UNEP 2010a, b).

Typical concentrations in the major applications were between 12 wt % and 18 wt %, with approximately 100,000 tonnes of c-OctaBDE at an application rate of 15 wt %. The primary treated polymers can be estimated at approximately 800,000 tonnes. Considering the recycling of c-OctaBDE in new plastic products (secondary contamination), the total quantity of impacted plastics is likely to be considerably higher than this. For more details, see chapter 2 of the *PBDE Inventory Guidance*.

2.4 Risks associated with POP-PBDEs

The risks associated with individual POPs have been assessed by the Persistent Organic Pollutants Review Committee (POPRC). The risk profiles on c-PentaBDE (UNEP/POPS/POPRC.2/17/Add.1) and c-OctaBDE

⁷ Automotive seating and trim foam compliance with MVSS 302 requires varying amounts of flame retardant content depending on whether raw foam materials or composite seating, headliners or floor coverings are tested. One major global seating supplier reports that between 0.5% and 1.0% flame retardant additives are required for moulded foam products as may be found in seating, arm and head rests. FR concentrations of 2-5% could be found in moulded carpet padding, and, depending on the headliner fabric and grade of foam substrate, up to 15% FR content could be found in foam for lamination to headliner fabric (Luedeka, 2011).

⁸ In some regions such as Europe and Japan, CRT monitor housing and copying machines are already normally treated separately.

(UNEP/POPS/POPRC.2/17/Add.4), and the risk management evaluation documents for c-PentaBDE (UNEP/POPS/POPRC.3/20/Add.1) and c-OctaBDE (UNEP/POPS/POPRC.4/15/Add.1), can be viewed and downloaded at www.pops.int.

In some regions, current exposures to POP-PBDEs are already at levels where serious health effects are being measured in epidemiological studies (Herbstman et al., 2010). The *Technical Review of the Implications of Recycling Commercial Pentabromodiphenyl Ether and Commercial Octabromodiphenyl Ether* for the POPRC (UNEP 2010a, b) concluded that the following groups are considered to be at high risk, if exposed to POP-PBDEs as a consequence of being involved in recycling activities:

- Workers in low-technology WEEE operations.
- Those living in areas of developing/transition countries where intensive low-technology WEEE operations are carried out (Wong et al., 2007).
- Workers involved in manufacturing/recycling/ installing foam materials (Stapleton et al., 2008).
- Toddlers and breast-fed infants – especially in countries or localities where body burdens are already high. In these scenarios, recycled products are likely to supplement those existing high levels of exposure.
- Workers in smelters and other industries processing WEEE (possibly exposed to PBDE from PWB or WEEE plastic, and related polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/PBDF) releases).
- Women of child-bearing age and those who are pregnant, in relation to neurodevelopmental impacts on the foetus (Herbstman et al., 2010).

The review also concluded that the formation of PBDD/PBDF throughout the life cycle of PBDE (Shaw et al., 2010) poses relevant risks that need to be considered in the assessments of risks associated with POP-PBDEs (UNEP, 2010a, b).

2.5 POP-PBDEs in material/recycling flows and at end-of-life

Even though POP-PBDEs are considered to be no longer produced, the main challenge for their elimination is the identification of existing stockpiles and articles containing POP-PBDEs, and the disposal of POP-PBDEs-containing materials at end-of-life.

Large volumes of these materials are in the global recycling flow and will continue to be used in consumer articles (UNEP, 2010a, b; Shaw et al., 2010). The existing reuse and recycling of materials and wastes containing POP-PBDEs was the trigger for the COP4 exemption that allows recycling and reuse under certain conditions. The *Technical Review of the Implications of Recycling Commercial Pentabromodiphenyl Ether and Commercial Octabromodiphenyl Ether* (UNEP 2010a, b) highlighted that it is clearly not sensible to risk increased exposure when serious health effects from POP-PBDEs are being measured in epidemiological studies in some regions. Therefore the recycling of materials containing POP-PBDEs into uses where further exposure cannot be effectively controlled needs to be controlled (UNEP, 2010 a, b). And at the end of their lifetimes, the articles become waste with the potential of causing additional releases (Hale et al., 2006). Therefore, any remaining stockpiles should be eliminated or be subject to environmentally sound management. In this respect consideration is also given to the COP5 recommendation that recycling of materials containing POP-PBDEs should be phased out where feasible.

Some technical details of appropriate technologies to address these challenges are included in the chapters and annexes of this document.

2.5.1 C-PentaBDE in reuse, recycling and waste flows

The main uses of c-PentaBDE were in PUR foam used in the transport sector (e.g. cars, buses, trains etc.) and furniture (e.g. couches, seats, cushions etc.), with limited use in mattresses and some other uses. Therefore, the reuse and recycling of these major material flows needs to be addressed by this BAT/BEP guidance (see chapters 5 and 6).

Other applications with former minor uses (e.g. insulation in construction, treated rubber, textiles, epoxy resins in e.g. printed circuit/wiring board, polyvinylchloride (PVC), etc.) might only be assessed if they appear relevant in a country.

The major use and recycling flows of materials containing c-PentaBDE are shown in figure 2-2.

Transport

The lifespan for cars in industrial countries is 10 to 12 years, while buses and trains might have a longer life expectancy. A considerable share of cars and other transport has been and is still being exported from industrial countries to developing countries and countries with economies in transition for reuse; the vehicles are often used for a long time before they finally break down (spare parts are also reused further). Today a large share of the transport fleet from 1970 to 2004 (cars, buses and possibly trains) containing c-PentaBDE is still in operation, likely in developing countries, and will need to be identified with respect to reuse and recycling when these vehicles reach end-of-life. Therefore, the transport sector needs specific BAT/BEP considerations for further management and control of c-PentaBDE-containing materials. The BAT/BEP treatment of this material flow is addressed in chapter 5. The PUR foam and plastic currently recycled to a minor extent are covered in chapters 4 and 7.

Furniture and mattresses

The use of c-PentaBDE (and other flame retardants) in furniture or mattresses depends on the flammability standards of a country (Shaw et al., 2010). Due to flammability standards for furniture in the United States and United Kingdom in particular, furniture in North America and the United Kingdom is often flame retarded. Therefore, older furniture and mattresses (in particular from institutions like prisons, military facilities, hospitals or hotels) in these region/countries may contain c-PentaBDE (and other flame retardants).

The lifespan of furniture in industrial countries is estimated at about 10 years. Therefore, it is estimated that a considerable share of furniture containing c-PentaBDE in these regions has been deposited or incinerated (ESWI, 2011) with a minor share recycled e.g. in carpet rebond (see below). The extent of furniture exported from North America and the United Kingdom for reuse or recycling to other regions has not been assessed and needs to be considered as a possible source for c-PentaBDE input for other countries.

C-PentaBDE was also used in rigid PUR foam in construction, but this is considered a minor use. Further recycling activities of rigid PUR foam are not known.

Textiles and rubber

C-PentaBDE has been used⁹ in limited quantities for the treatment of textiles for uses including back-coating, for curtains and for functional textiles (UNEP, 2009). Although the extent of recycling of POP-PBDEs-containing textiles is unclear, it can reasonably be assumed to be small for composite materials such as those

⁹ C-DecaBDE and HBCD are still used in the impregnation of textiles.

used in transport. There may be some limited recycling of other c-PentaBDE-containing textiles but it is likely that only relatively small quantities of POP-PBDEs-containing textiles are in use as the application of c-PentaBDE stopped about a decade ago. The POPRC decision to recommend hexabromocyclododecane (HBCD), for which the textile sector is a major application, to the Conference of Parties for listing as a POP (POPRC-5/6¹⁰) might imply that the management of textiles treated with brominated flame retardants (BFRs) with POPs-like properties could become more relevant in the near future. C-PentaBDE has also been used in rubber for conveyor belts and other minor uses. Because of the small quantities involved, BAT/BEP is not considered for these uses apart from end-of-life treatment (see chapters 7 and 8).

Printed circuit/wiring boards

The use of c-PentaBDE in printed circuit/wiring boards (PWBs) has been phased out.¹¹ PWBs are a component of WEEE that ends up in certain developing countries, where the metals are recovered using primitive methods in the formal sector, or by simple smelters. This can be the source of certain levels of pollution including POP-PBDEs and PBDD/PBDF (see e.g. Yu et al., 2008). Thus there is an urgent need for the definition and implementation of BAT and BEP for this material flow (see chapters 4, 7 and 8).

Recycling of PUR foam to new articles

PUR foams in furniture, transport, end-of-life vehicles and mattresses are partly recycled into new articles by processes such as carpet rebond and regrinding.

[Carpet rebond]

Large-scale recycling of PUR foam into carpet padding/rebond is currently practised in the United States and Canada (Luedeka, 2011; see chapter 6). The extent of this recycling activity in other regions is unknown but appears to be limited (DiGangi et al., 2011). Relevant exposure of PUR recyclers and carpet installers to PBDEs has been demonstrated in a first study in the United States (Stapleton et al., 2008), and there are obvious risks of further exposure of consumers.

[Other uses]

While the majority of PUR foam scraps is processed into carpet rebond (in the US market), scrap can also be shredded and used as packaging and stuffing for pillows, pet bedding, insulation and plush toys. Foam scraps might also be used for some furniture cushioning, sound insulation gymnastic mats, or school bus seats (UNEP, 2010b; USEPA, 1996; Zia et al., 2007).

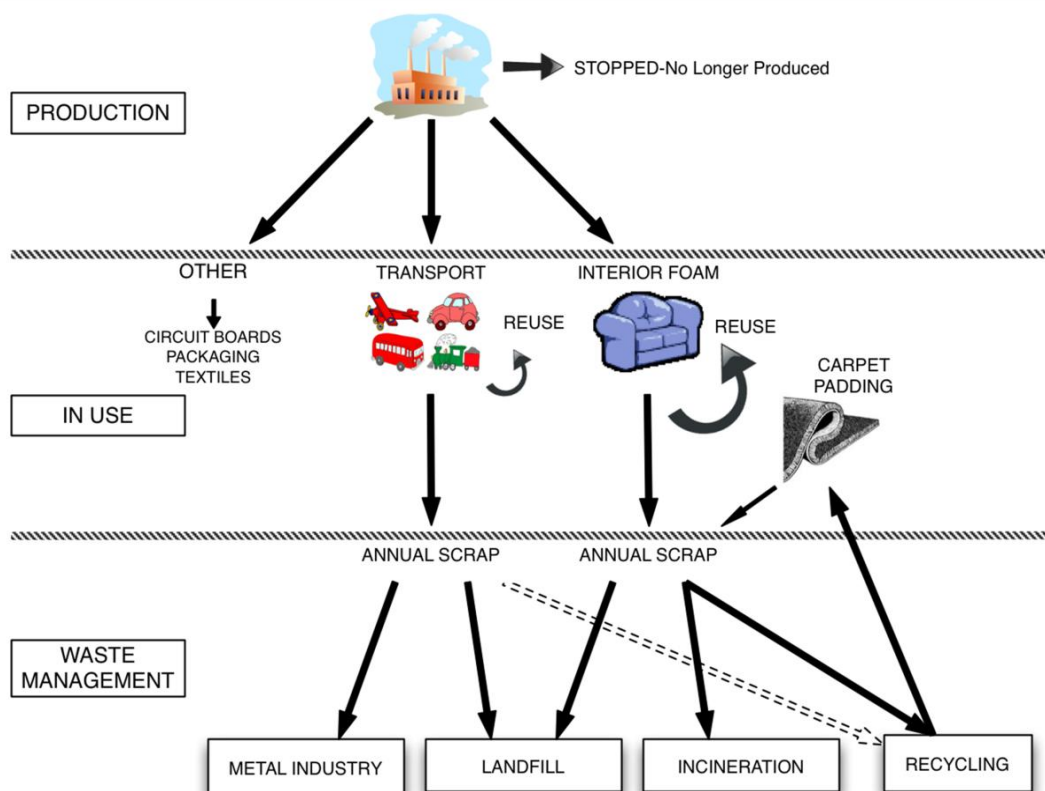
[Regrinding]

Eaves (2004) noted that this innovative process allowed manufacturers to non-cryogenically grind foam scrap into ultrafine powders that displaced approximately 20% of the virgin material in the manufacture of new foams.

BAT/BEP measures are required to reduce risks of exposure by separating POP-PBDEs-containing materials from PUR foam (as described in chapter 6).

¹⁰ http://informea.org/uploads/decisions/stockholm/3754_stockholm-POPRC-5-6-en_4df73f5fbb6d5.pdf

¹¹ The main flame retardant use in PWB is tetrabromobisphenol A and derivatives.



(adapted from Alcock et al., 2003; UNEP, 2010a, b)

Figure 2-2: Schematic diagram of the life cycle of c-PentaBDE

2.5.2 C-OctaBDE in reuse, recycling and waste flows

Europe and Japan stopped the use of c-OctaBDE in the 1990s. The production of c-OctaBDE in the United States stopped in 2004. The largest c-OctaBDE content is found in polymers (in particular ABS and HIPS) that are used in EEE and WEEE. The use of c-OctaBDE in polymers in the transport sector was limited.

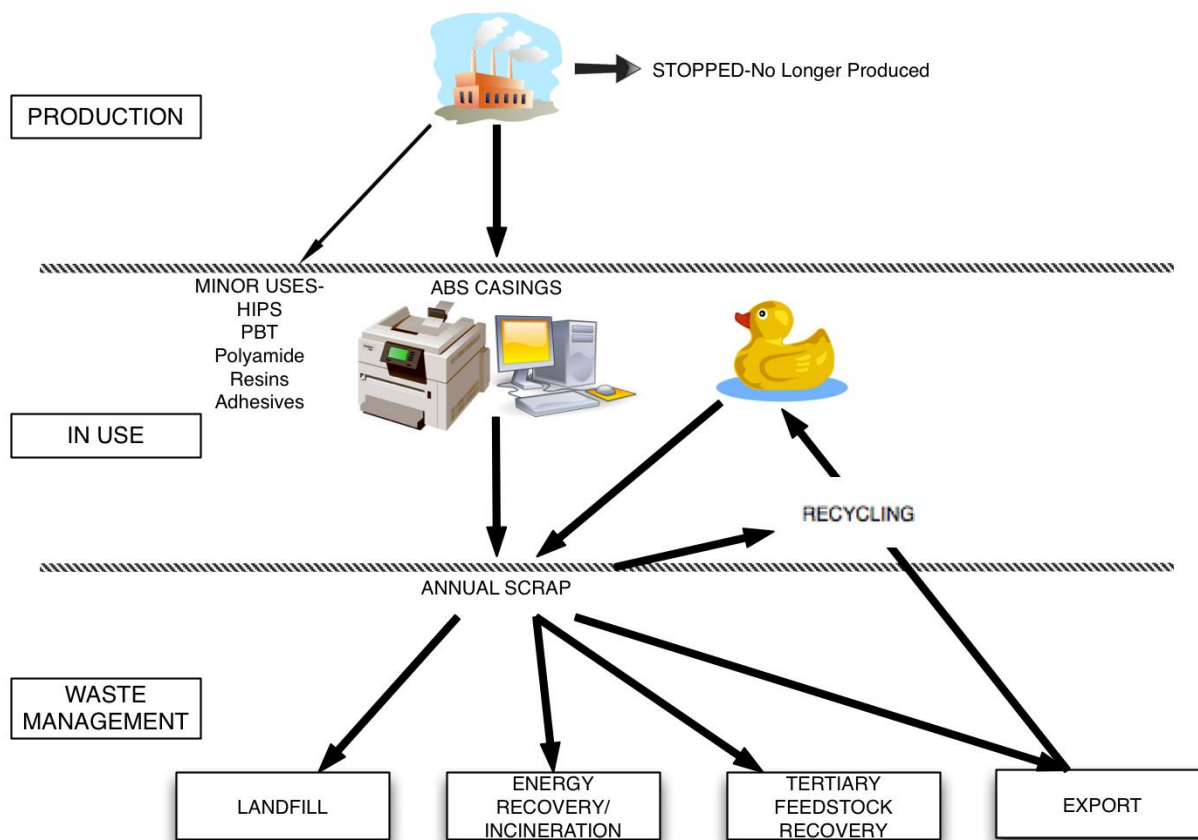
EEE in use, second-hand EEE and WEEE

EEE produced before 2005 may be flame retarded with c-OctaBDE. The main appliances are television and computer CRT monitors. Large quantities of old EEE and WEEE were - and in some cases still are - exported from industrial countries/regions (e.g. United States, Europe and Japan) to developing countries for reuse or recycling. Primitive recycling technologies for WEEE have resulted in large contaminated areas in developing countries and exposure of recyclers and the general population to the contaminants (Wong et al., 2007; UNEP, 2010a, b).

Plastics from WEEE recycling and production of articles from recycled plastic

The mechanical recycling of plastic for further use is strongly favoured from a waste hierarchy and life cycle assessment perspective. When plastics are contaminated with POPs and other hazardous materials, however, particular care has to be given to how the waste hierarchy is followed. The recycling of WEEE results in a fraction of flame-retarded plastic, possibly containing c-OctaBDE. Some plastic from WEEE is sent to developing countries such as China and India where it is recycled into new articles. Recent studies have shown that plastics containing POP-PBDEs and other BFRs have been recycled in the production of articles

for which no flame retardancy is required including children’s toys, household goods and video tapes (Hirai and Sakai, 2007; Chen et al., 2009; Chen et al., 2010). This shows that the flow of plastics containing POP-PBDEs and other flame retardants for recycling are not well controlled and that plastics containing POP-PBDEs are being mixed with non-flame-retarded polymers for the production of items with sensitive end uses. Therefore, in some cases, the use of recycled plastic may be significantly more hazardous than the original use (recycling from a printer housing into a toy that may be chewed by a child, for example).



(adapted from Alcock et al., 2003)

Figure 2-3: Schematic diagram of the life cycle of c-OctaBDE and potential for emissions

2.6 Separation of POP-PBDEs-containing materials

The recommendations of the POP Review Committee, which were accepted by COP5, emphasise the importance of separating POP-PBDEs-containing materials. This followed an extensive “Technical review of the implications of recycling commercial penta and octabromodiphenyl ethers” for the POPs Review Committee (UNEP 2010a, b). This review report and the related Annex should be referred to for detailed information about the background for the management of POP-PBDEs (UNEP 2010a, b).

The obligations arising from the Stockholm Convention apply only to BFRs listed under the Convention, i.e, POP-PBDEs and HBB. However, the separation of materials containing POP-PBDEs from those containing other brominated flame retardants not listed under the Convention is currently difficult due to technological

limitations. Therefore, in practice, in order to achieve the separation of materials containing POP-PBDEs, the separation of all materials containing BFRs/bromine from non-BFR/bromine materials is compelled¹².

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¹² Other advantages for separating plastics containing BFRs/bromine from those which do not are compiled in the Technical review of the implications of recycling commercial penta and octabromodiphenyl ethers (UNEP 2010a,b)

3 General principles and cross-cutting considerations for the recycling and disposal of articles containing POP-PBDEs

3.1 General BAT/BEP considerations

This chapter summarizes general safety measures or necessary precautions to manage POP-PBDEs. These safety precautions apply to all types of products and industries where POP-PBDEs are involved and they relate to waste management, life cycle management. Guidance that apply only to specific process categories are described in the following chapters.

The Stockholm Convention's BAT/BEP guidelines on unintentional POPs (Stockholm Convention, 2007) briefly describe principles such as sustainable development, sustainable consumption, the precautionary approach, integrated pollution, internalization of environmental costs, extended producer responsibility, cleaner production, life cycle assessment, and life cycle management. These principles are all relevant to secure BAT/BEP for the management of POP-PBDEs-containing material flows in recycling and disposal processes. Due to their particular importance for determining the optimal recycling and disposal options, the concepts of life cycle assessment and life cycle management are applied in this document throughout the key POP-PBDEs-containing material flows (see section 3.4).

3.2 Waste management

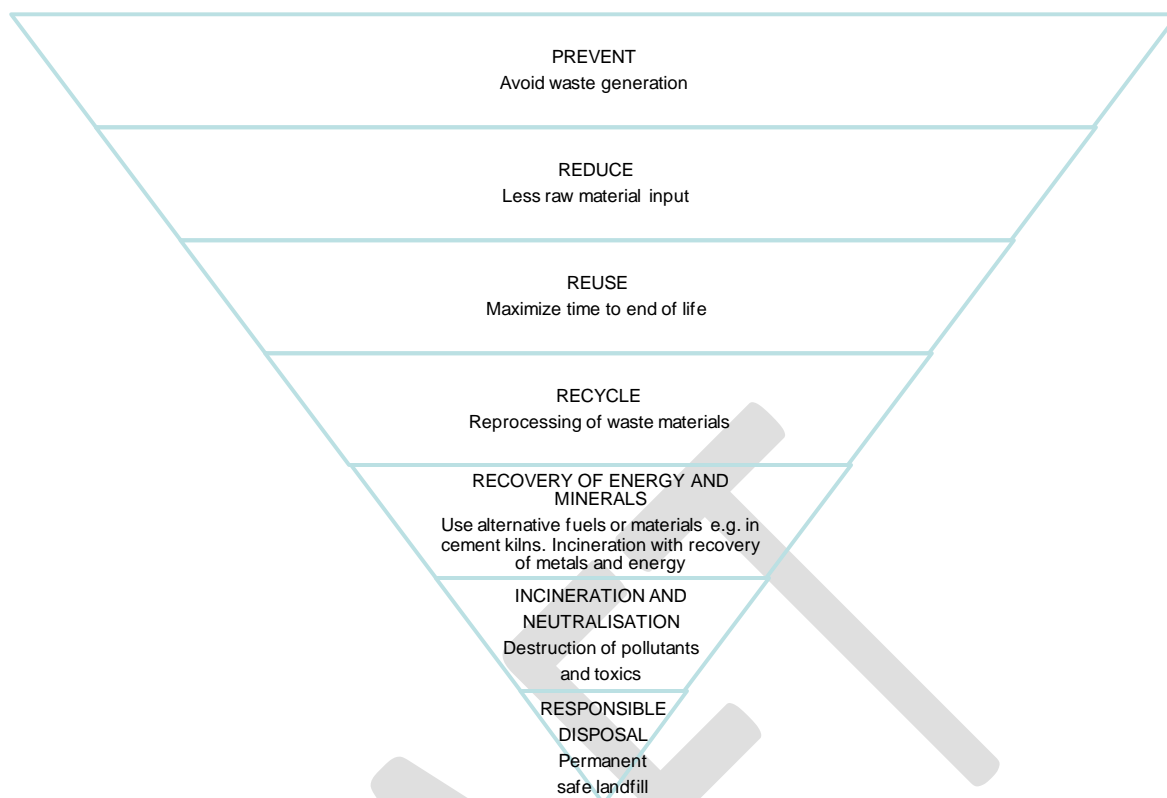
Waste management influences all parts of society and the economy. It concerns local, regional and national authorities and requires a legal framework, a financial mechanism, and an effective coordination between citizens and authorities at all levels. Furthermore, good waste management is not feasible without an adequate level of investment. To ensure a coherent waste management system, it is important all actions at different levels follow a commonly agreed strategy. It is therefore necessary, or at least useful, to discuss and decide upon a national waste management strategy.

The successful implementation of any waste management system, particularly in developing countries, may require the transfer of appropriate technologies and capacity-building in accordance with Article 12 of the Convention.

The COP of the Stockholm Convention sought to ensure that the principles of the waste management hierarchy would be followed wherever possible (Stockholm Convention, 2007). The BAT-BEP guidelines for Annex C of the Convention adopted the hierarchy shown in figure 3-1.

Each decision will always be influenced by local circumstances such as the availability of waste treatment facilities, alternative markets for materials, and the infrastructure available to safely collect, manage and transport waste materials.

When considering POP-PBDE-containing material management options, it is important that the principles of the waste hierarchy are reflected that are also included in the individual chapters. Key issues to be considered on the reuse of POP-PBDE-containing articles are described in the chapters, and the recycling options and separation technologies for POP-PBDE-containing articles/materials are described (chapters 4 to 6). The presence of POP-PBDEs and PFOS in the large associated material flows creates challenges associated with the reuse and recycling of articles containing those POPs. A more precautionary approach is needed for the reuse and recycling of materials containing hazardous chemicals wherever possible in closed material cycles at higher recycling rates. Thermal recovery options are also described and assessed including limitations of treating POP-PBDE-containing wastes. BAT/BEP is described for the disposal of POP-PBDE-containing materials (chapter 8 and annex 3).



(Stockholm Convention, 2007)

Figure 3-1: Waste management hierarchy

POP-PBDE-containing wastes, in particular WEEE and ELV, have been recognised during the last decade as a crucial part of national waste management schemes and strategies. Large PUR foam-containing consumer goods such as furniture, mattresses, and insulation foams are currently not managed in a sustainable manner in most countries.

Therefore the inventory, and in particular the BAT/BEP approach of recycling and end-of-life management of these large material flows containing all potential harmful chemicals, could be included as an important component of national waste management schemes taking into consideration the following life cycle concepts.

3.2.1 Producer responsibility

Producers and other stakeholders have responsibilities that can be established through initiatives such as the EU's integrated product policy;¹³ its thematic strategy on the prevention and recycling of waste¹⁴ and associated framework directives;¹⁵ the extended producer responsibility programme of the Organisation for Economic Co-operation and Development and related guidance (OECD, 2001); the concept of product stewardship; and through other initiatives. In some cases it may be useful to oblige producers to take back certain end-of-life products and to assure their environmentally sound treatment (Stockholm Convention, 2007).

¹³ <http://ec.europa.eu/environment/ipp/>

¹⁴ <http://ec.europa.eu/environment/waste/strategy.htm>

¹⁵ <http://ec.europa.eu/environment/waste/framework/index.htm>

POP-PBDE-containing articles include important material flows for which producer responsibility could be the key for their global management. Such regulatory schemes already exist in some regions for vehicles and EEE, giving the producer the responsibility for end-of-life management. Other POP-PBDE material flows, such as insulation foam, mattresses or furniture, could be addressed using this approach.

3.3 Life cycle management for POP-PBDE-containing materials

Life cycle management (LCM) has been defined as an integrated concept for managing the total life cycle of goods and services towards more sustainable production and consumption, building on the existing procedural and analytical environmental assessment tools and integrating economic, social and environmental aspects (Stockholm Convention, 2007).

Life cycle assessment (LCA) is a comprehensive technique that quantifies ecological and human health impacts of an article or system over its complete life cycle (UNEP, 2011; European Commission JRC, 2010). The main applications of LCA include analysis of the origins of problems related to a particular article, the comparison of improvement variants of a given article, the design of new articles, and the choice between existing comparable products. LCA can also be applied to comparisons of recycling and end-of-life scenarios.

LCA has been applied to recycling systems including a comprehensive assessment of the Swiss collection and recovery systems for WEEE (Hischier et al., 2005; Wäger et al., 2011). A targeted version of the LCA/LCM approach, which defines the boundaries, could be useful to formulate POP-PBDE management strategies in low- and middle income countries whose recycling technologies and approaches are different from developed countries and need to be more labour intensive. For example, this approach could lead to better separation and sorting of recycled materials at WEEE dismantling facilities, and thus achieve higher values and improved recycling business operations. Other examples of LCA/LCM considerations are briefly discussed below (see also table 3-1).

3.3.1 Life cycle considerations for the polymer fraction from vehicles

The light fraction of automotive shredder residue (ASR), containing most of the polymer fraction, is usually defined as the 15–25% mass remaining after depollution, dismantling, shredding of the hulk, and removal of metals from the shredded fraction from an end-of-life vehicle (Vermeulen et al., 2011).

To date only a few papers have addressed the LCA for this waste stream (Vermeulen et al., 2011). There is common ground that landfill should be the least preferred option, but general conclusions on alternatives differ slightly depending on the assumptions and system boundaries (Boughton and Horvath, 2006; Ciacci et al., 2010; Duval et al., 2007).

The LCA approach of Boughton and Horvath (2006) considered hydrolysis to light fuel oil (thermo-chemical treatment), co-combustion in a cement kiln and material recovery for recycling as alternatives to landfill of ASR. They concluded that the co-combustion of ASR in a cement kiln is the most advantageous and short-term practical option, assuming that co-combustion of ASR would not affect the net release of emissions, cement quality or kiln operation. As noted in section 7.3, however, these assumptions may not be robust.

Another LCA study compared five ASR management strategies (Ciacci et al., 2010): (i) landfilling, (ii) increased metal recovery before landfilling, (iii) increased metal recovery before thermal treatment with energy recovery, (iv) advanced material recovery by post-shredder treatments followed by energy recovery and (v) feedstock recycling. The study found that scenarios (iv) and (v) resulted in the highest environmental

benefits compared to the current practice. Scenario (v) feedstock recycling had a slight advantage because it achieved the highest recycling rate, making it the best solution for ASR management.

Both studies confirmed, however, that market conditions still need to be improved to allow profitable recycling of automotive plastics (Duval et al., 2007). These economic barriers or market uncertainties often hamper the full-scale application of alternative ASR treatment methods (Vermeulen et al., 2011). The price of polymers is likely to increase with decreasing oil resources and rising energy costs so recycling can be expected to be more economically attractive in the future and is likely to be BAT/BEP for ASR management.

3.3.2 Life cycle considerations for recycling of WEEE and WEEE plastic

Hischier et al. (2005) examined Swiss take-back and recycling systems, and demonstrated with LCA that the environmental impact of recycling of WEEE was much smaller than that of the alternative baseline scenario considering both incineration of WEEE and primary production of raw materials. This study was done in an industrialized country where the recycling is done in an environmentally sound manner. This may not be the case in most of the developing countries, and so life cycle considerations could be adopted in each case when designing WEEE recycling business processes to ensure the proposed processes will reduce the overall environmental impacts considering the country-specific situations.

3.3.3 Life cycle considerations for the management of PUR foam

Since PUR foam is sent to landfill or is incinerated in most countries, the current life cycle of PUR could be further improved in a more sustainable manner. There is potential for improvement with increased horizontal recycling of PUR foam. While PUR foam can be reused by grinding it into new polymer or recovered by glycolysis, the extent to which this can be done is limited. The large-scale use of PUR foam to make carpet rebond is currently carried out only in North America. The rebond material can again be recycled to rebond.

3.3.4 Life cycle considerations for bromine recovery

Some technologies have been developed to recover bromine from POP-PBDE/BFR-containing material flows (see annex 4). No full-scale facility has yet been operated for this purpose and there is no evidence of such closed-cycle recycling in prospect.¹⁶ For a sustainable substance flow this gap needs to be closed. The increased emphasis on separating bromine-containing plastics, due to current technical limitations for only separating POP-PBDE-containing plastics, could be triggered by the Stockholm Convention's related activities, which might offer options to collect more bromine-enriched materials, which could then motivate the development of bromine recovery processes.

The recovery of bromine (see annex 4) could offer income generation opportunities, if such a business environment was supported by policies and regulations, to contribute towards these costs in cases where the plastics cannot be directly recycled. To further encourage this option, the total costs (including external

¹⁶ Also the recycling rate of BFR-containing polymers is low (estimated for polymers from WEEE to 8% for the EU; PlasticsEurope, 2010) and only a part of these materials is recycled in flame-retarded polymers. Therefore the substance flow of BFRs cannot currently be considered sustainable.

costs) of thermal treatment and landfill or dumping need to be assessed. For thermal facilities this might include environmental costs of emissions, corrosion of facilities and appropriate disposal of the ashes. Hazardous waste incinerators charge approximately €10 per 0.1% of bromine (and chlorine) in their incoming waste streams (Fernwärme Wien GmbH, 2011), but this reflects only higher operational costs rather than environmental costs. In the case of residue disposal, the price needs to reflect the cost of engineered landfills with long-term aftercare (see chapter 8 and annex 3).

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Table 3-1: Comparative emissions and impacts of recycling and recovery technologies

<i>Scenario (Material)</i>	<i>Applied in practice</i>	<i>Waste Hierarchy</i>	<i>Economics **</i>	<i>BFR Removal/ Destruction</i>	<i>PBDD/DF</i>	<i>Worker Exposure</i>	<i>Consumer Exposure</i>
<i>Rebonding (PUF)</i>	Green	Green	Orange	Red	Yellow	Red	Red
<i>Regrinding (Polymer)</i>	Green	Green	Orange	Red	Yellow	Red	Red
<i>Moulding (Polymer)</i>	Green	Green	Orange	Red	Orange	Red	Red
<i>Creasolv (Polymer)</i>	Yellow	Green	Yellow	Green	Green	Yellow	Green
<i>Hydrolysis</i>	Orange	Yellow	Orange	Orange	Green	Yellow	Green
<i>Glycolysis</i>	Orange	Yellow	Orange	Orange	Yellow	Yellow	Green
<i>Pyrolysis for fuel/feed</i>	Yellow	Yellow	Orange	Orange	Red	Orange	Yellow
<i>Pyrolysis/ Gasification</i>	Green	Orange	Yellow	Yellow	Orange	Yellow	Green
<i>Blast Furnace (Polymer)</i>	Green	Orange	Green	Green	Yellow	Yellow	Green
<i>Copper Smelters (PWB)</i>	Green	Orange	Green	Green	Red	Orange	Green
<i>Antimony Smelter</i>	Green	Orange	Yellow	Green	Red	Orange	Green
<i>Electric Arc*</i>	Orange	Orange	Yellow	Green	Red	Orange	Green
<i>Secondary Aluminium*</i>	Orange	Orange	Yellow	Green	Red	Orange	Green
<i>Cement Kilns (All)</i>	Green	Orange	Yellow	Green	Yellow	Yellow	Green
<i>HW/MW Incineration (All)</i>	Green	Orange	Red	Green	Orange	Yellow	Green
<i>Landfill (All)</i>	Green	Red	Yellow	Red	Orange	Orange	Orange
<i>Open Burning (All)**</i>	Green	Red	Red	Red	Red	Red	Red

Green	Yes/ Scoring:
Dark Green	Positive – e.g. low emissions/ environmental/ health impacts
Yellow	Uncertain - probably OK
Orange	Uncertain - possibly negative
Red	No/Negative – high emissions/ environmental/ health impacts

(UNEP 2010a)

* The PBDE material is just introduced with the metal fraction. ** Economics includes external cost consideration.

3.4 Alternatives to POP-PBDEs

C-PentaBDE and c-OctaBDE were phased out about a decade ago and a number of replacements have been developed and introduced over the past 20 years or so. Since production and use of POP-PBDEs are no longer allowed under the Stockholm Convention, some knowledge on alternative flame retardants could be helpful to improve sound chemicals management of flame-retardant materials. An overview of the alternatives available for c-PentaBDE has been compiled (UNEP, 2009). The data illustrate that there are alternative, less hazardous, chemical and non-chemical flame retardants commercially available for both c-PentaBDE and c-OctaBDE. An overview of currently used commercial flame retardants has been compiled in a report for the European Commission (Arcadis EBRC, 2011).

The goal is to replace harmful substances with safer options; alternative flame retardants need to be carefully evaluated to achieve this. The persistence, bioaccumulation and toxicity of halogen-free flame retardants have recently been reviewed (Waaaijers et al., 2012). A case-by-case assessment is necessary to find the best alternative suitable for specific uses. It is important to consider all the available health and environmental data to obtain a comprehensive and robust understanding of the toxicological and ecotoxicological effects and recycling performance of the alternatives (see annex 5).

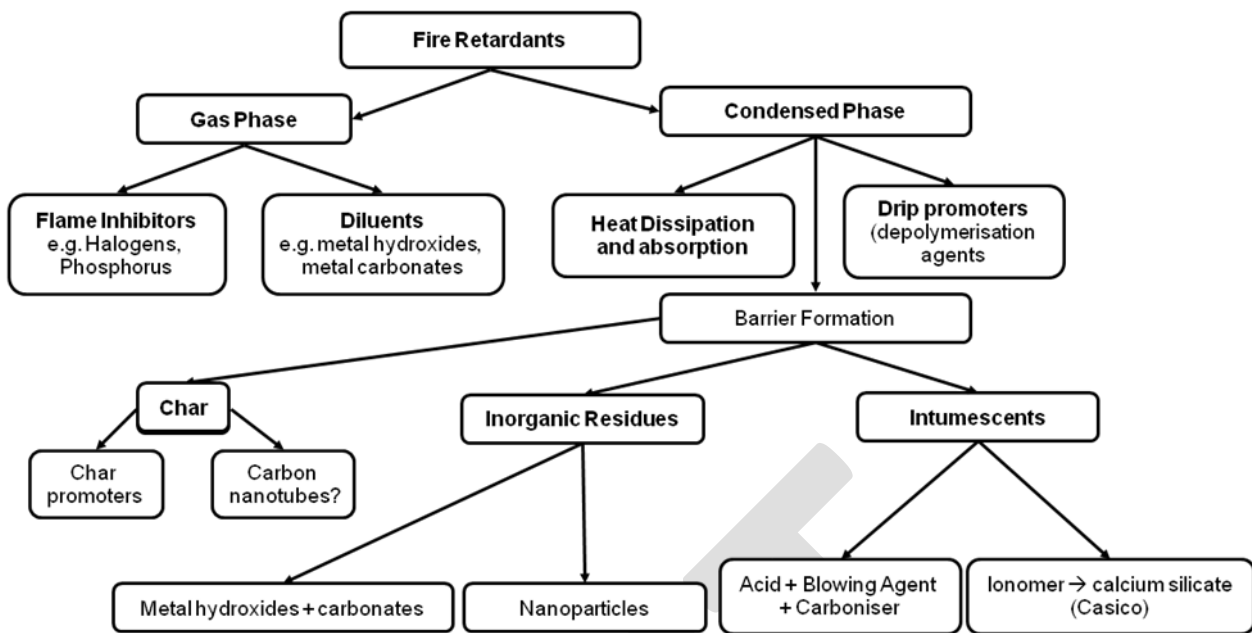
Some alternative flame retardants for the main applications of c-PentaBDE and c-OctaBDE are listed in table 3-2. Decision trees on flame-retardant materials are shown in figure 3-2. Ecological choices of flame retardants have been elaborated by the German Environmental Agency (UBA, 2008).

Table 3-2: Main use areas of c-PentaBDE and c-OctaBDE and some alternative flame retardants

Main use area of POP-PBDEs	Alternative BFR or CFR	Non-halogenated alternatives
Casings of EEE (c-OctaBDE)	c-DecaBDE and decabromodiphenyl Ethane (DBDPE) or tris(tribromophenyl)cyanurate (for ABS and HIPS); HBCD (for HIPS); TBBPA (for ABS); brominated polymers	Phosphorous based halogen-free flame retardants: bisphenol A-bis(diphenylphosphate) resorcinol-bis(diphenylphosphate) (for PC, PC/ABS, and PPE/HIPS)
Small components in EEE (c-OctaBDE)	DecaBDE and DBDPE (for PBT, PET, and PA); brominated polymers	Microencapsulated red phosphorus, magnesium hydroxide, melamine, metal phosphinate (for PA), and Metal phosphinate (for PBT and PET)
Printed circuit boards (c-PentaBDE)	Reactive TBBPA (for epoxy resin); Additive TBBPA (for phenol resin)	Phosphorus based halogen-free flame retardants: dihydrooxaphosphaphenanthrene (DOPO)/ aluminium hydroxide (for epoxy resin); Metal phosphinate/ DOPO/ silica dioxide (for epoxy resin); Polymer phosphonate (for epoxy resin); Flame-resistant thermosets Flame-resistant thermoplastics (under development)
Textile coatings (c-PentaBDE)	DecaBDE (for various fibres); HBCD (for various fibres); Halogenated phosphor organic flame retardants	Inherently flame-resistant synthetic fibres with integrated flame retardants (for PP and PE); Flame-resistant synthetic fibres (for polyaramide); glass fibres; Long-term integration of phosphonium compounds (for cellulose); Intumescent systems (for various fibres)
Polyurethane foam (c-PentaBDE)	Firemaster 550 and 600; Halogenated phosphor organic flame retardants	Various barrier technologies; Substitution of PUR foam in certain applications

ABS: acrylonitrile-butadiene-styrol; PA: polyamid; PBT: poly butylene terephthalate; PET: polyethylene terephthalate; PP: polypropylene; PPE: polyphenyl ether; XPS: extruded polystyrene; EPS: expanded polystyrene; HIPS: high impact polystyrene

PC: polycarbonate (derived from UBA, 2008)



(Hull, 2010)

Figure 3-2: Decision trees on flame-retardant materials

3.5 Monitoring of POP-PBDEs/bromine in polymers

The COP5 recommended that separation of POP-PBDE-containing articles require the screening and detection of POP-PBDEs or bromine-containing materials. One challenge, and prerequisite, is quick and reliable detection of POP-PBDEs in articles, which would allow the separation of POP-PBDE-containing materials in recycling processes. These technologies are discussed briefly in annex 5 and in the *Guidance on screening and analysis of POPs in Articles and Products*. Their applicability and potential use are then discussed in the sections describing BAT/BEP for treating material and recycling streams (see chapters 4 and 6). BAT/BEP technologies on screening (and separation) of POP-PBDEs are further evaluated for their practical applicability including developing country considerations in the following sections.

4 Specific BAT/BEP: POP-PBDE/BFR-containing plastic in WEEE

Since the main use of c-OctaBDE was for plastic casings of EEE (see sections 2.3.2 and 2.5), this is the largest stock and recycling flow of c-OctaBDE. It is therefore of particular relevance for BAT/BEP management.

4.1 Reuse of EEE

According to the waste management hierarchy, repair and reuse of used EEE is the preferred option for end-of-life management (see figure 3-1). Reuse and refurbishing of EEE extends the life span of products, hence saving energy for the manufacturing of new equipment and lowering the environmental impacts of mining for raw materials. Since most uses of c-OctaBDE were phased out before 2000, few remaining EEE items are still expected to contain POP-PBDEs. Therefore the reuse sector for many EEE items is likely not impacted significantly by POP-PBDEs. Exceptions are CRT monitors and TVs, which still appear in significant volumes on the reuse market, especially in developing countries. Some special attention also has to be given to EEE from the US market, where c-OctaBDE was produced until 2004 (UNEP, 2010b).

4.2 Material recycling considerations for plastics containing POP-PBDEs

Plastics recycling makes sense from an environmental and economic perspective as they are produced almost entirely from fossil fuel based petrochemicals.¹⁷ Their production also consumes similar quantities of fossil fuels as their raw materials (Hopewell et al., 2009). In spite of the fossil fuel intensity of plastics, and the low thermal efficiency of most energy recovery processes,¹⁸ some countries burn most of their plastic waste (Hopewell et al., 2009). Yet if 50% of the WEEE plastics from the European market were recycled, emissions of CO₂ could be reduced by nearly 2 million tons, and over 10 million kilowatt hours of energy would be saved in the energy required to convert petrochemicals into plastic (Slijkhuis, 2011). With this recycling level, WEEE recyclers would become more economic because their single largest waste stream would be turned into a resource. There would be significant environmental and social benefits from such recycling if the necessary measures to prevent exposures of workers and the appropriate use of the resulting plastics to protect consumers could be guaranteed. Additional jobs would be created, as plastic recycling is more labour intensive than the production of virgin polymers (Slijkhuis, 2011).

From an economic perspective, the combination of separation technologies can lead to an economic process for the plastic fraction from WEEE (see figure 4-3; section 4.4). Japan has established a Japanese Industrial Standard (JIS) for optimizing the recycling of plastics in electric home appliances, "marking for identification of plastic parts for electrical and electronic equipment (JIS-C9912¹⁹)" Aizawa et al., 2010. This standard requires the marking of plastic parts such as flame retardants, recycled plastics and dismantling procedures. Thus, the information flow is linked with the mass flow. In particular, the marking system includes plastics already recycled by "closed-loop recycling" (recycling from plastics of electric home appliances to plastics of electric home appliances). Target recycling rates for different electronic categories have also been set (Aizawa et al., 2010).

The management of POP-PBDE-containing plastics needs to be assessed and addressed in the larger frame of BAT/BEP for the management and treatment of EEE and WEEE. To describe BAT/BEP for the recycling of WEEE is beyond the scope of this document. BAT/BEP for the management of (selected) WEEE, however, is currently established e.g. in the framework of the Basel Convention and on a

¹⁷ Hopewell (2009) suggested that around 4% of annual petroleum production is converted directly into polymers from petrochemical feedstock.

¹⁸ 17-30% without combined heat and power for a modern incinerator (European Commission, 2006).

¹⁹ JIS-C9912 (Japan Standard Association 2007)

national level (e.g. in Germany the VDI 2343, 2007). The first international guidance in this respect has been established for information and communications technology (ICT) equipment under the Partnership for Action on Computing Equipment PACE (Basel Convention and UNEP, 2011).

The following guidance documents could be consulted for the management of EEE and WEEE:

- *Sustainable Innovation and Technology Transfer Industrial Sector Studies: Recycling from E-waste to Resources* (UNEP and StEP, 2009).
- *Technical Review of the Implications of Recycling Commercial Penta and Octabromodiphenyl Ethers and Annexes* (UNEP 2010a, b).
- *Guideline on Environmentally Sound Material Recovery/Recycling of End-of-Life Computing Equipment* (Basel Convention and UNEP, 2011).

The recycling of POP-PBDE-containing material is discouraged by the recommendations of COP5 and the reasons detailed in the POPRC reports (UNEP 2010a, b) and other studies (Wäger et al., 2010). Additionally for Europe, the RoHS (Restriction of Hazardous Substances) Directive triggers the end-of-life status of recycled plastic, also restricting c-DecaBDE in EEE.²⁰ Similar regulations have been established in other countries.

The exemptions listed in the Convention allow the recycling of POP-PBDE-containing materials if a country has registered for this exemption. For such recycling of POP-PBDE-containing polymers the following BAT/BEP could be further considered:

- Labelling of WEEE plastic fractions containing POP-PBDEs for further processing and labelling of articles produced from such plastic for recycling
- Minimization of occupational exposure in the processing stage (see annex 2; European Commission 2011a)
- Type of articles produced from such WEEE plastic fractions

4.2.1 Labelling of POP-PBDE-containing plastic fractions and articles

BEP can imply that plastic fractions or mixed plastic for recycling from WEEE are labelled or otherwise marked so that their origin is known when they are exported/imported or used by industries for producing new articles. For further recycling, fractions need to be specifically classified or labelled to ensure that the plastic fraction containing POP-PBDEs and other plastics fractions from WEEE recycling²¹ are not recycled into sensitive uses including e.g:

- Toys and other plastic goods with exposure risk to babies and children
- food packaging; food containers;
- silos, storage and piping for food and animal feed;
- kitchen equipment;
- refrigerator interior; freezer interior;²²
- water tanks and water pipes, in particular tanks used for drinking water pipes;
- plastic parts with direct contact such as furniture, handles of tools and doors.

Although not recommended by COP5, plastic fractions containing POP-PBDEs might be down-cycled to materials with non-sensitive use such as lumber or pallets. Such products made from POP-PBDEs-

²⁰ C-DecaBDE can still be recycled into applications different than EEE.

²¹ These polymers can contain other hazardous substances like heavy metals (including antimony, cadmium), other BFRs, PFRs or softeners.

²² The recycling of polymers from WEEE polymers containing no critical chemicals is encouraged following cradle-to-cradle principle e.g. polymers from refrigerators/fridges to refrigerators/fridges.

containing materials could be labelled (see *POPs Labelling – considerations*) to guarantee their appropriate end-of-life management as required by the Stockholm Convention (see Stockholm Convention text, Annex A part IV and V. In this respect it must be ensured that the recycling and final disposal is carried out in an environmentally sound manner (see chapters 7 and 8).

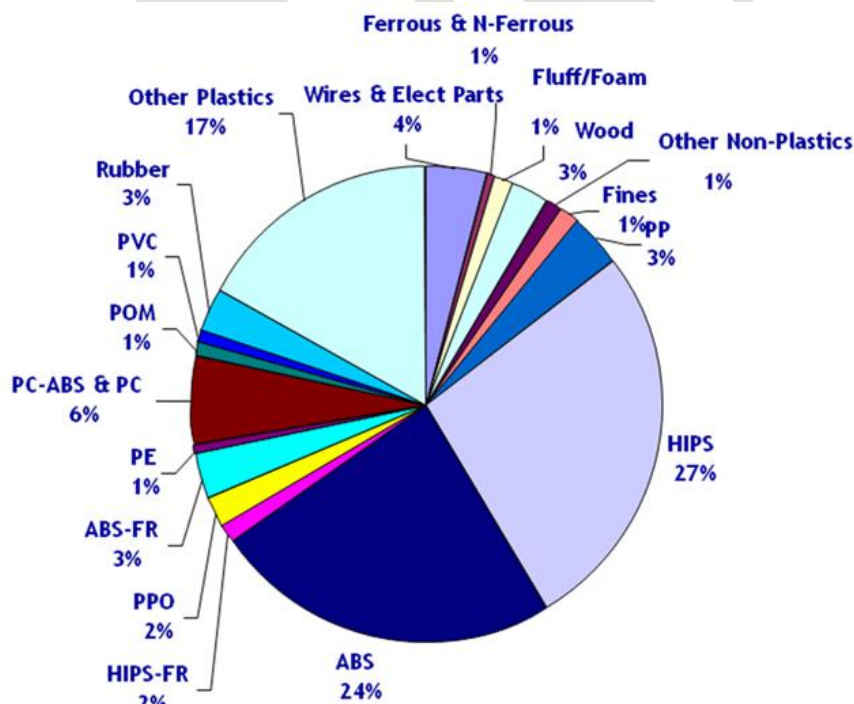
4.2.2 Processing technologies for plastics to minimise exposure

Processing technologies are used to convert polymers and recycled plastics into the required shape of the final product. The processing step itself is mainly a physical transformation step using different technologies often under elevated temperature. Environmental and health concerns of moulding or extruding recycled plastics are emissions of volatile and semi-volatile organic compounds including POP-PBDEs. Preliminary BAT/BEP considerations for such technologies have been listed in annex 2 and are to some extent described in an EU BAT Reference Document (BREF) (European Commission, 2011a).

Some facilities generate wastewater with the potential for high loads of organic compounds, spent solvents and non-recyclable waste that could contain POP-PBDEs. Generic BAT/BEP management for these releases are described in annex 1. Specific BAT/BEP management considerations for energy or material recovery POP-PBDE-containing materials are described in chapter 7 and disposal of POP-PBDE containing wastes in chapter 8 and annex 3.

4.2.3 Types and composition of POP-PBDE-containing plastics

WEEE recycling and recycling activities are normally not optimised for the separation of PBDE-containing plastics (UNEP 2010a, b). In most facilities WEEE shredding results in a mixed plastic fraction as the recycling industry processes different categories (TV/monitors, PCs, white goods, small electronics, lamps, etc). This final polymer rich fraction from WEEE can have an average composition (see figures 4-1 and 4-2).



(Slijkhuis/MBA polymers, 2011)

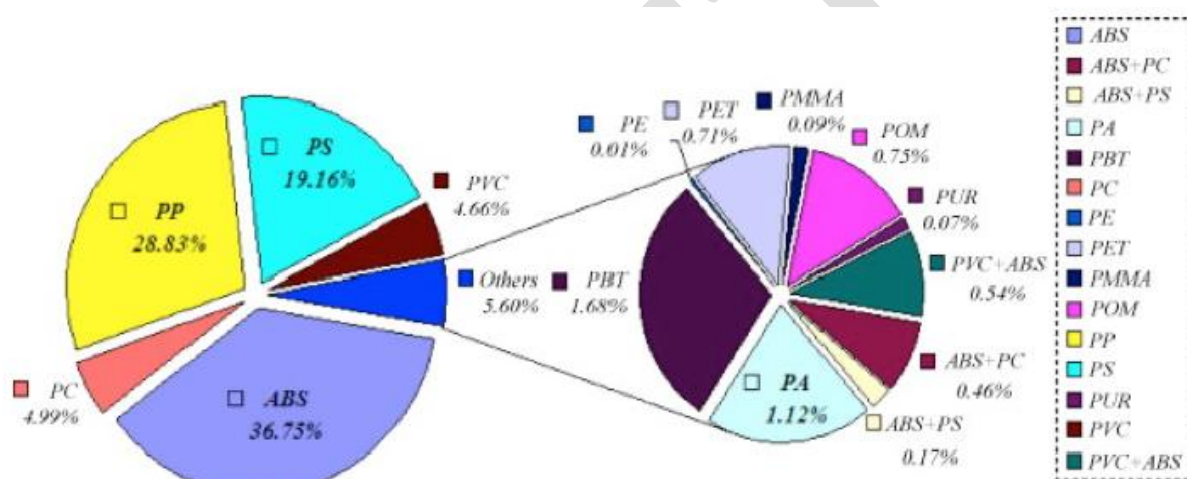
Figure 4-1: Composition of the polymer rich mixture after metal recovery from e-Waste shredding

A large proportion of WEEE plastics is sold as mixed polymer for export, mainly to China or India (UNEP, 2010b). In many parts of the world, however, the polymer fractions and particularly shredder

residues are then sent to landfill (see chapters 6 and 8) or incinerated (see chapter 7), often in non-BAT/BEP facilities.

The four main reasons for the limited recycling of mixed plastics from WEEE are (UNEP 2010b):

- Industry using secondary plastic materials has tight specifications in relation to plastic quality, both chemically (RoHS compliance) and with respect to material properties.
- WEEE plastic fractions often contain 15 or more different plastic types and a degree of cross-contamination is inevitable in practice (see figure 4-2; Dimitrakakis et al., 2009). While three polymers (ABS, PS, PP²³) account for between 70% and 85% of the total, the efficient sorting of the mixtures presents difficult technical challenges.
- WEEE plastics could contain Convention listed POP-PBDEs and also RoHS listed c-DecaBDE²⁴. Potential customers are therefore at risk due to contaminated plastic articles recycled from WEEE.
- Many major manufacturers require production of larger volumes with identical properties and performance and this is difficult from heterogeneous plastic from WEEE.



(Dimitrakakis et al., 2009)

Figure 4-2: Polymer types identified in small WEEE polymer samples (% w/w).

Some of the plastics used in WEEE equipment are high-value engineered thermoplastomers that can be repeatedly softened by heat and hardened by cooling. If these thermoplastomers can be recovered in a usable condition they can be sold for a profit.

TV and computer monitors provide two of the richest sources of plastics: the plastic content in these two product groups varies between 10 wt % and 40 wt %. The major plastic part of a monitor is the rear part of the housing; this is separated for recycling and to gain access to the cathode ray tube. These plastic parts are normally removed by hand in the facilities and this gives a clean polymer fraction consisting mainly of ABS and HIPS, which can then be recycled. To maximize resale value, polymers must then be sorted by polymer type (e.g. HIPS, ABS thermoplastic), and by colour.

After the plastic has been cleaned and sorted into a specific type, it will need to be compacted for storage and transportation (annex 1), or further processing (see annex 2). This can be done by hand tools such as scissors, shears, etc., or, better, by baling, shredding and size grading. Some mechanized operations combine heating, rapid cooling and cutting into grain. These smaller pieces are then typically heated and extruded through a die to form strings and pellets for final sale as raw materials. This polymer fraction is normally traded at prices that only allow a limited number of treatment steps,

²³ Normally no/low POP-PBDE or PBB.

²⁴ But normally no PBB that is also listed in RoHS and the Stockholm Convention.

especially when the cost of incineration of residual POP-PBDE-containing plastics has to be covered. Therefore the disposal of residual contaminated plastics needs to be covered by the revenue from WEEE recycling (e.g. noble metals) or by legal implementation of the extended producer responsibility (e.g. European WEEE or Chinese WEEE regulations).

While initial collection and handling of unbroken plastic parts and cases should not involve exposures of concern to hazardous substances, all subsequent processing involves higher exposure risks. Plastic particles, additives and brominated flame retardants may be released, causing exposures to workers (UNEP 2010a, b). Size reduction and granulation can also generate heat and, if not properly managed, open smoke and fire. After granulation, the plastic will be moulded under elevated pressure and temperature with risks of exposure to substances contained in the plastic and new substances such as halogenated dioxins and furans (Ota et al., 2009).

4.3 Technologies to separate POP-PBDE-containing polymers

Separation technologies are designed to pick POP-PBDE-free plastics out of WEEE plastics with the aim of recovering valuable and marketable products, the sale of which generates much of the process revenues. Thus, development and running and combining these technologies is driven mainly by economy of the overall process chain. That means that separation of POP-PBDEs is only a part of the overall strategy to produce valuable products with a reasonably high yield and a quality accepted by producers of new products (see figure 4-3).

WEEE plastics may be transformed into valuable plastic for recycling by a chain of optimized processes sometimes performed by more than one company. The process is only economically feasible if the cumulative cost of processing is lower than the revenues for the recycled product (see figure 4-3). Therefore, separation of POP-PBDE-containing plastic needs to be effectively integrated with the main driving forces of a recycling plant: the technologies used for shredding of WEEE and separation of polymers for polymer material recycling and for metal recycling.

The following techniques could be used at a plant recycling plastics from WEEE as BAT/BEP:

- Manual dismantling approaches or shredding technologies.
- Sorting technologies to separate possibly POP-PBDE-containing bulk and shredded plastics as listed in figure 4-3.
- Combinations of technologies to optimise the separation process (see 4.3.3 and table 4-1).
- Full-scale plants to separate WEEE and POP-PBDE-containing plastics (see 4.3.5)

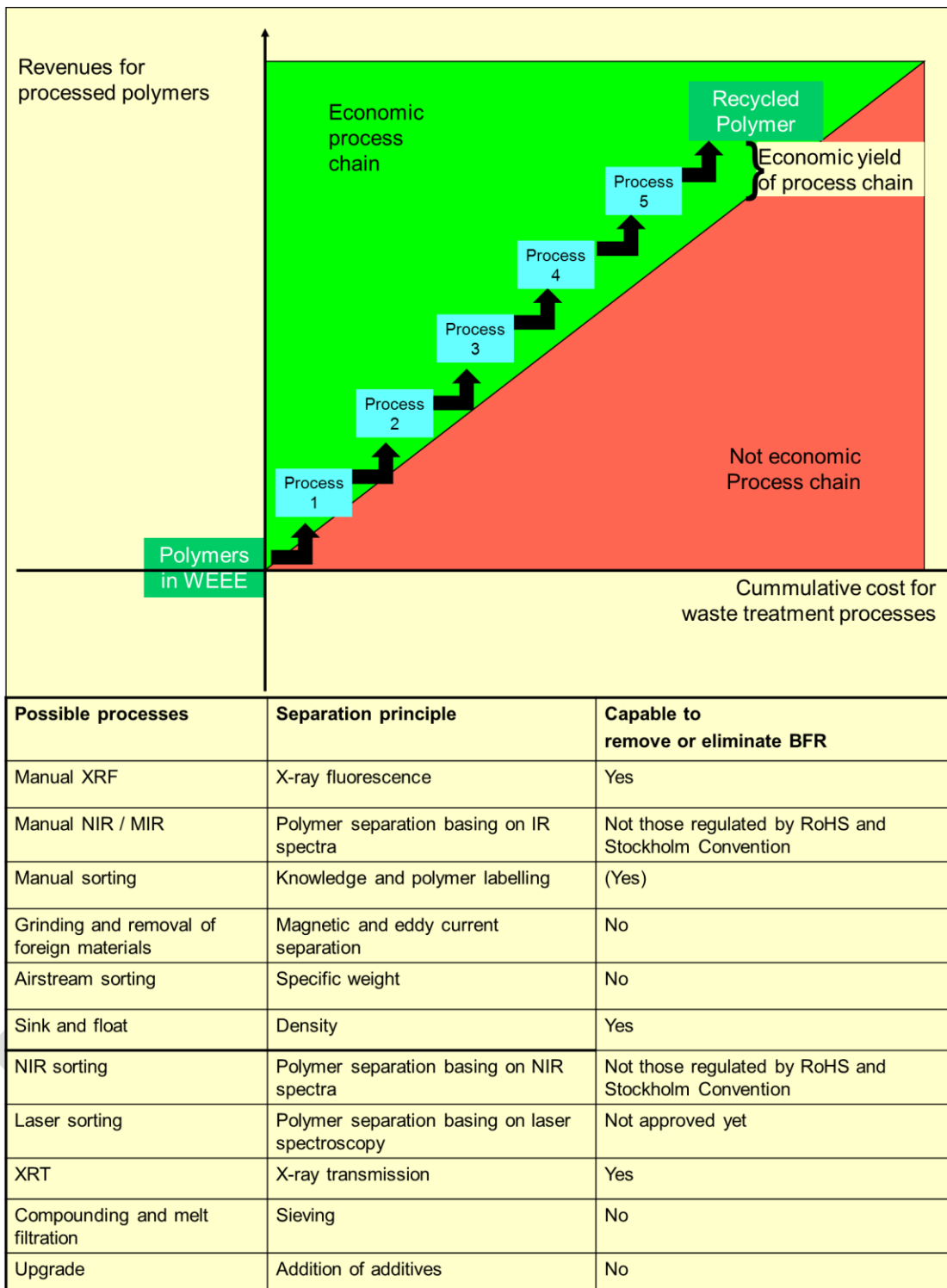


Figure 4-3: Stepwise separation of polymers from waste of electrical and electronic equipment and their transformation into valuable plastic-for-recycling.²⁵

(Numbers of process/separation steps are indicative and vary depending on process combinations used (see examples below in 4.3.3 and table 4-1). The above list includes possible separation technologies and methods.)

²⁵ There is no stringent rule for the choice of processes; however, for the purpose of this guidance at least one principle of POP-PBDE removal should be applied. Further, the processes may be performed by more than one company.

4.3.1 Manual dismantling approaches

Recycling companies handling CRT monitor housings often manage these plastics separately based on their experience of the specific type of polymers and type of flame retardant, thus keeping these streams "cleaner". Colours of plastics could influence the effectiveness and efficiency of the sorting technologies engaged after sorting processes; therefore it is important to separate plastics into different colours considering, in particular, challenges with separation of black/dark plastic materials.

BEP approach applied in Sweden

Retegan et al. (2010) describe the current principal method used in the Swedish recycling industry for the separation of plastics from TVs and computer monitors containing POP-PBDEs. This approach is used only for TVs and monitors; however, it is not clear how many of the non-marked plastics do contain POP-PBDEs. The listed items are removed manually from the waste stream. Training and experience in manually sorting WEEE plastics and parts containing POP-PBDEs is needed to effectively sort polymers and remove those components. Even experienced manual sorting operatives cannot, however, determine which types of POP-PBDE are incorporated in the polymers. Thus, the report recommends that manual sorting be supervised by spot-checks using XRF measurements. Although this report does not include information on the effectiveness of this approach, it claims that, for waste TV and PC monitors, the accuracy of these sorting methods is satisfactory for complying with European directives/legislation.

The compliance with legislation is not surprising as the number of residual articles still containing PBDEs has now dropped to low levels in Europe (Wäger et al., 2010).

Applicability of manual separation for other regions

The effectiveness of manual separation needs to be evaluated in other countries or regions where the composition of POP-PBDEs in the different WEEE categories is likely to be different before a BEP recommendation can be given.

The separation of a larger share of potentially POP-PBDE-containing equipment might be possible in particular for regions where POP-PBDEs were phased out in the 1990s (e.g. Japan or Europe). Here mainly older electronics produced in the 1990s and earlier could be separated.

For regions where c-OctaBDE (and c-PentaBDE) was used until 2004, and particularly in the United States where volumes were very high, even relatively new equipment can contain POP-PBDEs and manual separation of POP-PBDE-containing equipment is likely to be less effective.

Manual separation of POP-PBDE-containing plastic in developing countries

Manual separation of POP-PBDE-containing materials without instrumental help could be an option, to some extent, if the flow was to largely stem from the period in which c-OctaBDE was not used any more in the region and only a few older equipment items have to be sorted out. Developing countries often have large stocks of WEEE from the 1990s and early 2000s with a high percentage of POP-PBDE-containing TV casings and computer monitors (Sindikú et al., 2011). Therefore, such pure manual pre-sorting without a bromine screening seems currently not to be a feasible approach to removing POP-PBDEs in developing countries (or at least the African region). Practical tests, however, are missing.

Manual separation also seems challenging considering the complexity of the different electronics (different types, different producers and different series from the same type and producer) and the uncertainty of producers that have used a POP-PBDE type. Although the simplicity of this approach has obvious attractions, a more detailed analysis of the correlation between the visual assessments and XRF screening would be necessary before it could be recommended as BAT/BEP.

4.3.2 Individual screening technologies to separate possibly POP-PBDE-containing bulk and shredded plastics

Screening technologies to determine plastics containing POP-PBDEs/BFRs need to be easy to use, reliable and economical for developing countries. The XRF and sliding spark technology available are relatively simple and robust methods (WRAP, 2006a) and therefore appear appropriate for use in developing countries in WEEE recycling and similar facilities (UNEP, 2010a, b). Both methods are labour intensive; although this is a disadvantage in industrial countries because of the associated labour costs, it is not a barrier in developing/transition countries with lower wages.

The sliding spark technology for the detection of halogens (Seidel et al., 1993; IoSys, 2010; Seidel, 2012) costs around US\$6,000. A German producer of sliding spark technology has confirmed that equipment has been supplied to China and South Africa (Seidel, 2010), thus indicating it is already used in developing/transition countries.²⁶ Such handheld sliding spark equipment is available with additional detectors (near infrared; NIR) for determination of the polymer type (at a cost of approximately US\$33,000) and could be used for producing clean polymer fractions with associated higher market values. The manual determination of polymer type to produce clean polymer fractions could be an attractive option for recovery of high-quality polymer from developing and transition countries and could be combined with the separation of POP-PBDE/BFR containing plastic.

The use of these technologies needs to be further assessed for their practicability.²⁷ Alternatively, such equipment could be used for confirmation of other separation techniques (e.g. sink and float or manual separation based on experience) (UNEP 2010a, b).

Sliding spark spectroscopy

The lowest detection limit for bromine with this technology is 0.1%. For practical reasons the recyclers normally set the system at 1% bromine to screen out POP-PBDE/BFR-containing plastics, which normally contain between 3% and 20% POP-PBDEs/BFR (Seidel 2010).

Sliding spark spectroscopy using handheld instruments is used in WEEE dismantling plants and other fields for screening halogens in plastic. It allows operators to distinguish between BFR-containing (halogen-containing) and almost BFR (halogen) free components. The scanning time is quick and takes only a few seconds. Also the instrument needs a direct contact to the material surface and coated materials need to be specifically addressed by scratching the coating.

With dual-function equipment including NIR, this method can also distinguish different polymer types. Instruments with this integrated function therefore have the potential for practical separation not only of PBDE/BFR and non-PBDE/BFR plastic but also for polymer types at e-waste dismantling and recycling facilities at the dismantling stage. As mentioned above, NIR has difficulties with recognizing black plastic.

XRF technology

WEEE may contain components that originate from previous recycling of POP-PBDE-containing polymers. These may contain mixtures of different BFRs, including c-OctaBDE, but exhibit bromine levels in the range of 100-1000 ppm (Bantelmann et al., 2010; Chen et al., 2009, 2010; Sindiku et al., 2011). Only XRF is sensitive enough to trace these materials.

The XRF technology has been described in section 2.6. It can be used for detection and separation of POP-PBDE-containing plastic with a bromine detection limit of 10 to 100 ppm. The time requirement

²⁶ The tasks for which the equipment is used in South Africa and China are not documented.

²⁷ International projects on WEEE recycling in developing/transition countries could determine whether such equipment is already used for selection of the polymer types and if there is already any experience in determining bromine content in practical operations.

for a measurement when applying handheld items is less than a minute. With a cost of approximately US\$30,000 to US\$50,000, its use in small size enterprises may be limited. Since the handheld XRF instrument needs a direct contact to the material surface, it is not applicable for use in automated sorting systems but is used in the dismantling stage. Coated materials need to be specifically addressed by scratching the coating.

XRT technology

The X-ray transmission has been described in annex 5. It has been developed to separate materials with different optical densities. In contrast to the handheld screening instrument (XRF and SSS) normally applied in dismantling plants, it is intended to sort scrap automatically. Industrial machines sort up to 1 tonne of scrap per hour. The technology is used to separate PBDE/BFR-containing plastics from BFR free types in Switzerland. It may, therefore, play a role in WEEE plastic recycling plants particularly if combined with NIR.

One of the companies claims its system is able to clean and separate alumina fractions, CRT glass fractions (Pb vs non-Pb), and RDF fractions from metals, glass and PVC, and to remove halogen-containing materials (Schlummer 2011). Limited information, however, exists on the separation success with mixed WEEE plastic scrap, the waste fraction containing the majority of WEEE plastics.

XRT is not a stand-alone technique as the produced bromine-reduced fractions require further treatment with respect to producing marketable recycled polymer. Sorting machines based on X-ray transmission are available at an industrial scale (for example one of the existing systems costs approximately €400,000).

Raman spectroscopy

Raman spectroscopy equipment in combination with sorting to separate PBDE-containing polymers has been developed in Japan (Tsuchida et al., 2009; Kawazumi et al., 2011). The pilot equipment can sort 400 kg of plastic shredder/hour. Practical performance of the equipment need to be further verified before recommendations can be given.

Separation of polymers by sink and float technologies

Polymer types exhibit different specific weights, and therefore liquid media with appropriate densities allow for separation of different thermoplastics into density groups. The salinity, and hence the density, of the liquid media can be changed by adding different salts. If water is being used, for example, the density can be raised 15% by the addition of magnesium sulphate. BFR additives increase the density of the ABS and HIPS materials significantly, when added at typical concentrations (> 3%). If treated in an appropriate liquid medium, bromine-free polystyrene will float while bromine-containing polystyrene will sink, thus separating the polymers containing bromine from other polymers (Schlummer and Maeurer, 2006).

A simple two-stage separation has recently been tested successfully in a German collaborative project (SpectroDense; InnoNet, 2009). At first the mixture is treated in a liquid with a density of around 1,100 kg/m³. The float fraction will mainly consist of PP, PE and BFR free PS, and ABS; whereas BFR-containing styrenics, but also PPO/PS and PC/ABS (both flame retarded with phosphate based FR) and highly filled PP items will sink. The float fraction is further treated with water (density 1,000 kg/m³) to separate HIPS and ABS from PP and PE.²⁸ Valuable polymers as PC/ABS and PPO/PS (normally free of POP-PBDEs) could be separated from the heavy fraction by downstream NIR techniques, as these materials are grey in many cases.

For selected input fractions, the sink and float technology produces very clean and qualitatively good products in respect to separation of BFR-containing materials. TV housings are mainly HIPS. Since about 30%²⁹ of the casings in Europe contain BFR, sink and float (S/F) is a good way to separate them,

²⁸ These two binary mixtures could further be separated by NIR or electrostatic separation.

²⁹ The content of BFR will depend on the region and the legislation for flammability standards - in the United States/Canada most of the casings contain flame retardants.

and the high yields of BFR free materials suggest the process is economic (Schlummer, 2011). In Africa this share seems higher (Sindikou et al., 2009).

With respect to BFRs, and especially POP-PBDEs, S/F has been reported to effectively separate BFR-containing materials from non-BFR types of ABS and/or HIPS (Schlummer and Maeurer, 2006). S/F has been reported used in separation of BFR rich fractions of TV/PC from low BFR fraction intended for recycling purposes in Sweden (Retegan et al., 2010). One challenge of the S/F technology is that the fractions of HIPS/PPO (1,150 kg/m³) and PC/ABS (1,180 kg/m³) are present containing phosphorus flame retardants and must be considered in the overall separation strategy (see below).

With respect to plastics from small electronic equipment and mixed WEEE plastic from recycling of mixed WEEE, S/F can produce almost bromine-free plastic fractions, consisting largely of ABS, PS (incl. HIPS) and polyolefins. Due to a large share of black plastics in these low-bromine fractions, which inhibit a downstream NIR separation, it is challenging to produce high quality polymers with a good market price as useful output. Currently, the yield of these techniques does not normally allow economic recovery of polymers. Thus unless the bromine-free fraction can be converted into valuable plastic for recycling, S/F is unlikely to be widely used. Operators are (understandably) unwilling to use a separation technique to produce what might be, in effect, two new waste streams without adding value to the output (Schlummer, 2011).

4.3.3 Combinations of technologies for producing marketable products

None of the individual techniques described above has the ability to separate mixed plastic from WEEE: to ensure that the plastic is separated into marketable polymer fractions and that, at the same time, POP-PBDE/BFR-containing plastics are separated. Therefore, combinations of the techniques need to be used in practice.

In addition, no technique achieves a 100% separation, leading to residual POP-PBDE levels in the intended bromine-free fraction. In the case of handheld sorting this is due to errors by the operatives. For automated systems, the sorting efficiency with blowing bars has its limits and the purity of sorted fractions is normally below 95%.

This section describes process chains, which include steps suitable (in principle) for the separation of POP-PBDEs/BFRs followed by technologies focusing on polymer separation and upgrade of fractions (whereas section 4.3.5 lists existing plants). The process combinations are based only on technical considerations and do not take into account the economic feasibility, which may vary significantly in different countries. Local costs and revenues therefore need to be calculated for the different combinations of technologies.

Dismantling → NIR → Sink and float (→ Electrostatic separation)

Dismantling sites usually recover CRT glass from computer monitors. As these products contain rather large plastic housings, which are in most cases built by PS, ABS or blends of these polymers with polycarbonate (PC/ABS) or polyphenylene oxide (PPO/PS), dismantling personnel can easily produce a polymer fraction from these items upon the established glass recycling process.

After a coarse crushing process, the material waste plastics can be separated into the following polymer fractions by online NIR: light PS, light ABS, light PC/ABS, light PP, light PPO/PS and dark materials that cannot be identified with NIR.

The light PS and light ABS, as well as the dark fraction, are most likely containing higher amounts of BFR, which can be separated by the sink and float technology when performing two separation runs in density media of 1,000 and around 1,100 kg/m³. The sink and float technology is based on the fact that BFR rich ABS and PS exhibit significantly higher densities compared to non-BFR ABS and PS.

As the dark density fraction 1,000-1,100 kg/m³ is intended to contain both ABS and PS, a subsequent separation of both materials is preferred and can be performed by electrostatic separation. The latter technique is available on an industrial scale and works best for binary and well dried plastic mixtures. In this process, the plastic mixture is fed via a vibrating conveyor into a so-called tribo-electric charging unit. Different plastics are charged here selectively and specifically according to the material, taking on a positive or negative charge. After charging has taken place, the plastic mixture reaches a high tension field where the components are separated electrostatically into pure sorted fractions according to their charges: positive particles are attracted by a negative electrode, while negative particles are rejected and vice versa.

Dismantling -> Sink and float (→ Electrostatic separation)

Dismantling sites usually recover CRT glass from TV sets. As TVs typically include large plastic housings predominately composed of PS and only rarely by ABS or PP, dismantling personnel can easily produce a polymer fraction from these items to supplement the established glass recycling. Recent research has shown that it is possible to reduce the amount of non-BFR-ABS in this fraction to a minimum by appropriate training. This is important, since TVs contain dark plastics unsuitable for NIR sorting. After a grinding process, the PS rich fraction is separated in a BFR rich and almost BFR free fraction by S/F. As the dark density fraction 1,000-1,100 kg/m³ contains both ABS and PS, a subsequent separation of both materials is preferred and can be performed by electrostatic separation. The latter technique is available on an industrial scale and works best for binary and well dried plastic mixtures (Hamos, 2012; Wersag, 2012; see table 4-1).

Dismantling -> Manual sorting (→ Sink and float)

The most elaborative approach is manual sorting, preferably assisted by handheld NIR and a handheld bromine identification tool (SSS or XRF). In addition to these tools, sorting personnel should check casing for materials stamps indicating the type of material. By using these techniques, trained personnel may be able to collect a high share of (almost) BFR free materials from plastic streams. Subsequently NIR technologies will enable production of fractions of defined polymer types for further processing. A disadvantage of this approach may be that large items like housing of printers, monitors and TVs with high levels of BFRs are side products requiring a sound waste treatment. In contrast, plastics parts from non-BFR or low BFR equipment are normally smaller and not often dismantled and treated by shredder techniques.

Shredder → Sink and float → Electrostatic separation

Shredded plastics from mixed WEEE (especially small WEEE appliances) have to pass removal steps for Fe and non Fe metals and dust before they may be treated by a two-step sink and float process in density media of around 1,100 kg/m³ and 1,000 kg/m³. The fraction smaller than 1,000 kg/m³ is intended to be rich in PP and minor amounts of PE. The intermediate density fraction is considered to contain BFR free ABS and PS as well filled PP types. These three fractions may be subsequently separated by electrostatic separation (Hamos, 2012; Wersag, 2012; see table 4-1).

Shredder → XRT → Spectroscopy

From mixed WEEE fraction, a plastic fraction is recovered in state of the art WEEE treatment plants by a set of smashing, grinding and mechanical separation processes. Since this fraction has a typical particle size below 20 mm, automated online rather than manual separation processes are required for further upgrading this fraction for polymer recovery.

Bromine and chlorine may be removed by online XRT technology producing a low-bromine fraction of mixed plastics composed of up to 16 polymer types. The main polymer types (PS, ABS, and PP) may be

recovered subsequently by online NIR; however, this technique is limited to the fraction of light materials, which is unfortunately not the major fraction of WEE plastics.

In a current pilot test, Fraunhofer IVV (Freising, Germany) and Unisensor (Karlsruhe, Germany) are testing and optimizing a new automated sorting technique based on laser spectroscopy. Results obtained so far clearly indicate that this technique is able to separate several polymer types out of a mixed input stream of shredded plastics automatically with high throughput rates (~1 ton per hour). Laser spectroscopy (in contrast to NIR) can identify black and dark plastics and might therefore become a key technology to transform BFR free plastic shred from WEEE into marketable sorted polymer type fractions. Further investigations are focusing on the identification of BFRs with laser spectroscopy applying comparable high throughput rates. (Schlummer, 2011; Unisensor, 2012).

4.3.4 Comparison of technologies to separate polymer streams

Some practical combinations of technologies used for separation of polymers for different input materials are listed in table 4-1. Also the possible product output, the status of development and the economy or available commercial systems are mentioned

Table 4-1: Combinations of separation techniques, input materials, products, status of development and remarks on related economy

Combination	Suitable input	BFR free products	Status of development	Economy	Reference
Dismantling → NIR → sink and float (→ Electrostatic separation)	Plastics from dismantled WEEE items	ABS, PS	Approved	Economy depends on the yield of BFR free products	Schlummer (2011)
Dismantling → Sink and float (→ Electrostatic separation)	TV casings	HIPS	Approved	Approved	Schlummer (2011)
Dismantling → manual sorting (→ sink and float)	Plastics from dismantled WEEE items	ABS, PS, PC-ABS	Approved	Not approved in industrial countries	
Shredder → Sink and float (→ Electrostatic separation)	Mixed WEEE (small appliances)	ABS, PS, PP	Approved	System runs successfully at wersag AG (Großschirma, Germany)	Hamos (2012) Wersag GmbH (2012)
Shredder → XRT → spectroscopy	Mixed WEEE	BFR and PVC "free" plastic mix	Approved	No information	Schlummer (2011) Unisensor (2012)

4.3.5 Full-scale plants to separate WEEE and POP-PBDE-containing plastics

Table 4-2 lists some of the WEEE treatment plants in operation and their potential to separate POP-PBDE-containing plastics.

Table 4-2: Full-scale WEEE/WEEE-plastic treatment plants and their potential to separate POP-PBDE-containing plastics.

WEEE input	Separation techniques	Polymers Separated	Quality of separated polymers	PBDE/BFR Elimination (RoHS compliant)	Development Stage*	Reference
Mixed plastic from WEEE (Austria, China)	Not disclosed	A) Low-BFR types of ABS, HIPS and PP	A) Good (Customer specified)	Yes BFR rich fraction incinerated	Industrial scale	MBA Polymers (2012)
Small EEE, White goods (Switzerland)	Includes XRT	BFR and PVC free polymers	Good	Yes	Industrial scale	RUAG Technology (2012)
WEEE plastics (UK)	Undisclosed	Low-BFR types of ABS and HIPS	Good	Yes	Industrial scale	Morton (2007)
WEEE plastics (Germany)	Undisclosed (incl. S/F and Electrostatic)	Low-BFR types of PP, ABS, HIPS	Good	Yes	Industrial scale	Wersag GmbH (2012)
TV and computer casings (Sweden)	Manual, not disclosed	Low-BFR types of ABS and HIPS	Good	Yes	Industrial scale	Retegan et al. (2010)
Mixed plastic from WEEE (Germany)	Successive Grinding and XRT	BFR and PVC free polymers	Not yet approved	Yes	Industrial scale	Adamec Recycling (2012)

(UNEP 2010a with modifications)

4.4 Energy recovery and end-of-life management of POP-PBDE plastics

Energy recovery in appropriate BAT/BEP incinerators or possibly in other thermal BAT/BEP facilities offers energy/material recovery³⁰ options for POP-PBDE-containing plastic fractions. The treatment technologies and requirements are described in chapter 7.

BAT/BEP considerations for landfilling of POP-PBDE-containing materials are described in chapter 8 and annex 3. As noted previously (section 3.3) this option is least favoured by life cycle considerations since POPs are not destroyed but stored for the next generation.)

³⁰ Material recovery is considered for metals in WEEE including co-processing of a share of the polymer fraction.

5 Specific BAT/BEP: POP-PBDE/BFR materials in the transport sector

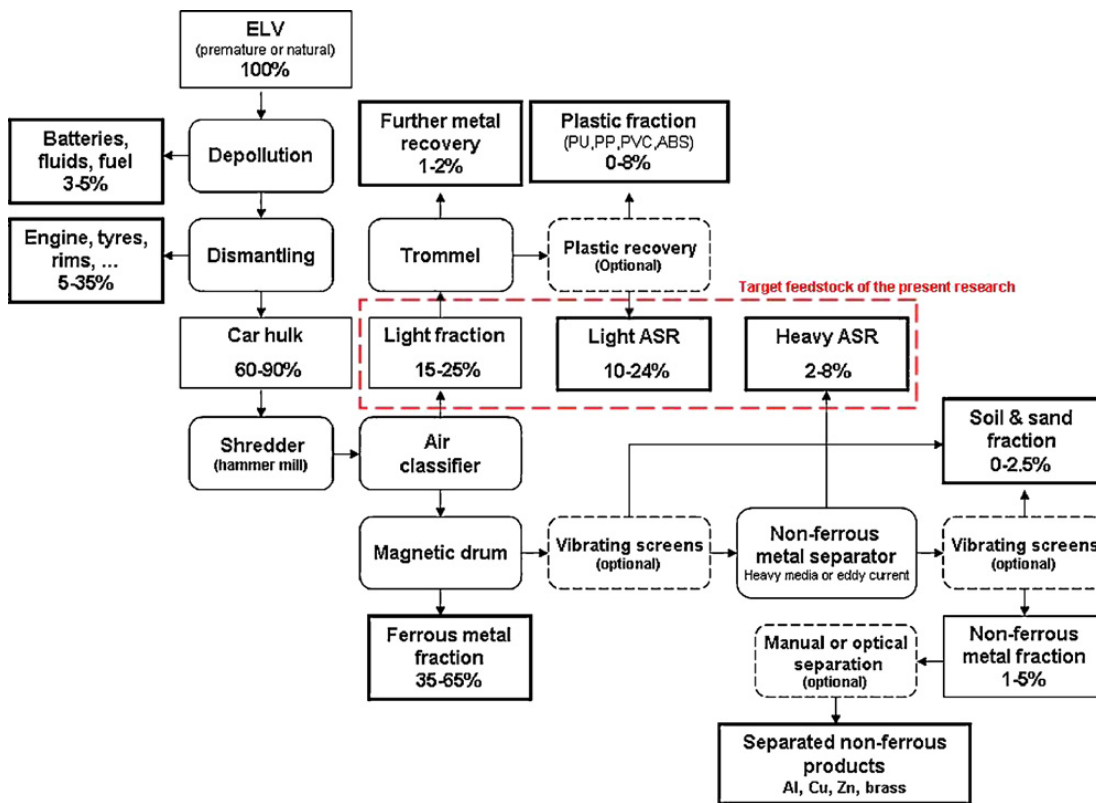
The transport sector (cars, busses, trucks, trains, ships³¹, and planes) is one of the largest global material and waste flows. One of the main uses of c-PentaBDE was in PUR foam for the transport sector. C-PentaBDE was used in upholstery of seats, headrests and ceilings, and application in textile back-coating. Some c-OctaBDE was also used in plastic parts (e.g. dashboard, steering wheel). The transport sector can be considered as a large stock and reuse/recycling flow for POP-PBDEs because of the relatively long lifetime of vehicles (in particular in developing countries) and high reuse and export rate.

POP contaminants in end-of-life vehicles (ELVs) could also include polychlorinated biphenyls (PCBs)³² and PCDD/PCDF (*Stockholm Convention BAT/BEP Guidelines (Stockholm Convention 2007)*; Vermeulen et al., 2011). Other hazardous substances found in ELVs are heavy metals, such as copper, cadmium, lead, nickel and zinc, which also need to be considered for proper assessment of final waste management of ASR. Due to these contaminants, some countries have classified ASR as hazardous waste and have established legislative controls. Total (heavy) metal concentrations in ASR are reported to be up to 22% (Lanoir et al., 1997; Vermeulen et al., 2011). ASR also contains significant levels of chlorine - normally from 1 wt % to 4 wt % - mainly due to the presence of PVC or halobutyl rubber (Boughton, 2007; Vermeulen et al., 2011). ELVs also contain waste oil, and ozone depleting substances (ODS) like CFC refrigerants and climate active refrigerants like HFC, which need specific pre-treatment before the shredding step.

Developing countries have recently begun implementing BEP measures to manage vehicles and ELVs. One BEP approach is the concept of environmentally friendly village mechanics addressing the waste management of vehicle repairs and end-of-life vehicles (Nwachukwu et al., 2011).

³¹ Ship dismantling is addressed by the Basel Convention (<http://www.basel.int/ships/index.html>)

³² The data available indicate that polychlorinated biphenyls released from shredder plants are from industrial/intentional polychlorinated biphenyl production and have been introduced with the oils and dielectric fluids, etc., contained in the vehicles or more probably in consumer goods which are shredded in particular white goods (*BAT/BEP Guidance Stockholm Convention*).



(Vermeulen et al., 2011)

Figure 5-1: Schematic of the processing of an end-of-life vehicle

5.1 Reuse of vehicles containing POP-PBDEs

Repair and reuse is the preferred end-of-life management for vehicles when considering the waste management hierarchy. Reuse saves energy from new manufacturing and avoids the environmental impact of the production of new raw materials, which is particularly important for such resource intensive material flows.

Since the use of POP-PBDEs ended in most regions before 2000 (e.g. Europe, Asia³³), a large share of these vehicles are not in operation any more in industrial countries but have reached end-of-life or have been exported to developing/transition countries. Therefore the reuse sector for vehicles in industrial countries in these regions is not impacted significantly by POP-PBDEs (Morf et al., 2003). Some special care has to be taken for vehicles in/from North America where c-PentaBDE and c-OctaBDE was used until 2004 with the largest POP-PBDE use volume (see chapter 2).

In developing countries, where vehicles are used for decades, many cars from the 1970s, 1980s and 1990s are still in operation (*POP-PBDE Inventory Guidance*). In these regions POP-PBDEs in the transport sector could be of particular relevance. Human exposure, particularly taxi drivers or other professional drivers, to POP-PBDEs from POP-PBDE-containing vehicles could be relevant, especially for aged vehicles with bridal PUR foam considering results of exposure studies from United States (Imm et al., 2009; Stapleton et al., 2008, Betts, 2003). Therefore the reuse of vehicles containing POP-PBDEs is not recommended.

³³ Some uncertainty exists about the production and use of c-PentaBDE in China.

5.2 Treatment and recycling of end-of-life vehicles

End-of-life vehicles contain valuable materials (in particular metals) and therefore the recycling rate of ELVs has always been high (about 70%). The environmental impact of the non-recycled fraction of an ELV should nevertheless not be overlooked, as it often exhibits hazardous characteristics due to the presence of spent oils and lubricants, heavy metals, and POPs (Vermeulen, 2011). Many ELVs today also have air conditioners containing ODS and/or GHG. Thus the dismantling and depollution step (see section 5.4.1) is of crucial importance for environmentally sound management of ELVs.

Normally the materials containing POP-PBDEs end up in the ASR fraction when processing ELVs (see figure 5-1). The ASR is normally further separated into a “light ASR” and a “heavy ASR” where the PUR foam is contained in the light ASR fraction and makes up 4% to 20% of this fraction (see figure 5-2).

In industrial countries the light shredder residues from ELVs are normally not recycled but subject to thermal destruction/energy recovery (see chapter 7) or disposal in landfills (see chapter 8 and annex 3).

Some industrial countries have introduced legislation requiring recycling quotas for ELVs (and other materials), e.g. the Japanese Government introduced the Law on Recycling of ELVs (ELV Recycling Law) in 2002, which requires manufacturers to retrieve CFCs, airbags, and ASR from ELVs and to properly recycle the remaining materials. Europe has introduced the ELV Directive requiring a recycling quota of 95% from 2015 onwards (European Commission, 2010).

More recently, some facilities recycle the polymer fractions as described below.

5.2.1 Dismantling and depollution of the vehicle

Before dismantling, the potentially hazardous and toxic parts need to be removed from the ELV. Fluids, like brake fluid, petrol, steering fluid, motor oil, coolants (ODS and GHG) and transmission fluid, should generally be removed from the ELVs or other devices before shredding. This is especially applicable in the case of PCBs, which should be identified and removed from any device to be shredded. Specific attention should be given to transformers and condensers. More detailed measures are described in the Stockholm Convention’s BAT/BEP guidelines for Annex C chemicals (Stockholm Convention, 2007).

This depollution step offers the option to remove POP-PBDE-containing materials for further treatment. These materials could be separated using bromine screening technologies (see section 3.6), particularly if the non-impacted polymers are further considered for material recycling.

In the dismantling step, reusable and recyclable components are removed, with special emphasis on components with a sufficient market value or containing valuable materials (e.g. catalytic converters). Table 5-1 lists parts of an ELV that can easily be recycled, indicating also possible end products.

In general, 5–35% of an ELV’s mass can be removed for reuse or recycling, depending on the age of the ELV, the market value of the removed parts, and the labour costs to remove these parts (Vermeulen et al., 2011). A large difference exists between, for instance, European countries, where only about 5–10% of an ELV’s mass is removed during dismantling, and South Korea, where up to 35% of an ELV’s mass is removed during this stage (Ferrão et al., 2006; Joung et al., 2007; Forton et al., 2006). This demonstrates the large potential of the dismantling step as a BEP measure.

Exposure to pollutants (including POP-PBDEs) should be minimised by appropriate procedures (e.g. with low dust generation) and the use of appropriate personal protection equipment.

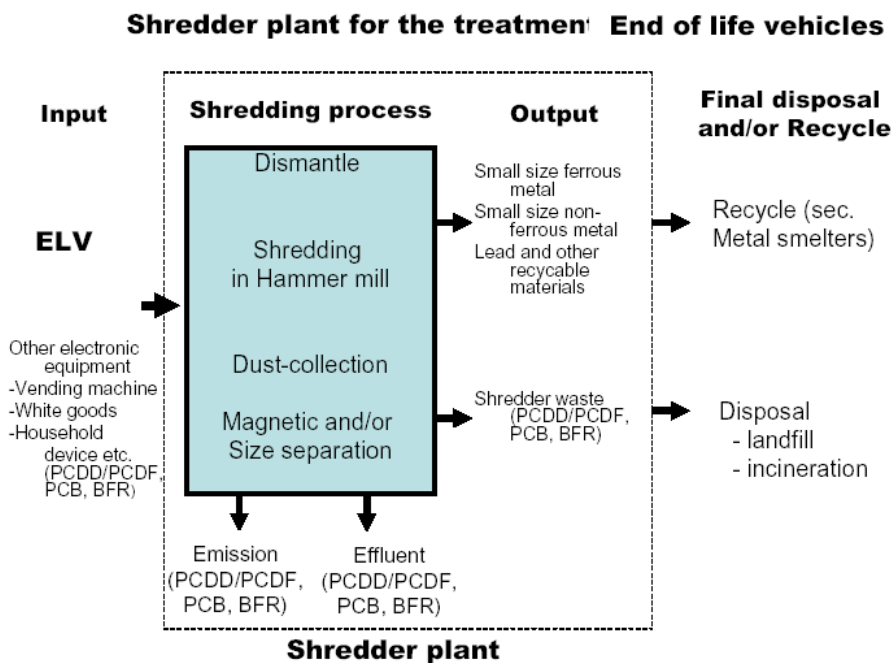
Table 5-1: Parts that can be recycled from ELVs

Part	Material	Recycled as
Window	Glass	Tiles
Seat	Foam and fibre	Soundproofing materials for vehicles
Body, trunk, hood and door	Steel	Car parts and general steel products
Wire harness	Cu	Cu and engines products (cast Al reinforcement)
Bumper	Resin	Bumper, interior parts, toolbox, etc.
Radiators	Cu and Al	Gun metal ingots and Al products
Coolant, engine and gear oil	Oil	Alternative fuel for boilers and incinerators
Engine transmission, suspension and wheel	Steel and Al	General steel and Al products
Catalytic converter	Precious metals	Catalytic converters or precious metal (e.g. platinum) recycling
Tire	Rubber	Raw material and energy recovery (e.g. cement kilns)

(Zameri and Saman; 2006; Vermeulen et al., 2011)

5.2.2 Shredder plants

Shredder plants for the treatment of end-of-life vehicles are listed in Annex C of the Stockholm Convention as a source that has the potential to form and release unintentionally produced POPs; they are therefore described in the Stockholm Convention BAT/BEP guidelines (Stockholm Convention 2007, Part III Source category (k)). An overview of the process is shown in figure 5-2.

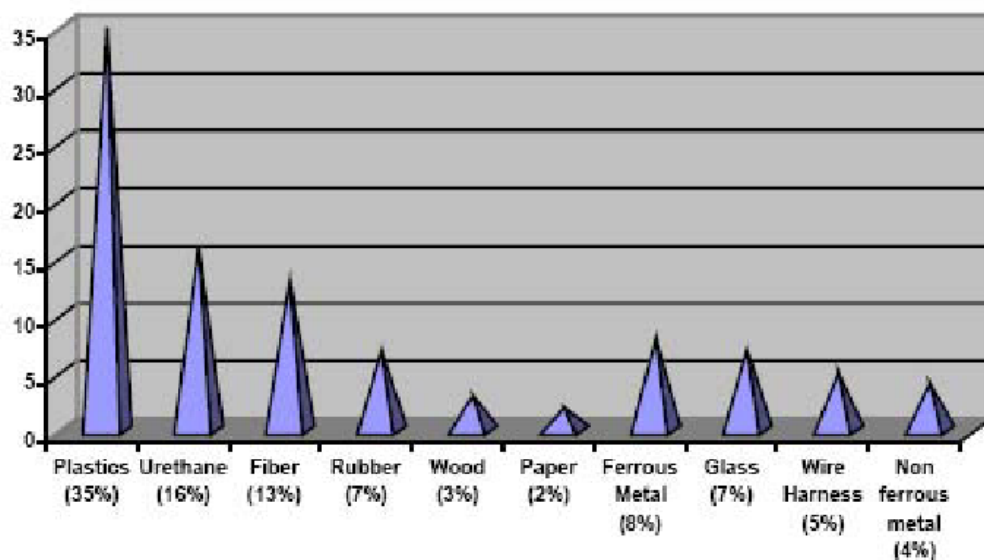


(Stockholm Convention, 2007)

Figure 5-2: Overview of the shredder process

Many components of vehicles are made of non-ferrous materials, such as copper, aluminium and zinc. In the shredding process, magnetic separation is used to remove the magnetic ferrous fraction from other materials. The non-ferrous metals, such as copper and aluminium, are normally sorted out at a later stage by manual or optical separation. The remainder is the ASR and is estimated at between 15% and 30% of the weight of ELVs (Stockholm Convention, 2007; Vermeulen et al., 2011). ASR consists of glass, fibre, rubber, automobile liquids, plastics, PUR foam and dirt (see figure 5-3) and is normally further separated in the “light fraction” (containing PUR foam, most of the textile and plastic) and a “heavy fraction” (see figure 5-1).

Since shredder plants can generate dust and other releases (including the above-mentioned pollutants) appropriate personal protective equipment should be used.



(Stockholm Convention, 2007)

Figure 5-3: Composition of shredder waste

5.2.3 Recycling by improved depollution and post-shredding techniques

As mentioned in section 5.2.1, a significant share of materials can be recycled. The possible POP-PBDE-containing materials (PUR foam and plastic/textiles from the interior) are normally not listed as materials being recycled (see table 5-1). Due to the increased pressure on material recycling, however a higher share of the polymer fraction will need to be recycled in future. According to Ferrão et al. (2006), increasing the recycling of the polymers from ASR is the key objective e.g. the European reuse and recycling target of 95% by 2015. Since polymers are increasingly used in cars, this fraction will become even more relevant in future. Therefore several BAT/BEP facilities to process ASR have been established in Europe (see table 5-2).

The PUR foam (considered to contain the main POP-PBDE fraction)³⁴ is approximately 5%, and up to 15%, of the ASR fraction (in average approximately 16 kg PUR foam/car); however, it makes up over 30% of its volume (Hoffman, 2008). The US industry says that the viability of foam recovered from shredder residue for the foam-rebond market depends on two key factors: (i) development of an economical process for recovering foam from shredder residue, and (ii) confirmation that the recovered foam meets quality requirements (Hoffman, 2008). The POP-PBDE-content could become one of the quality requirements.

Argonne National Laboratory has developed a polymers separation system based on froth flotation (Hoffman, 2008). A series of six tanks is used, each with a specific function, depending on the polymer being recovered. The chemical solutions in each tank are chosen for the particular application. This system has been used for recovering selected polymers from ASR, disassembled car parts, industrial scrap plastics, and consumer electronics (Selke, 2006). Argonne has found that the highest-quality foam comes from dismantling and then washing the foam from seats. But it claims that manual separation of foam is not economical for industrial countries (Hoffman, 2008; UNEP, 2010b).

In 2004 NV Salyp of Ypres, Belgium commissioned the Salyp ELV Centre, which operated the Argonne technology under licence, to recover PUR foam and other polymers from shredder residue. It is

³⁴ In the United States, the main PUR-foam applications in transport (seat, arm/head rest) were treated with approximately 1% c-PentaBDE to meet MVSS 302 (Luedeka, 2011; see chapter 6).

reported to have an operational process capacity of 6 tonnes of ASR per hour. The plant also used technology licensed from a German firm, KUTEC, for separating different types of thermoplastics from the Argonne technology reject stream. The Argonne technology separates the fluff into three streams: fines, foam, and a thermoplastic-rich stream. The foam stream is cleaned and sold for markets such as rebond foam in carpet underlay and for padding in automobiles (Selke, 2006; UNEP 2010b).

Other facilities take polymer-enriched fractions from the shredding process of vehicles. One precondition here is a pre-processing step to generate a polymer enriched fraction with 70% to 80% polymers so that the transport to a plastic recycling facility becomes economically viable (Slijkhuis, 2011).

Table 5-2: Overview of post-shredder technologies³⁵

	Argonne	Galloo	MBA-polymers	Salyp process	Stena	R-plus (WESA-SLF)	VW-Sicon
Separation techniques							
Air classification	X	X	X	X	X	X	X
Magnetic separation	X	X	X	X	X	X	X
Eddy current separation	X	X	X	X	X		X
Screening		X		X	X	X	X
Trommel separation	X	X		X	X		
Optical sorting				X			X
Manual sorting					X		
Drying						X	
Float/sink separation		X		X	X		X
Froth flotation	X						
Thermo-mechanical sorting				X			
Wet grinding			X				
Hydrocyclone			X				
Static, hydrodynamic separation tanks		X					
Heavy media separation					X		
Status of development	Operating plants	Operating plants	Operating plants	Operating plants	Operating plants	Operating plants	1 trial plant + 2 under construction
Overall recovery rate	90% of polymers > 6 mm 90% of metals > 6mm	90%	Not given	86%	80%	92%	95%

(Vermeulen et al., 2011)

5.3 Energy recovery and disposal of ASR and other ELV residues

5.3.1 Energy recovery

ASR has a high calorific value (14–30 MJ/kg), which is favourable for energy recovery. The high chlorine content, however, together with the presence of brominated flame retardants and the high heavy metal concentration and ash content, limits its use as a fuel substitute (Vermeulen et al., 2011).

ASR therefore requires BAT waste incinerators for proper treatment. In Switzerland all ASR is co-incinerated with a maximum co-incineration rate of 5%. Non-BAT incineration or treatment by pyrolysis lead to the formation of PCDD/PCDF and other unintentionally produced POPs (Sakai et al., 2007; Weber and Sakurai, 2002).

The aim of advanced secondary recovery techniques for production of refuse derived fuel is to segregate ASR and isolate the combustible materials with low ash content and with low halogen and contaminant concentrations. The halogen and heavy metal rich fractions need further treatment and sound waste management, which can be challenging. The finest fraction of ASR generally has the highest ash and mineral oil content, combined with the lowest calorific value. Screens, shaker tables, rotary drums or float/sink separation techniques can be applied to remove this fine sized fraction and thus improve the fuel characteristics of the ASR (Morselli et al., 2010; Boughton and Horvath, 2006; Hjelmar et al., 2009). Halogenated polymer components such as POP-PBDE/BFR-containing materials, PVC, or (halobutyl) rubber are the main sources of the high halogen concentrations often found in ASR. PVC removal from ASR is a simple way of lowering the overall chlorine concentration. Several

³⁵ Other operating facilities recovering polymers from ELVs are TBS in Enns (Austria) and SRW in Espenhain (Germany).

studies have pointed out that density separation, using a bath density of 1,100–1,200 kg/m³, can remove the majority (up to 68%) of chlorinated and POP-PBDE/BFR-containing plastic (density of about 1,400 kg/m³ or more) from the combustible materials of ASR (Hwang et al., 2008; Boughton, 2007). In some cases heavy metals must be removed from ASR before recycling or energy recovery to meet the regulatory limits of the final application (Vermeulen et al., 2011).

Thermal treatment technologies for energy/material recovery are described in chapter 7.

Another “recycling” approach for ASR is the direct incorporation of the fine sized ASR fraction into materials such as composites, concrete or asphalt, which might be considered a temporary storage.

5.3.2 Disposal of ASR

In ASR the concentrations of some heavy metals, such as Cu, Cd, Pb, Ni, Zn, may exceed the limit values of applicable landfill regulations and pose a threat for the environment as these metals can leach from deposited ASR (Gonzalez Fernandez et al., 2008). Similar consideration can be given for POP-PBDEs and PCBs. Disposal of ASR is therefore problematic and is regulated e.g. in the European Union ASR is classified as hazardous waste according to the list of hazardous wastes (2000-532-EEC)³⁶. Despite this pollutant reservoir, however, even industrial countries currently mainly deposit ASR in landfills. BAT/BEP considerations for deposition of POP-PBDE-containing materials are described in chapter 8 and annex 3.

5.4 Developing country considerations

There is limited evidence of recycling of POP-PBDE-containing materials from ELVs in developing countries. The first preliminary new POPs country assessment in Nigeria found no specific recycling activities of POP-PBDE-containing materials from the transport sector (plastic and PUR foam). Currently there is hardly any appropriate BAT/BEP incineration capacity (see chapter 7) in developing countries to treat POP-PBDE-containing ASR. Most landfills in developing countries also do not meet even the standards for sanitary landfills and thus are far from meeting the criteria of landfills to which POP-PBDE-containing materials might be disposed (see chapter 8 and annex 3). Therefore developing countries do not currently have an appropriate end-of-life treatment option for POP-PBDE-containing polymers from ELVs, and support is evidently needed to ensure that these wastes are treated in an environmentally sound manner.

³⁶ Section 1910, an annex of the European Directive 91-689-EEC on hazardous waste.

6 Specific BAT/BEP: POP-PBDEs-containing PUR foam

Flexible polyurethane foam (FPF) is a manufactured article with a multitude of end uses (Luedeka, 2011; UNEP, 2010b). The main uses of FPF products are in:

- Residential and commercial upholstered furniture (coach, chairs)
- Residential and institutional mattresses and top-of-bed products including pillows and mattress pads
- Vehicles (cars, trucks, trains, ships, planes; see also chapter 5) as interiors for seating, upholstered trim and acoustic panels
- Military and defence applications to help prevent fuel-related flash fires in vehicles, vessels and aircraft

Minor use volumes are in:

- Protective packaging applications
- Healthcare for restraining, support, pressure-relief, fluid absorption and wound care applications
- Air and fluid filtration
- Laboratories and testing instruments as absorption medium
- Apparel padding and insulation
- Cushion underlayment for residential carpet installation, particularly in the United States

While FPF may appear to be a generic commodity product, it is, in fact, often a technical article with specific performance attributes created through proprietary formulations and fabrication processes. Many FPF manufacturers produce more than 150 different FPF products, each having unique characteristics appropriate for specific end uses (Luedeka, 2011).

The FPF industry uses two basic production methods: slabstock (outside the United States, referred to as “block foam”) and moulding. Each method requires unique product formulations using a number of raw materials including, but not limited to, a polyol, diisocyanate, surfactant, catalyst, auxiliary blowing agent and numerous optional specialty additives including, in some instances, fire retardant products (Luedeka, 2011). Formulations for slabstock and moulded products may require adjustment prior to or during production to respond to ambient production conditions including humidity, temperature and barometric pressure. Such formulation adjustments may include variations in concentration and/or changes in the selection of various raw materials including additives such as optional fire retardants (Luedeka, 2011).

The regional use of POP-PBDEs (chapter 2) is particularly relevant for recycling considerations of PUR foam for regions possibly impacted by those markets because of vehicle or furniture export/imports.

6.1 Reuse of furniture and mattresses possibly impacted by POP-PBDEs

The reuse of FPF-containing furniture (e.g. couch, (arm)chair), mattresses or textiles is the preferred end-of-life management when considering the waste management hierarchy. Reuse saves energy of new manufacturing and avoids the environmental impacts of production of new raw materials.

Markets with flammability standards for furniture at the time of production of c-PentaBDE (before 2005) are the United States and the United Kingdom. Mattresses for private consumers were not significantly treated with c-PentaBDE, which was mainly used for those from public/governmental institutions like prisons, military facilities or hospitals (Luedeka, 2011).

For most other countries, no specific flammability standards have been established in the past for furniture. These countries/regions, therefore, are not, or only to a minor extent, impacted by c-PentaBDE in PUR foam applications depending on the import of such articles from countries with

specific flammability standards (United States and United Kingdom). Thus the reuse sector for furniture and mattresses is likely not (significantly) impacted by POP-PBDEs in most countries/regions. If an aged couch, pillow or vehicle, however, contains c-PentaBDE, human exposure to POP-PBDEs could be relevant (Betts, 2003; Imm et al., 2009; Stapleton et al., 2008; UNEP, 2010b) and the reuse would not be recommended.

The assumption that most regions are not impacted by POP-PBDEs in these use areas requires some confirmation before the unrestricted reuse of these articles can be considered as BEP. Parties discovering relevant c-PentaBDE in such articles in use or reuse might need to assess if further steps for the protection of human health are necessary.

6.2 Recycling/recovery of PUR foam

Recycling of articles containing PUR foam such as furniture, vehicles, mattresses, and construction need management considerations such as the geographic origin and the production years of the articles. The use of flame retardants and the type of flame retardants used highly depend on the region and country. It is assumed that more than 90% of c-PentaBDE in PUR foam, and also most hexabromobiphenyl (HBB), has been produced/used in the United States and is largely either already deposited in landfills, in use or recycled in carpet rebond (UNEP, 2010a, 2010b). Therefore it can also be assumed that most other regions and countries (excluding United States/North America) have a low content of c-PentaBDE and HBB in their current PUR foam.

Recent monitoring of POP-PBDEs in baby products in the United States, however, has revealed that these products can contain POP-PBDEs (Stapleton et al., 2011). In all facilities dealing with recycling or end-of-life of PUR foam, the general BAT/BEP considerations (annex 1) should be taken into account. Considering the finding of high c-PentaBDE blood levels in workers at a US PUR foam recycling facility (Stapleton et al., 2008), occupational safety measures, such as elimination of contaminated PUR foam before processing foams and the use of appropriate personal protective equipment, could be considered in facilities known to process c-PentaBDE-containing PUR foam.

For flexible PUR foam categories known to partly contain POP-PBDE impacted material, such material could be screened for bromine (see section 2.6) to separate the POP-PBDE-containing materials. Such separation can either be at the state of collection or in the facility recycling PUR foam.

While the separation of POP-PBDE/BFR-containing polymers by separation of BFR-containing fractions has been developed to full scale for WEEE plastics (see chapter 4), there is no information on such separation for other POP-PBDE/BFR-containing materials including PUR foam. For larger polyurethane foam items like mattresses or furniture, the same screening methods used for WEEE plastics items could be applied with handheld XRF or sliding spark spectroscopy. A screening study, possibly supported by government, could reveal if such an approach was needed in a country.

If facilities for thermal recovery are not available in the country, POP-PBDE-containing material could be stored (annex 1) until appropriate treatment technologies are available or they are disposed in sanitary landfills, which is the least preferred option (see chapter 8 and annex 3).

The decision on the final treatment of non-impacted PUR foam should be based on LCA considerations. Depending on the local circumstances (available market, logistics, quality of thermal facilities), recycling or energy recovery could be the preferable option.

6.2.1 Rebond: Recycling PUR foam with phase-out of c-PentaBDE

Rebonding is the process whereby scrap PUR foam is shredded into small pieces and then reconstituted with a polyurethane prepolyol binder to produce an aggregated polyurethane foam product (USEPA, 1996). The main use is in the production of carpet cushions (Eaves, 2004). The vast majority of carpet cushion is used in English-speaking countries, specifically the United States, United Kingdom and Australia. Little carpet cushion is yet used in the rest of the world (Luedeka, 2011). Other uses of rebond include school bus seats (USEPA, 1996) and floor mats for gymnasias (Zia et al., 2007). Other recycling uses for foams that are not reused in the refurbishment of mattresses or for rebond include pet bedding, stuffed animals and insulation (UNEP, 2010b). Relevant exposure of PUR recycling and carpet installers to POP-PBDEs has been demonstrated in a first study from the United States (Stapleton et al., 2008) and there are obvious risks of further exposure of consumers.

6.2.2 Material recovery from mattresses

As mentioned in section 6.1, mainly mattresses in specific institutions (e.g. prison, hospital, military) are flame retarded, even in countries with specific flammability standards. Such specific sources could be monitored for bromine/PBDE for an overview of the presence of POP-PBDEs/BFRs. If POP-PBDEs are detected in these uses, they could be excluded from recycling or be screened (e.g. XRF) and separated.

A review of mattress recycling by the International Sleep Products Association summarises some of the key issues with materials recovery for mattresses (International Sleep Products Association, 2004):

- The economics of recycling are finely balanced and the value of the recovered mattress materials alone cannot sustain a mattress disposal operation. Finding a sustainable income source to supplement the scrap revenue is therefore key to a successful operation (fees from consumers, retailers, manufacturers or municipalities equal to the “tipping fee” that a landfill would otherwise have charged had the mattress instead been dumped at the landfill).
- Facility location and security are critical as it is important to minimise the cost of moving product to the facility and when selling the recovered materials to potential customers.
- Preparing recovered scrap in saleable form can be challenging – particularly for the steel scrap, which is by far the most valuable and easily recovered mattress material.
- Consistent product volume is necessary to maintain an efficient dismantling operation.
- Low-tech manual dismantling appears to be more efficient than more automated alternatives. Although new technologies are under development, a manual approach using relatively low-skilled manual labourers equipped with box-cutters is the preferred approach at present. Capital expenditures are still needed, however, to shred product that cannot be quickly dismantled by hand. These include magnetic separators, bailers, forklifts to handle the product and the scrap, etc.

6.2.3 Regrinding

Eaves (2004) notes that the declining use of scrap foam in North American carpet cushion has spurred the uptake of innovative processes allowing manufacturers to non-cryogenically grind foam scrap from the manufacturing process. The ultrafine powder can then be used to displace approximately 10% of the virgin chemicals in the manufacture of new foam. Specific care has to be taken for occupational safety when workers are exposed to this fine powder (particulate respirator). With minor formulation adjustment, the resulting foam is said to have properties equal to the original foam. The economics are driven largely by the difference between the value of scrap and the price of chemical raw materials (Eaves, 2004). Regrinding, however, currently does not have a significant use in the PUR foam industry (Luedeka, 2011).

6.2.4 Chemical recovery (glycolysis)

The chemical recycling of polyurethane foam is still in an early stage. A few companies have developed the reprocessing of polyurethane, e.g. thermal glycolysis of PUR foam is applied in Germany (<http://www.rampf-ecosystems.de/en/home/>).

6.3 Labelling of articles produced from recycled PUR foams

If POP-PBDE-containing PUR foam is recycled, it has to be assured that this does not lead to human exposure as observed e.g. for staff in recycling of PUR foam and carpet installers working with rebond (Stapleton et al., 2008). Also no/low exposure to consumers would need to be guaranteed. Finally environmentally sound management at the end of life of such articles would need to be assured. Such articles could be labelled as a precondition for further environmentally sound management in the life cycle can be implemented (see *Guidance on labelling of products or articles that contain new POPs or use new POPs during manufacture – initial considerations*).

6.4 Other materials possibly impacted by POP-PBDEs

Some other minor uses of POP-PBDEs have been applied in the past:

- Textiles (e.g. back-coated textiles in vehicles)
- Rubber (e.g. for conveyer belts)
- Coatings/lacquers

Although no specific BAT/BEP has been developed for these minor uses: the same basic approach as described for PUR foam could be considered:

- Country/region survey of the presence of POP-PBDEs in these sectors
- Assessment of recycling activities of these materials
- Exclusion of specific impacted streams from recycling
- Screening and separation by bromine screening approaches in the recycling
- Recycling of POP-PBDE free material flows
- Energy recovery of POP-PBDE-containing material streams (see chapter 7)

If the above listed options are not available in a country, the material might be stored (see annex 1) until appropriate treatment technologies are available or it is disposed of in sanitary landfills, which is the least preferred option (see chapter 8 and annex 3).

7 Energy/material recovery from POP-PBDE-containing materials

The BAT/BEP guidelines in this document cannot describe each BAT/BEP for individual thermal treatment technologies since meaningful BAT/BEP descriptions of each of the processes would require several hundred pages. Such descriptions, however, are compiled in the Best Available Techniques Reference Documents (BREFs) developed for respective industrial processes (<http://eippcb.jrc.es/reference/>) and described, to some extent, in the Stockholm Convention BAT/BEP Guideline document with emphasis on reduction of unintentionally produced POPs (uPOPs) (Stockholm Convention, 2007). Also refer to Chapter 4.4 and chapter 5.3.1.

7.1 General remarks on thermal treatment of POP-PBDE-containing materials

7.1.1 Calorific value and halogen content of POP-PBDE-containing materials

POP-PBDEs are mainly used in materials with high calorific values (plastics, polyurethane foam, polystyrene foam, textiles). One option for the recovery of such materials is to utilize the energy present in the material and the metals attached to the POP-PBDE-containing polymers. The potential energy value of polymers is nearly 40 MJ/kg, which corresponds to €80/mton (at €2/GJ) (Tange and Drohmann, 2005).

The *Technical Guidelines for the Identification and Environmentally Sound Management of Plastic Wastes and for their Disposal* (Basel Convention, 2002) recommend feedstock recycling and thermal energy recovery for POP-PBDE-containing polymers. The guidelines state: "Plastic wastes which contain polybrominated diphenyl ethers (PBDE) should be excluded from material recycling because of the possibility of emitting dioxins and furans. Instead such plastic wastes should be treated in feedstock recycling facilities or in controlled incinerators recovering energy."

The thermal treatment of POP-PBDE-containing wastes (ASR or plastics from WEEE recycling) is a challenge for thermal facilities because of its high halogen content. For such wastes with a halogen content above 1%, in some countries hazardous waste incinerators may need to be used.³⁷ When using other facilities for recovery of energy or treatment, special care needs to be taken to avoid the release of unintentionally produced POPs.

7.1.2 Monitoring of PBDD/PBDF and PXDD/PXDF release

Since POP-PBDE-containing materials are flame retarded, their flammability is reduced, which can result in increased formation of products of incomplete combustion in facilities not equipped with optimally efficient combustion chambers, as specified in the BAT/BEP (Weber and Kuch, 2003). Since materials containing PBDE are excellent precursors of PBDF, the formation of the more toxic PBDF is also a crucial parameter to be considered and evaluated during thermal recovery and destruction operations (Sakai et al., 2001; Weber and Kuch, 2003; WHO, 1998; Vehlow et al., 2002; UNEP, 2010b). Because chlorine is normally present at relevant levels in PBDE-containing materials (e.g. WEEE plastic, ASR, PUR foam), the formation of polybrominated-chlorinated dibenzo-*p*-dioxin and dibenzofurans (PXDD/PXDF) can also comprise the highest share of dioxin-like compounds (Hunsinger et al., 2002, Zennegg et al., 2009). Therefore the measurement of only PCDD/PCDF in such operations is not sufficient and rather misleading.³⁸ The instrumental analysis of >5000 PXDD/PXDF congeners with several hundred 2,3,7,8-substituted congeners, however, is complex and can currently not give a TEQ. To overcome this dilemma of instrumental analysis of the mixed halogenated PXDD/PXDF, support of such monitoring by using accredited bio-assays measuring total dioxin-like toxicity like CALUX,

³⁷ The combination of chlorine, bromine and catalytic metals such as copper risks the generation of high levels of PCDD/PCDF, PBDD/PBDF and PXDD/PXDF in other facilities.

³⁸ The addition of bromine can result in reduced levels of PCDD/PCDF, partly by bromination of the chlorinated aromatics.

DRCALUX or EROD is recommended (Stockholm Convention, 2007). Their ability to assess such complex dioxin-like mixtures has been demonstrated e.g. with the assessment of e-waste recycling sites (Yu et al., 2008).

7.1.3 Considerations on corrosion caused by bromine/HBr

Bromine/HBr has a high potential to cause corrosion, in particular of metal parts. Thus corrosion effects need to be considered when larger amounts of bromine-containing waste are thermally treated in facilities. The process needs to be closely observed and the economic benefits and drawbacks assessed, including the cost of maintenance and repairs. In particular the boiler section is of concern from an economic perspective. Since all halogens enhance corrosion, operators of facilities with boilers are reluctant to burn large amounts of bromine-containing waste (Rademakers et al., 2002).

7.1.4 Considerations for removal of HBr and bromine in flue gas treatments

For all thermal treatment technologies, the behaviour of bromine within the facility and the flue gas line need to be considered. Due to similar redox potential of bromine and oxygen (see table 7-1), bromine is present in the flue gas partly as HBr and partly as elemental bromine. The ratio is influenced by, for example, the level of sulphur present.

HBr (together with HCl and other acid gases) can be removed by the usual removal technologies (dry/semi dry scrubbing with basic adsorbents, scrubbing with a NaOH solution, etc.). The technique to remove elementary bromine (and iodine) from the flue gas is a reductive wet scrubber stage with the addition of sulphite or bisulphite.

Table 7-1: Redox potential of halogens and boiling/melting point³⁹ of potassium and sodium halogenides

	Fluorine	Chlorine	Bromine	Iodine
Boiling Point Potassium halogenides (°C)	1505	1500	1380	1330
Boiling Point Sodium halogenides (°C)	1704	1465	1393	1304
Melting point Potassium halogenides (°C)	858	790	732	686
Melting point Sodium halogenides (°C)	995	801	755	662
Redox potential (Standard potential O ₂ +1,23)	+2.87	+1.36	+1.09	+0.54

7.2 Energy recovery of POP-PBDE-containing materials in incinerators

Basic BAT/BEP for waste incineration is specified in Section V for Source category A of the Stockholm Convention BAT/BEP guidelines (Stockholm Convention, 2007). Further details are described in the EU BREF document on waste incineration (European Commission, 2006)⁴⁰.

In general, shredder waste from the transport or electronic sectors is not suited for mono-incineration (Moakly et al., 2010). Co-incineration of such high shredder waste can be conducted in various types of incinerators, such as grate furnaces, fluidized bed incinerators and rotary kilns.⁴¹ Considerations need to be given to materials with a halogen content exceeding 1%. Such wastes should be disposed

³⁹ GESTIS-Substance database of IFA.

⁴⁰ ftp://ftp.jrc.es/pub/eippcb/doc/wi_bref_0806.pdf

⁴¹ Mark (1998) compared different alternatives (co-incineration with MSW, co-incineration in a cement kiln and co-incineration with hazardous waste) and concluded that co-incineration of ASR with MSW was most appropriate.

of in hazardous waste incinerators.⁴² BAT/BEP municipal solid waste incinerators (MSWI) or cement kilns (see below) could be used for the treatment of this waste material. Pilot tests have demonstrated that all emission parameters do not increase compared to normal operation procedures.

Small-scale incinerators and mobile incinerators can normally not be used for the destruction of POPs-containing wastes in particular due to their limitations in operation stability, secondary combustion quality and flue gas cleaning technology. To assure that these criteria are met and that long-term emissions of unintentional POP and POPs are low, continuous dioxin/UPOPs and respective POPs monitoring could be performed at least for some months (Reinmann et al., 2010; Weber, 2007).

As mentioned above, the corrosion of boilers (and other parts) must be taken into consideration when incinerating POP-PBDE/BFR-containing waste. If bromine is considerably lower compared to the chlorine input, the corrosion is mainly caused by chlorine (Rademakers et al., 2002).

7.2.1 Co-incineration of plastics from WEEE

BAT waste incinerators operating according to BEP can co-incinerate POP-PBDE-containing waste material without significant releases of POP-PBDEs or unintentionally formed brominated or chlorinated dioxins (Sakai et al., 2001; Vehlow et al., 2002; Weber and Kuch, 2003). It must be highlighted, however, that during the solid fuel burnout of WEEE with a mixture of municipal waste (Hunsinger et al., 2002) extremely high levels of PCDD/PCDF can be formed. The formation of mixed brominated-chlorinated PXDD/PXDF in relation to PCDD/PCDF strongly depends on Cl/Br ratio of the waste mixture⁴³ (Hunsinger, 2010). These PCDD/PCDF and PXDD/PXDF were efficiently destroyed during controlled flue gas burnout in the secondary combustion zone, finally resulting in moderate PCDD/PCDF and PXDD/PXDF levels in the raw gas and low levels in the clean gas (Nordic Council of Ministers, 2005; Tange and Drohmann, 2005; Vehlow et al., 2002). These tests demonstrated that BAT incineration can cope with the addition of POP-PBDE-containing polymers and that resulting high levels of unintentionally formed chlorinated, brominated and brominated-chlorinated dioxins can be destroyed in the secondary combustion zone operated according to BAT (sufficient residence time (2 seconds), temperature (>850°C) and turbulence (Stockholm Convention, 2007; European Commission, 2006).

7.2.2 Co-incineration of ASR in municipal solid waste incinerators

Extensive co-incineration tests have been carried out in municipal solid waste incinerators to assess the technical feasibility and environmental impact. In a test in Switzerland up to 10% of shredder residue was co-incinerated (Jody et al., 2006; Keller, 1999; Disler and Keller, 1997) and in a test in Sweden up to 20% (Aae Redin et al., 2001). The co-incineration was reported to meet the regulatory environmental limits. In Switzerland currently all ASR (55,000 t/year) is treated in MSW incinerators (at a cost of 150 €/t). It has been shown that flue gas emissions did not change significantly compared to the incineration of MSW.

In another study involving the co-incineration of ASR (31%), the concentrations of Zn, Pb, Sn, Sb, Cu and Co in the fly and boiler ashes increased significantly: the respective concentrations of Pb and Zn were up to 18 and 16 times higher than the average baseline level (Mark et al., 1998). In Switzerland some incinerators leach the ashes by acidic washing to remove the heavy metals.

While the co-incineration with MSW in the above-mentioned test of ASR were conducted in grate furnaces, ASR could also be co-incinerated in kinds of furnaces such as fluidized bed incinerators (Vandecasteele, 2011).

⁴² The EU Waste Incineration Directive, for example, requires that if hazardous wastes with a content of more than 1% of halogenated organic substances, expressed as chlorine, are co-incinerated, the temperature has to be raised from 850 °C to 1100 °C (European Commission, 2000).

⁴³ In another experimental series in this incinerator an addition of 0.06% bromine to the fuel feed (containing approximately 0.6% chlorine) resulted in the formation of high levels of PXDD/PXDF (mainly mono bromo- and dibromo-polychloroDD/DFs) in the first combustion zone at levels higher than the PCDD/PCDF. This demonstrates that despite the high Cl/Br ratio of >10 in the fuel input, considerable PXDD/PXDF can be formed (Hunsinger et al., 2001).

In many countries, bottom ashes from MSW incinerators are used as a secondary raw material in construction (Arickx et al., 2007; Vandecasteele et al., 2007). Therefore, it is important to monitor toxic components (heavy metals, POPs) in the bottom ashes when ASR is co-incinerated (Vermeulen et al., 2011) and avoid environmental contamination in further use and deposition. Legal concentration limits for toxic elements in bottom ashes are needed to limit the amount of ASR that can effectively be co-incinerated (Moakly et al., 2010).

7.2.3 Recovery of metals

The shredder fractions of ASR and WEEE still contain considerable amounts of heavy metals. BAT/BEP is used to recover the metals in the heavy ASR fraction in metal smelters (see below) while the light ASR fraction needs to be incinerated or if appropriate thermal treatments are not available deposited in secured landfills (see chapter 8 and annex 3). In almost all incinerators, the heavy metals, other than some bulk metal parts, are not recovered from the ashes. Promising pilot tests to comprehensively recover metals from bottom ashes are currently being conducted in Switzerland (ZAR, 2011).

7.2.4 Developing country considerations

If incinerating POP-PBDEs-containing materials then only BAT incinerators should be used considering the high unintentional POPs formation potential of WEEE plastic and ASR; however, there are hardly any BAT incinerators available in developing countries. The construction of BAT incinerators in developing/transition countries is questionable, considering the high final cost of waste treatment (normally above US\$100 / tonne) (Brunner and Fellner, 2007; World Bank, 2005). Therefore waste incinerators are unlikely (at least currently) to be a feasible option for treatment of POP-PBDE-containing waste in developing countries.

7.3 Cement kilns

Some key BAT/BEP considerations for cement kilns are described in Section V for Source category 2B of the Stockholm Convention BAT/BEP guidelines (Stockholm Convention, 2007). Further details are described in the EU BREF document on waste incineration (European Commission, 2010)⁴⁴. This chapter addresses specific considerations for treatment of POP-PBDE-containing materials.

Cement kilns are increasingly used in waste management schemes in both industrial and developing countries (Holcim and GTZ, 2006; Reijnders, 2007). Major POP-PBDE-containing materials like WEEE plastic, ASR and potentially other POP-PBDE/BFR-containing materials are also partly treated.

The Stockholm Convention BAT/BEP Guidelines (Stockholm Convention, 2007) includes “Electronic Waste” on the negative list of “waste not recommended for co-processing in cement plants”. The guidelines expand upon this by saying:

Electronic waste is composed of computer and accessories, entertainment electronics, communication electronics, toys and also white goods such as kitchen devices or medical apparatus. The average composition shows that electronic waste contains, on the one hand, substances potentially harmful to health and the environment such as Cl, Br, P, Cd, Ni, Hg, PCB and brominated flame retardants in certain concentrations, often higher than threshold limit values. On the other hand, electronic waste contains such a high scarce precious metal content that all efforts have to be undertaken to recycle it. Co-processing of the plastic parts of electronic waste would be an interesting option, but requires disassembling and segregation first (after Holcim and GTZ 2006).

⁴⁴ ftp://ftp.jrc.es/pub/eippcb/doc/clm_bref_0510.pdf

(Stockholm Convention, 2007)

This reflects industry interest in cement kilns as a possible energy recovery option for polymer waste containing POP-PBDEs from electrical and electronic equipment (Tange and Drohmann, 2005).

ASR (and other PBDE-containing wastes) is also a potential alternative fuel and mineral feedstock for cement production as about 50 wt % of ASR consists of combustible matter such as plastics or rubber; and another 40 wt % is made up of silicates, calcium, aluminium and iron (Boughton, 2007; Vermeulen, 2011). When the fuel of the cement kiln contains 50% of ASR, instead of the regular fossil fuel mix, strong negative effects on the quality of the clinker have been noted (Gendebien et al., 2003). In this case the concentrations of Cl, Pb, Cd, Cu and Zn in the clinker increased by one order of magnitude or more (Gendebien et al., 2003); and the Swiss product specification for clinker was not met for Cl, Cd, Cu, Pb and Zn. Other problems related to co-incineration of ASR in cement kilns include increased ash formation, clogging of the fuel injection zone, volatilization of mercury, and increased concentrations of hazardous elements in the cement kiln dust (Reijnders, 2007; Fink, 1999). In general, upgrading and purification of ASR is required before its use as a fuel substitute in high percentages in a cement kiln (Vermeulen, 2011).

Unfortunately no study has yet been published on monitoring releases of POP-PBDEs and PBDD/PBDF when PBDE/BFR-containing waste materials are co-incinerated. It is therefore not possible to be confident about the effectiveness of cement kilns for wastes containing POP-PBDEs, particularly since the feeding point is in the colder kiln inlet area. The destruction efficiency of POP-PBDEs in the waste will depend to a significant extent on the feeding point in the kiln. Stable molecules (and dioxin precursors) like PCB or POPs pesticides need to be fed at the "hot end" of the kiln into the burner flame with temperature up to 2000° C and residence time of more than 2 seconds is required above 1100° C to guarantee a high destruction efficiency. This also assures the destruction of POP-PBDEs in secondary fuels and the suppression of PBDD/PBDF formation at this feeding point. POP-PBDE-containing waste (e.g. WEEE plastic, automotive/transport shredder, polyurethane foam from furniture, insulation or mattresses), however, are solid waste fractions that are challenging to feed at the "hot end". Such solid waste fractions are normally fed at the colder kiln inlet where temperatures between 700° C and 1000° C exist and the residence time depends strongly on the plant configuration of the respective cement kiln (Waltisberg, 2010).

Therefore the current situation of accepting and treating POP-PBDE/BFR-containing waste in cement kilns requires a detailed and site-specific assessment including feeding points, temperature, residence time, POP-PBDE destruction efficiencies (in particular if fuel is fed at the kiln inlet) and related emissions. A properly configured test-burn, together with the establishment of the destruction efficiency, which incorporates an analysis of all emissions from the process including from products and the bypass stack, should always be carried out before any POPs waste is considered for routine disposal.

A second important consideration in treating POP-PBDE/BFR-containing waste in cement kilns is the sensitivity to halogen input, particularly with BAT cement kiln types with pre-heaters to halogen input. For pre-heater kilns (with or without a pre-calciner) – the main kiln type considered from the Stockholm Convention BAT/BEP guidelines as an option for waste treatment (Stockholm Convention, 2007) – the average total chlorine input from the combination of raw material, fuel and other materials (including waste) should stay below 0.03% (of total input recalculated to the clinker) to avoid clogging (Waltisberg, 2010). Here, chloride entering the cement kilns builds up within the kiln (around the kiln inlet zone), resulting in hot meal (meal at kiln inlet) levels of up to 2% chlorine within this area. This circulates within the system with possible negative impact on the operation by clogging at the colder areas at the kiln inlet and lower cyclone stages (Waltisberg, 2010).

Since cement kilns with pre-heaters normally have PCDD/PCDF emission levels well below 0.1 ng TEQ/Nm³ (Karstensen et al., 2006) but with high chlorine levels, wet and (long) dry kilns can reach emission levels well above 1 ng TEQ/Nm³. Levels as high as 136 ng TEQ/Nm³ have been reported (Stockholm Convention, 2007; Karstensen, 2008).

The behaviour of bromine in cement kilns and associated releases of unintentionally produced POPs/by-products or elemental bromine have not been investigated or described (UNEP, 2010b). As

bromine has similar physico-chemical properties to chlorine (e.g. boiling point of the potassium salt (see table 7-1) for KBr/KCl) crucial for the adsorption/desorption and therefore accumulation behaviour of a halogen in a cement kiln, bromine will probably act in a similar way to chlorine within a cement kiln.

With increased input of bromine via POP-PBDE- and other BFR-containing waste fractions, the risk of increased clogging in pre-heater kilns and possible formation of brominated and brominated-chlorinated PXDD/PXDF and other brominated organics for all kiln types (but in particular for wet and long dry kilns) needs to be considered and assessed.

Options and limitations for the destruction of wastes containing POP-PBDEs (such as plastics from WEEE, automotive/transport shredder, polyurethane foam from furniture insulation or mattresses) in cement kilns need a detailed evaluation of the individual kiln to decide on the options and limits of recovery energy from POP-PBDE/BFR-containing materials in such kilns. Such assessment should include comprehensive monitoring of the release of POP-PBDEs and other unintentionally produced brominated and brominated-chlorinated toxic substances including PBDD/PBDF and PXDD/PXDF. Considering that the build-up of chloride within a cement kiln can take weeks, an assessment of the fate of POP-PBDE/BFR-containing materials on associated POPs releases could best be performed through long-term monitoring (Reinmann et al., 2010).

7.3.1 Developing country considerations

Cement kilns are increasingly used in waste management schemes in developing /transition countries for energy and material recovery (Holcim and GTZ, 2006).⁴⁵ The facilities have been and are used for destruction of PCB-contaminated oil. In some pilot tests they have also been used to destroy pesticide stockpiles in developing countries (Karstensen et al., 2006). Since studies on the effectiveness of cement kilns in destroying POP-PBDE/BFR-containing wastes have yet to be published (POP-PBDEs and PBDD/PBDF), no final recommendation can currently be given even for dry BAT kilns.

For long dry kilns without pre-heaters and pre-calciners, as well as for wet kilns, the PCDD/PCDF formation and release potential is known, particularly when chlorine-rich (alternative) fuel/feed is brought into such kilns. Therefore these two types of kilns cannot be considered BAT and are not recommended for use in destruction/thermal recovery of POP-PBDE-containing materials.

Only BAT/BEP cement kilns with multi-stage pre-heaters/pre-calciners that are already operating in compliance with their authorized parameters/permits should be considered for such waste management (Holcim and GTZ, 2006).

A properly configured test-burn, including the assessment of the destruction efficiency of the kiln, which incorporates an analysis of emissions (including a sampling for POP-PBDEs and PXDD/PXDF) from the process and the bypass stack together with the concentrations in clinker and cement kiln dust, should always be carried out before POP-PBDE waste is considered for routine disposal. The routine disposal of POP-PBDE-containing materials can be supervised by long-term monitoring of unintentionally produced POPs and PBDD/PBDF or POP-PBDE in stack emissions (Reinmann et al., 2010).

7.4 Melting systems

In Japan a study of a direct melting system (shaft-type gasification and melting technology) has been found to be appropriate for ASR treatment, indicating the effective decomposition of brominated flame retardants and polybrominated dioxins (Sakai et al., 2001). The long-term operation of this technology, however, needs to be documented it could be considered as BAT/BEP for energy recovery of POP-PBDE-containing materials.

⁴⁵ <http://www.coprochem.com/>

7.5 Pyrolysis and gasification of POP-PBDE-containing materials

In its simplest definition pyrolysis is the degradation of polymers at moderate to high temperatures under non-oxidative conditions to yield marketable products (e.g. fuels, oils or activated carbon). Pyrolysis is capable of converting plastic waste into fuels, monomers, or other valuable materials by thermal and catalytic cracking processes (Tange and Drohmann, 2005; Scheirs and Kaminsky, 2006). This method can be applied to transform both thermoplastics and thermosets in fuels and chemicals. Moreover it allows the treatment of mixed, unwashed plastic wastes (Scheirs and Kaminsky, 2006).

Considering the results from laboratory thermolysis, however, elevated concentrations of PBDD/PBDF can be expected from pyrolysis processes when POP-PBDEs are present in the waste (Ebert and Bahadir, 2003; Weber and Kuch, 2003). Thus for the feedstock recycling of POP-PBDE-containing waste via pyrolysis/gasification, the formation of PBDD/PBDF could be problematic. Also the possible formation of brominated-chlorinated PXDD/PXDF needs to be considered (Weber and Kuch, 2003; Weber and Sakurai, 2001).

Furthermore, since pyrolysis and gasification are thermal processes in reducing atmospheres, debromination and dechlorination processes could take place. This could lead, for example, to high PCDD/PCDF releases for pyrolysis of chlorine-rich automotive shredder waste (Weber and Sakurai, 2001). During pyrolysis/gasification significant debromination of DecaBDE to lower-brominated PBDEs (including POP-PBDEs) takes place (Hall and Williams, 2008). Therefore, in all pyrolysis and gasification processes the fate of debromination of DecaBDE to POP-PBDEs needs to be considered and assessed for feedstock recycling of PBDE-containing materials (c-PentaBDE, c-OctaBDE and c-DecaBDE). The conversion to PBDF during thermal degradation of c-PentaBDE, c-OctaBDE and c-DecaBDE-containing materials in feedstock recycling also needs to be taken into consideration and evaluated.

Another issue to consider is the halogen content of the resulting oil. Only if the pyrolysis oil has below 50 ppm (Cl or Br) can it be possibly used as a fuel with an acceptable impact on corrosion.

Currently pyrolysis and gasification cannot be considered BAT/BEP for treatment of POP-PBDE-containing materials until long-term full-scale applications have shown to result in products and product flows that can be considered environmentally sound.

An option for possibly utilizing pyrolysis is for the treatment of POP-PBDE/BFR containing materials in the recovery of bromine (see annex 4).

7.5.1 Developing country considerations

No positive recommendation can currently be given for using pyrolysis or gasification technologies for the treatment of POP-PBDE-containing materials for developing/transition countries due to the lack of reported long-term full-scale operation of such technologies for wastes even from industrial countries. Since most pyrolysis projects in industrial countries have failed or have been stopped due to technical or economic reasons (Gleis, 2011), it can (currently) be recommended that developing countries do not aim to establish full-scale plants for the pyrolysis of waste.

7.6 Metal industries

Some POP-PBDE-containing materials are treated or end up in integrated metal smelters/copper smelters and other metal industries. These are used to recover metals from printed circuit/wiring boards (PWBs), cables and other polymer materials from WEEE, which are firmly combined with the metals to be recovered. In most cases such material is mixed with other primary (ore concentrates, anode slimes, etc.) or secondary materials (e.g. catalysts, industrial residues). Releases of POP-PBDEs have been reported from electric arc furnaces, sinter plants and aluminium, smelters revealing that POP-PBDE-containing materials are being processed in these facilities (UNEP, 2010b). The main sources of such releases are probably the recovery of materials from ELVs or electronic wastes (UNEP, 2010b).

For PCB-containing materials, thermal treatment options need to be assessed for their destruction efficiency for POP-PBDE-containing materials. In this regard the formation and release of chlorinated, brominated and mixed halogenated dioxins and furans need to be considered (Weber and Kuch, 2003; Weber, 2007; UNEP, 2010b).

Recent studies have reported that releases of POP-PBDEs,⁴⁶ polybrominated dioxins and furans (PBDD/PBDF) and brominated-chlorinated dioxins and furans (PXDD/PXDF) from these metal industries also reveal POP-PBDE-containing materials (Du et al., 2010a, 2010b; Odabasi et al., 2009; Wang et al., 2010). Although the type of feeding materials was not specifically documented,⁴⁷ these emissions indicate that POP-PBDE-containing waste has been processed in these facilities and this has resulted in such emissions.

At this point only limited conclusions can currently be drawn about the effectiveness and environmental impact of these processes for recovering energy and materials from articles containing POP-PBDEs. These processes need further assessment before final conclusions on BAT/BEP for treatment of POP-PBDE-containing materials in such facilities can be stated.

7.6.1 Copper smelters and integrated smelters-refineries

Category 2D “Thermal processes in the metallurgical industry” in Section V of the Stockholm Convention BAT/BEP Guidelines (Stockholm Convention, 2007) describes some key BAT/BEP issues for secondary copper production. In particular, BAT/BEP of reducing unintentionally produced POPs emissions in that document would be considered. BAT/BEP details on the technologies are described in the EU BREF document on non-ferrous metal industries (European Commission, 2001)⁴⁸ as well as the updated draft of the document (European Commission, 2009).⁴⁹

Smelters treat a wide range of mixed waste streams, such as shredder residues, which can contain high concentrations of PBDE, other BFRs, PVC, and catalytic metals such as copper (Hwang et al., 2008). Other flame-retarded materials, notably PWBs,⁵⁰ are often processed in secondary copper smelters for recovery of the copper and other precious metals including WEEE plastics. PWBs have an average composition that includes 15-20% copper, 200-250 ppm gold, 1000 ppm Ag and 80-100 ppm palladium (Hagelüken, 2006). This can be compared with gold ores, which can be economically mined with concentrations as low as 0.5 ppm.⁵¹ The attraction of recycling precious metals including gold from PWBs is thus self-evident.

PWBs also contain a wide range of other base and special metals, many of which can be co-recovered in modern integrated smelter-refineries (Ni, Pb, Sn, Bi, Sb etc.). Details of such processes have been described (Hagelüken, 2006) The scale of these PWB feedstock recycling operations involves tens of thousands of tonnes/year (see table 7-2) and is recommended by the industry for treatment of BFR-containing polymers from electronics (Mark and Lehner, 2000; Hagelüken, 2006; Brusselsaers et al., 2006). Thus releases of POP-PBDEs, PBDD/PBDF and PXDD/PXDF could be substantial depending on the destruction efficiency of the respective facilities. Also the European “Draft Reference Document on Best Available Techniques for the Non-Ferrous Metals Industries” states: “If major amounts of electronic scrap with brominated flame retardants are used as feedstocks, this may result in the formation of mixed halogenated dioxins” (European Commission, 2009).

⁴⁶ Since thermal processes can lead to debromination of DecaBDE to lower-brominated PBDE, the emission patterns of PBDE in these studies only allow limited conclusions on the actual input of c-PentaBDE and c-OctaBDE into these processes. Nor, without specific details of the concentration levels of brominated compounds in the inputs, can the destruction efficiency or appropriateness of treatment for PBDE-containing waste be assessed (UNEP, 2010b).

⁴⁷ The Du et al. (2010) study does provide some limited information on feedstock in the supporting information .

⁴⁸ ftp://ftp.jrc.es/pub/eippcb/doc/nfm_bref_1201.pdf

⁴⁹ ftp://ftp.jrc.es/pub/eippcb/doc/nfm_2d_07-2009_public.pdf

⁵⁰ [PWB is used as an acronym instead of PCB to avoid confusion with Polychlorinated biphenyls\).](#)

⁵¹ <http://en.wikipedia.org/wiki/Gold>

The use of polymers/resin serves a dual function as a reducing agent and as a source of energy for the smelting process. Further antimony can be recovered in integrated smelters. While the temperature in the molten metal bath is high (above 1100°C) and appropriate for the destruction of POP-PBDEs, the temperature from the charging point to the surface of the bath ranges through a full temperature gradient from ambient conditions to the bath temperature. Smelters can be described as thermal processes with incomplete combustion occurring at the charging of the material. While coke is mainly oxidized in the melting bath, the more flammable resins of printed circuit boards and plastics from WEEE charged to the smelter are ignited and burn/pyrolyse to some extent on top of the melting operation. Experience with waste incinerators demonstrates that the concentration of PCDD/PCDF and the brominated and brominated-chlorinated PXDD/PXDF in the off-gas of the first combustion zone is high (up to 1000 ng TEQ/Nm³) when adding a high proportion of WEEE. These were destroyed in the secondary combustion zone (Hunsinger et al., 2002; Hunsinger, 2010). From this evidence, together with a basic consideration of dioxin formation, high levels of brominated PBDD/PCDF and brominated-chlorinated PXDD/PCDF can be formed and released from smelter furnaces treating POP-PBDE- and other BFR-containing polymers. Therefore effective afterburners are required as BAT/BEP. Moreover information from the industry suggests that afterburners are needed for the treatment of exhaust gases from smelting processes in which PWBs are treated (Kegels, 2010).

The use of a BAT afterburner (850° C; 2 seconds residence time; sufficient turbulence) in smelters could possibly substitute for a secondary combustion chamber. PCDD/PCDF emissions of up to 5 ng/m³ are reported in the updated EU Draft BREF (European Commission, 2009) even with afterburners. Two larger pilot studies at full-scale plants on BFR WEEE plastic recovery utilizing brominated flame-retarded material in smelters as substitute for coke/oil as reduction agent have been documented in Europe (Mark and Lehner, 2000; Hagelüken, 2006; Brusselaers et al., 2006). One was in an integrated smelter in Sweden⁵² and the second in an integrated smelter in Antwerp, Belgium⁵³. Although PCDD/PCDF values were mentioned for both case studies, this is not very useful and can be rather misleading for inputs of PBDE/BFR.⁵⁴ Levels of POP-PBDEs and brominated-chlorinated PXDD/PXDF, which would have been much more informative, were not measured or at least were not reported in these studies.

No study has been published that assesses the release of POP-PBDEs and the formation and releases of PBDD/PBDF and PXDD/PXDF from the feedstock recycling of PBDE/BFR-containing materials in smelters. This is a major omission as this type of feedstock recycling is used for tens of thousands of tonnes of printed circuit boards every year and has been recommended for PBDE/BFR-containing polymer from electronics (Mark and Lehner, 2000; Hagelüken, 2006; Brusselaers et al., 2006).

For the individual smelters that want to process PWB and possibly utilize POP-PBDE/BFR-containing polymer as a reducing agent, the release levels of POP-PBDEs and halogenated dioxins/furans (PCDD/PCDF, PBDD/PBDF and PXDD/PXDF) need to be measured carefully before deciding on the appropriateness of the respective smelter or the effectiveness of the afterburners and flue gas treatments.

State-of-the-art integrated smelters require investments of well above US\$1 billion. Currently, only 5 to 10 plants feature the technological performance necessary for the described operations. These include the plants run by Umicore (Belgium), Aurubis AG (former Norddeutsche Affinerie AG) (Germany), Boliden (Sweden/Finland), Johnson Noranda (Canada), and DOWA (Japan). Using BAT/BEP metallurgical facilities has significant benefits beyond their good environmental performance. One major benefit is that a much wider range of metals can be recovered with higher yields and less energy requirements than in less sophisticated installations (Hagelüken, 2006; Hagelüken and Meskers, 2008). Final waste streams are usually small, since the depleted, inert slags from the

⁵² <http://www.boliden.com/>

⁵³ <http://www.unicore.com/en/>

⁵⁴ The value in the fuming plant during recycling of PC scrap in the Swedish study was found to be 0.08-0.12 ng TEQ/m³ (around the limit of stack emissions for waste incinerators) (Mark and Lehner, 2000), and therefore above the German workplace level of 0.05 ng TEQ/Nm³ (TRGS 557 2000) even without considering the PBDD/PBDF or PXDD/PXDF. Also in the pilot test at the smelter in Belgium only PCDD/PCDF were measured and only at the stack after flue gas treatment (Hagelüken, 2006; Brusselaers et al., 2006).

smelting operations can possibly be used as construction material (after consideration of their leaching properties) or as additives for the cement industry.

Table 7-2: European Smelter Capacity

Existing Plants	Recycling capacity (per year)
Boliden, Sweden	35,000 tons of EandE scrap (25% polymer)
Umicore, Belgium	Can treat >10,000 tons per year (mainly circuit board)
Norddeutsche Affinerie AG, Germany (now Aurubis AG)	Treats 10,000 tons of PWBs, plus another >15,000 tons of WEEE plastics

(BSEF, 2000)⁵⁵

Specific BAT/BEP considerations to reduce or eliminate POP-PBDEs and PXDD/PXDF release from copper smelters include:

- **BAT post-combustion afterburners:** the Stockholm Convention BAT/BEP guidelines mentions post-combustion afterburners as BAT to minimize PCDD/PCDF releases from secondary metal installations (Stockholm Convention, 2007). The efficiency of the post-combustion needs to be assessed to decide on its appropriateness to safely process POP-PBDE/BFR-containing material input.
- **Off-gas treatment:** BAT/BEP also includes as a primary measure the adequate off-gas handling and appropriate off-gas conditioning to prevent conditions leading to de novo synthesis formation of PCDD/PCDF. The same measures reduce the formation of PXDD/PXDF unless they are emitted from the furnace.

Key secondary measures for the reduction of unintentional POPs include:

- Adsorbent injection (for example, activated carbon)
- High-level de-dusting with fabric filters (to <5 mg dust/Nm³)

Further details can be found in the Stockholm Convention BAT/BEP guidelines (Stockholm Convention, 2007) and the EU BREF (European Commission, 2009).

7.6.2 Material recovery and energy recovery in electric arc furnaces

Some key BAT/BEP measures to be considered for reduction of unintentional POP release from electric arc furnaces (EAFs) are described in Section VI Part III Source category (b) “Thermal processes in the metallurgical industry not mentioned in Annex C, Part II” of the Stockholm Convention BAT/BEP guidelines (Stockholm Convention, 2007). Details on the BAT technologies used are described in the EU BREF for the Iron and Steel Industry (European Commission, 2011b)⁵⁶.

EAFs have not been considered to be facilities for recovery of POP-PBDE/BFR-containing wastes. For a number of years it has been demonstrated that EAFs processing scrap metals can generate high levels of PCDD/PCDF in solid wastes and dust from flue gas cleaning (ENDS, 1997). More recently, PBDE and PBDD/PBDF emissions from EAFs have been reported for China, Taiwan and Turkey (Du et al., 2010a, b; Odabasi et al., 2009; Wang et al., 2010). The levels from metallurgical processes were higher than from incinerators (Du et al., 2010a, b). This demonstrates that feedstock wastes containing PBDE is entering EAFs and needs to be addressed in the Stockholm Convention implementation. Since EAFs

⁵⁵ BSEF, 2000. <http://www.bsef.com/science/brominated-flame-retardants-and-recycling/technical-recycling-and-wastesolutions/>

⁵⁶ ftp://ftp.jrc.es/pub/eippcb/doc/IS_11_17-06-2011.pdf

can facilitate the recovery of metals, such cases might fall into the category of recycling and recovery of materials containing POP-PBDEs.

Specific BAT/BEP considerations to reduce or eliminate POP-PBDEs and PXDD/PXDF release from EAFs include:

- **Separating POP-PBDE-containing-materials from scrap:** this separation step is particularly important for electric arc furnaces that do not have BAT. As materials recovered/recycled through EAF might contain POP-PBDEs, the following types of waste need to be considered:
 - Automotive scraps and components from other transport vehicles (buses, trains, aeroplanes) containing POP-PBDEs in polyurethane foam from seats, head/arm rest and roofs, as well as plastics from interiors or cables.
 - White goods and other WEEE containing POP-PBDEs in plastic parts.
- **BAT post-combustion afterburners:** The Stockholm Convention BAT/BEP guidelines (Stockholm Convention, 2007) mentions post-combustion afterburners as BAT to minimise PCDD/PCDF formation and release for EAF. As for the smelters the efficiency of the afterburner needs to be assessed to decide to which extent EAFs using BAT (including afterburners) are able to safely process POP-PBDE/BFR-containing material input. It is recommended that, also for BAT/BEP EAFs, the input material containing POP-PBDEs might need an additional separation step before recovering the metals in the furnace.
- **Off-gas treatment:** BAT/BEP also recommends adequate off-gas handling and appropriate off-gas conditioning to prevent de novo formation of PCDD/PCDF. The same measures may include the use of post-combustion afterburners, followed by rapid quench of off-gases.

Key secondary measures to reduction UPOPs include:

- Adsorbent injection (for example, activated carbon)
- High-level de-dusting with fabric filters (to <5 mg dust/Nm³)

Details can be found in the Stockholm Convention BAT/BEP guidelines and the respective EU BREFs.

7.6.3 Feedstock recycling of POP-PBDE polymers in primary steel industry

The Stockholm Convention BAT/BEP guidelines (Stockholm Convention, 2007) do not include BAT for blast furnace operations since they are not listed as a relevant source of UPOPs; however, blast furnaces are covered by the EU iron and steel BREF (European Commission, 2001, 2011).

Plastic and possibly other polymers are used in the primary steel industry either i) directly in blast furnaces as coke substitutes or ii) as substitutes for coal in the production of coke (Japan National Institute for Environmental Studies, 2010; European Commission, 2011b). An LCA for POP-PBDE-containing TV casings (Hirai et al., 2007) compared four scenarios: material recycling, feedstock recycling, incineration and landfilling. It concluded that feedstock recycling of POP-PBDE-containing material in the primary steel industry could be preferable compared to the second best option of material recycling but noted that the capacity is limited because of the Br content of the plastics.

According to the European BAT reference document for iron and steel, shredder residue are feedstocks in primary steel production (European Commission, 2011). There are no data published for emissions from an operating blast furnace with explicit co-treatment of POP-PBDE-containing materials. The BAT/BEP document, however, emphasizes that to assess the options and limitations of the feedstock use of such polymer rich fractions (from mixed electronics and/or automotive shredder) it is necessary to ascertain heavy metal content of the polymer feedstock⁵⁷ in order to assess its suitability and limitation for use⁵⁸ (European Commission, 2011b). Hirai et al. (2007) found that

⁵⁷ Particularly mercury, but also of cobalt, chromium, arsenic, lead, nickel, cadmium and zinc.

⁵⁸ The European Steel BREF specifies the limits for cobalt, chromium, arsenic, lead, nickel, mercury, cadmium and zinc in plastic feedstock recycling in blast furnaces (European Commission, 2009).

bromine/halogen content was one factor limiting the extent of use in the primary steel industry⁵⁹ as the Japanese steel industry only accepts a halogen content of up to 0.5% (bromine or chlorine). In Europe the allowable halogen content appears higher.⁶⁰

The conditions in a blast furnace are likely to destroy POP-PBDEs and other halogenated organics in furnaces with high efficiency. Emissions of POP-PBDEs and PBDD/PBDF, however, need to be assessed in detail to ensure compliance with the Stockholm Convention obligations.

7.6.4 POP-PBDE-containing materials in secondary aluminium industries

Some key BAT/BEP recommendations to be considered for secondary aluminium production facilities focusing on UPOPs release reduction are described in Section V for Source category 2D “Thermal processes in the metallurgical industry” of the Stockholm Convention BAT/BEP guidelines (Stockholm Convention, 2007). Details on the technologies are described in the EU BREF documents on non-ferrous metal industries (European Commission, 2001)⁶¹.

PBDD/PBDF and PXDD/PXDF have been detected in stack gas emissions from secondary aluminium smelters (Du et al. 2010 a, 2010b). PBDEs have also been found in a waste input of an aluminium recycling plant. Samples were taken from waste from handling of WEEE plastics, filter dust from an electronic crusher, cyclone dust from an electronic crusher and light residues from a car shredder. In the screening analyses, PBDEs were identified in all samples in amounts of 245–67,450 ng/g. The highest levels were found in the plastics from electronics. Other brominated flame retardants were also observed in all samples. The major PBDE congeners found were pentaBDE (150 ng/g), hexBDE (20 ng/g) and decaBDE (10 ng/g) (Sinkkonen et al., 2004).

Thus, secondary aluminium plants should be properly assessed for the release of POP-PBDEs, PBDD/PBDF and PXDD/PXDF into the air and solid residue.

7.6.5 Antimony smelters recycling WEEE plastics

Some flame-retarded WEEE plastics can be recovered in antimony smelters in which Sb_2O_3 ⁶² is recovered and the plastic serves as a reducing agent (UNEP, 2010b). Unfortunately no data on the volumes treated, destruction efficiency for POP-PBDEs, or the amount of POP-PBDEs and PBDD/PBDF released are available from these processes. There are no reports published on the monitoring of PBDE and PBDD/PBDF release during antimony recovery from WEEE plastic.

The BAT for processing POP-PBDE/BFR containing plastics in antimony smelters requires afterburners for appropriate flue gas treatment. Measurements can determine then the appropriateness of using a respective antimony smelter to process POP-PBDE-containing plastics.

7.6.6 Developing/transition country considerations

Recent studies in China, Taiwan and Turkey have reported releases of PBDE and PBDD/PBDF from metal industries (copper smelters, electric arc furnaces, sinter plants, secondary aluminium industry), revealing that PBDE/BFR-containing materials are being treated in these facilities (Du et al., 2010; Odabasi et al., 2009; Wang et al., 2010). Since many developing/transition countries have some of

⁵⁹ The bromine content of waste TV casings generated in Japan each year is 705 tons or nearly twice the 400 tonnes of total halogen that could be accepted/managed by plastic feedstock recycling in the Japanese primary steel industry. Consequently, a maximum of about 50% of the TV plastics could theoretically be recovered via this route for Japan (Hirai et al., 2007).

⁶⁰ In Europe chlorine content of up to 1.5% (Bremen/Germany) (Tukker, 2002) and 2% (Linz/Austria) (European Commission, 2009) is reportedly acceptable to the steel industry.

⁶¹ ftp://ftp.jrc.es/pub/eippcb/doc/nfm_bref_1201.pdf

⁶² Used as a flame-retardant synergist with halogenated flame retardants.

these industries, there are likely to be releases from such facilities. But it might also be possible for these facilities to recover metals and energy from such material/waste streams with the associated benefits of resource conservation and energy efficiency.

The metal industries in most developing countries, however, are at a low technological level and abatement technologies are generally underdeveloped. Therefore it is currently not clear whether metal industries in developing countries are appropriate to treat materials containing POP-PBDEs.

Since there are still considerable knowledge gaps in the different metal industries even in industrial countries (copper smelters, electric arc furnaces, secondary aluminium, and antimony smelters), currently no recommendations can be given for such practices for developing and transition countries. Monitoring the releases from facilities treating POP-PBDE/BFR-containing material is a vital first step.

DRAFT

8 Disposal of POP-PBDE-containing materials to landfills

Most developing countries do not have established recycling schemes to separate POP-PBDEs from large material flows such as end-of-life vehicles, WEEE plastics, furniture and mattresses. Nor do they have the capacity, human or financial resources,⁶³ for sophisticated waste management practices, treatment and disposal options. Therefore in many developing countries a high proportion of wastes is still disposed of to landfills and open dump sites, sometimes with open burning, which has severe negative impacts on human health and the environment. For more information, annex 3 provides information on landfilling of POP-PBDE-containing wastes primarily aimed at developing countries and countries with economies in transition.

8.1 Drawbacks of landfilling of POP-PBDE-containing materials

Several studies show that POP-PBDEs along with other POPs (PCBs, PCDD/PCDF and other semi-volatile compounds) are leaching, together with heavy metals and other substances from non-sanitary landfills and dumps, into the soil and hydrosphere (Osako et al., 2004; Odusanya et al., 2009; Danon-Schaffer, 2010; Danon-Schaffer and Mahecha-Botero, 2010; Weber et al., 2011; Zennegg et al., 2010; Götz et al., 2012). POP-PBDEs have also been detected in soils adjacent to landfills in various regions of Canada (Danon-Schaffer, 2010), indicating atmospheric POP-PBDE release from landfills and subsequent deposition. POPs and heavy metal releases from dumps containing shredder residues of end-of-life vehicles and e-waste might ultimately require costly⁶⁴ remediation (Takeda, 2007).

These findings highlight that disposal of POP-PBDE-containing articles to landfills is only an option if all available BAT/BEP with advanced air pollution or alternative equivalent treatments (see chapter 7; Stockholm Convention, 2007) have already been explored and applied where possible.

8.2 Sanitary landfill for disposal POP-PBDE-containing materials

Only well-designed sanitary landfills, with at least the engineered measures described below, should ever be considered for the deposit of POP-PBDE-containing materials (see annex 3; BIPRO, 2007; Keet et al., 2010):

- Appropriate landfill siting taking into account proximity to residents and other sensitive receptors, local groundwater, surface water and flood risks.
- Strict site security and full control of wastes entering the landfill site for disposal.
- Management of the landfill to minimise fire risks by appropriate compaction, cover etc. (see Stockholm Convention, 2007).
- Operation of the landfill with daily cover.
- State-of-the-art bottom liners to minimise leakage.
- Profiling and capping to minimise infiltration.
- Collection, control and treatment of leachate.
- Collection, control and treatment of landfill gas.
- Comprehensive monitoring regime with long-term aftercare (possibly centuries).

8.3 Long-term aftercare considerations for sanitary landfills

The life expectancy of engineering and containment measures for sanitary landfill is limited with estimates varying between decades and centuries. Current practical experiences are not

⁶³ A survey of waste management costs across different regions demonstrates that expenditures on municipal waste management amount to between 0.2% and 0.4% of GDP for most countries and the financial resources available for waste management span a range with a factor of 500 (Brunner and Fellner, 2007).

⁶⁴ The high cost of remediation or excavation of POPs-containing landfills (Weber et al., 2011; Götz et al., 2012) is another reason that countries should avoid landfilling these wastes whenever possible.

comprehensive enough to provide long-term aftercare considerations for sanitary landfills (Buss et al., 1995; Allen, 2001; Simon and Mueller, 2004); however, it might be expected that landfilled POP-PBDE-containing articles and others will be released via the soil and leachate into environmental systems over time (Weber et al., 2011). The time period of the life of PBDEs and other persistent toxic chemicals in landfills have been modelled (e.g. Danon-Schaffer, 2010), and it has been indicated that the threat of POP-PBDEs to the environment will outlive the engineering containment of the landfill. For more is needed on the long-term behaviour and fate of PBDEs and other persistent toxic chemicals to assess the threat of POP-PBDEs to the environment, including climate change and extreme weather events (Laner et al., 2009; Weber et al., 2011).

BAT landfill design should consider higher precipitation, infiltration and erosion rates with enhanced leachate production; mobilization of a larger waste fraction; more rapid degradation of liners; and higher volatilization rates. The situation is of particular concern for flood plains, low lying and coastal areas where flooding and interaction with river and/or seawater poses a threat to environment and human health by bioaccumulation (Bebb and Kersey, 2003). For new landfill settings, flooding risks (and groundwater and surface contamination risk) should be considered over a long time scale (e.g. 10,000 years) if POP-PBDE (and other POPs-) -containing waste is to be landfilled. Furthermore, all current and former landfills where POP-PBDE- (and other POPs-) containing wastes have been disposed could be mapped and assessed in a national database, including flooding risk assessments (Laner et al., 2009). These data would be linked to the inventory of contaminated sites containing POP-PBDEs (see chapter 7 of the *POP-PBDE Inventory Guidance*), PFOS (see chapter 7 of the *PFOS Inventory Guidance*) or other POPs (UNEP, 2005; UNIDO, 2010; Hatfield Consultants and World Bank, 2009).

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DRAFT

Annexes

Annex 1: General BAT/BEP considerations

Environmental management systems (EMS)

These are techniques related to the continuous improvement of environmental performance. They provide the framework for ensuring the identification, adoption and adherence to BAT options that nevertheless remain important and can play a role in improving environmental performance at facilities. Indeed, these good house housekeeping/management techniques/tools often prevent emissions.

A number of environmental management techniques are determined as BAT. The scope and nature of an Environmental Management System (EMS) will generally be related to the nature, scale and complexity of the installation, and the range of environmental impacts it may have.

BAT/BEP in this respect include:

Implementing and adhering to an EMS that incorporates, as appropriate to individual circumstances, the following features -

- a. definition of an environmental policy for the installation by top management (commitment of the top management is regarded as a precondition for a successful application of other features of the EMS)
- b. planning and establishing the necessary procedures
- c. implementation of the procedures, paying particular attention to
 - structure and responsibility
 - training, awareness and competence
 - communication
 - employee involvement
 - documentation
 - efficient process control
 - maintenance programme
 - emergency preparedness and response
 - safeguarding compliance with environmental legislation.
- d. checking performance and taking corrective action, paying particular attention to
 - monitoring and measurement
 - corrective and preventive action
 - maintenance of records
 - independent (where practicable) internal auditing in order to determine whether the environmental management system conforms to planned arrangements and has been properly implemented and maintained.
- e. a commitment to continuously increase the energy efficiency of the installation, by:
 - aa. developing an energy efficiency plan
 - bb. using techniques that reduce energy consumption and thereby reduce both direct (heat and emissions from on-site generation) and indirect (emissions from a remote power station) emissions
 - cc. defining and calculating the specific energy consumption of the activity (or activities), setting key performance indicators on an annual basis (e.g. MWh/tonne of material/waste processed).

Within the EMS, have a noise and vibration management plan in place where needed.

Management of the process generated materials and residues BAT/BEP is to:

Have a residue management plan as part of the EMS including:

- a. basic housekeeping techniques
- b. internal benchmarking techniques

Material/Waste management in facilities and processes

Many processes described in this document are related to products/materials after their product lives are complete. In other words, they involve recycling, material/energy recovery or disposal as these are the most relevant for POP-PBDE containing material flows. Concerning material/waste management, the generic BAT/BET for material/waste management systems described herein seek to increase the knowledge of incoming materials and waste, and of how to properly store, handle, and dispose of wastes as well as the improvement of knowledge of material and waste leaving the facility are listed.

Material/Waste management system

The object of BAT/BEP is to put in place a system to guarantee the traceability of materials and wastes treatment containing the following features:

- a. A procedure to document the use and treatments of materials and wastes by flow charts and mass balances.
- b. A procedure to carry out data traceability through several operational steps (e.g. pre-acceptance/acceptance/storage/treatment/dispatch). Records can be made and kept up-to-date on an ongoing basis to reflect deliveries, on-site treatment and dispatches. Records are typically held for a minimum of six months after the waste has been dispatched.
- c. A clear reference and recording system on waste characteristics and the source of the waste stream that it is available at all times.
- d. This may consist of a computer database or a series of database, which are regularly backed up. The tracking system for a material/waste inventory/stock control system should include the date of arrival on-site, waste producer details, an unique identifier code, pre-acceptance and acceptance analysis results, a description of package type and size, intended treatment/disposal routes, an accurate record of the nature and quantity of materials/wastes held on-site including all hazards details on where the material/waste is physically located in relation to a site plan, at which point in the designated treatment route the material/waste is currently positioned.
- e. Drums and other mobile containers should be moved between different locations (or loaded for removal off site) only under instructions from the appropriate manager, ensuring that the waste tracking system is amended to record these changes.

Have and apply mixing/blending rules oriented to restrict the types of wastes that can be mixed/blended together in order to avoid increasing pollution emission of down-stream waste treatments. These rules need to consider the type of materials/waste (e.g. hazardous, non hazardous), waste treatment to be applied as well as the following steps that will be carried out to the waste OUT (see below).

A segregation and compatibility procedure should be in place that includes:

- a. Detailed and accurate records of the testing, including any reaction giving rise to safety parameters (increase in temperature, generation of gases or pressure spikes); a record of the operating parameters (viscosity changes and separation or precipitation of solids) and any other relevant parameters, such as the generation of odours.
- b. packing containers of chemicals into separate drums based on their hazard classification. Chemicals which are incompatible (e.g. oxidisers and flammable liquids) should not be stored in the same drum.

Have an approach for improving waste treatment efficiency. This typically includes the finding of suitable indicators to report waste treatment efficiency and a monitoring programme.

Produce a structured accident management plan and have and properly use an incident diary.

Incoming materials and wastes

To improve the knowledge of the incoming material and waste, the BAT/BEP should record accurate information about incoming material/wastes in respective facilities. Such knowledge needs to take into account the outgoing material/waste, the treatment to be carried out, the type of material/waste, the origin of the material/waste, the recommended procedures and the risks involved.

Implement a pre-acceptance procedure containing at least the following items:

- a. tests for the incoming material/waste with respect to the planned treatment.
- b. making sure that all necessary information is received on the nature of the process(es) producing the material/waste, including the variability of the processes. The personnel having to deal with a possible pre-acceptance procedure need to be able due to his profession and/or experience to deal with all necessary questions relevant for the treatment of the materials/wastes in the facility.
- c. a system for providing and analysing a representative sample(s) of the material/waste from the production process producing such material/waste from the current holder. If e.g. a WEEE recycling facility want to send plastics for further recycling it could be required that they provide data on the POP-PBDE content. A methodology for sampling and analysis of POP-PBDE in WEEE plastic is described in the Guidance on analysis of new POPs in articles and in Wäger et al. (2010)⁶⁶.
- d. a system to carefully verify, if not dealing directly with the waste producer, the information received at the pre-acceptance stage. This should include the contact details for the waste producer and an appropriate description of the material/waste regarding its composition and hazardousness.
- e. making sure that the classification is according to the national legislation and is provided.
- f. identifying the appropriate treatment for each waste to be received at the installation by identifying a suitable treatment method for each new material/waste enquiry and having a clear methodology in place to assess the treatment of waste. This should consider the physico-chemical properties of the individual material/waste and the specifications for the treated material/waste.

Implement an acceptance procedure containing at least the following items:

- a. a clear and specified system allowing the operator to accept material/wastes at the receiving plant only if a defined treatment method and disposal/recovery route for the output of the treatment is determined.

Regarding the planning for the acceptance, it needs to be guaranteed that the necessary storage treatment capacity and dispatch conditions (e.g. acceptance criteria of the output by the other installation) are also respected.

- b. measures are in place to fully document and deal with acceptable material/wastes arriving at the site, such as a pre-booking system, to ensure e.g. that sufficient capacity is available.
- c. clear and unambiguous criteria for the rejection of wastes and the reporting of all conformance violations.
- d. a system be in place to identifying the maximum capacity limit of material/waste that can be stored at the facility.
- e. visually inspect the incoming material/waste to make sure it complies with the description received during the pre-acceptance procedure.

Implement different sampling procedures for all different incoming material/wastes delivered in bulk and/or containers. These sample procedures may contain the following items:

⁶⁶ Wäger P, Schluep M, Müller E. 2010. RoHS substances in mixed plastics from Waste Electrical and Electronic Equipment. Final Report September 17, 2010.

- a. sampling procedures based on a risk approach. Some elements to consider are the type of materials/waste (e.g. hazardous or non-hazardous) and the knowledge of the customer (e.g. waste producer).
- b. check on the relevant physico-chemical parameters. The relevant parameters are related to the knowledge of the material/waste needed in each case to register of all waste/materials.
- d. have appropriate sampling procedures. The procedure should contain a system for recording the number of samples and degree of consolidation.
- e. sample prior to acceptance.
- f. a system for determining and recording.
- g. a system to ensure that the material/waste samples are analyzed if needed. POP-PBDE might be analysed in case that the material is considered for further recycling and the material. The screening of bromine (see section 3.6) can be used as a surrogate parameter for further decisions.

Have a reception facility that meets at least the following criteria:

- a. A laboratory to analyse the samples at the speed required by BAT. Typically this requires having a robust quality assurance system, quality control methods and maintaining suitable records for storing the analyses results. Particularly for hazardous wastes, this often means that the laboratory needs to be on-site. Since POP-PBDEs require a rather sophisticated analysis (see Guidance on analysis of new POPs in articles) such monitoring is normally not done on-site.
- b. have a dedicated quarantine waste storage area as well as written procedures to manage rejected waste. If the inspection or analysis indicates that the wastes fail to meet the acceptance criteria (including, e.g. damaged, corroded or unlabelled drums) then the material/wastes can be temporarily stored there safely. Such storage and procedures should be designed and managed to promote the rapid management (typically a matter of days or less) to find a solution for that material/waste.
- c. have a clear procedure dealing with wastes where inspection and/or analysis prove that they do not fulfil the acceptance criteria of the plant or do not fit with the material/waste description received during the pre-acceptance procedure. The procedure should include all measures as required by the permit or national/international legislation to inform competent authorities, to safely store the delivery for any transition period or to reject the material/waste and send it back to the waste producer or to any other authorized destination.
- d. move material/waste to the storage area only after acceptance.
- e. mark the inspection, unloading and sampling areas on a site plan.
- f. have a sealed drainage system if needed.
- g. a system to ensure that the installation personnel who are involved in the sampling, checking and analysis procedures are suitably qualified and adequately trained, and that the training is updated on a regular basis.
- h. the application of a waste tracking system unique identifier (label/code) to each container at this stage. The identifier will contain at least the date of arrival on-site and the waste code.

Storage and handling

POP-PBDE-containing materials (e.g. electronic waste, shredder residues, PUR foams) and wastes often have to be stored and handled prior to treatment or final disposal. BAT/BEP storage should include the following techniques:

- a. locating storage areas away from water courses and sensitive perimeters, and in such a way so as to eliminate or minimise the double handling of wastes within the installation.

b. ensuring that the storage area drainage infrastructure can contain all possible contaminated run-off and that drainage from incompatible wastes cannot come into contact with each other.

c. using a dedicated area/store which is equipped with all necessary measures related to the specific risk of the wastes for sorting and repackaging laboratory smalls or similar waste. These wastes are sorted according to their hazard classification, with due consideration for any potential incompatibility problems and repackaged if needed. After that, they are moved to the appropriate storage area.

g. considerations is given to appropriate fire safety measures required for storage of plastic wastes (see Basel Convention 2002)⁶⁷.

h. storing organic waste liquid with a low flashpoint under a nitrogen atmosphere to keep it inert. Each storage tank is put in a waterproof retention area. Gas effluents are collected and treated.

Apply the following techniques when handling waste.

a. having systems and procedures in place to ensure that wastes are transferred to the appropriate storage safely.

b. having in place a management system for the loading and unloading of materials/waste in the installation, which also takes into consideration any risks that these activities may incur.

c. ensuring that a qualified person attends the waste holder site to check the old original waste, waste from an unclear origin or undefined waste (especially if drummed), to classify the substances accordingly and to package into specific containers. In some cases, the individual packages may need to be protected from mechanical damage in the drum with fillers adapted to the packaged waste properties.

Maximise the use of re-usable packaging (drums, containers, IBCs, palletes, etc.)

Outgoing materials and wastes

To improve the knowledge and management on the outgoing waste/material BAT/BEP is to:

- analyse and guarantee the quality and composition of the material/waste OUT according to the relevant parameters important for the receiving company/facility.
- assess how and where wastes could be re-used, consistently with environmentally sound management, as feedstock for another industry.
- assure that the materials and wastes are labelled according to the waste management catalogue and other labelling criteria of the country.
- assure that contaminated materials are only delivered to companies with appropriate treatment capacity and management frames in place. For wastes the appropriateness of the treatment technologies is to be assured (e.g. landfill category, co-incineration in BAT cement kilns, BAT incinerators).

Crushing, shredding, sieving and washing operations

Within the management and treatment of POP-PBDE-containing materials crushing, shredding and sieving operations are common.

BAT/BEP is to:

Perform crushing, shredding and sieving operations in areas fitted where needed with extractive vent systems linked to abatement equipment when handling materials that can generate emission to air (e.g. dust, VOCs, odours).

Perform washing processes considering:

⁶⁷ Basel Convention. 2002. Technical Guidelines for the Identification and Environmentally Sound Management of Plastic Wastes and for their Disposal.

- a. identifying the washed components that may be present in the items to be washed (e.g. solvents, oil, refrigerants).
- b. transferring washings to appropriate storage and then treating them in the same way as the waste from which they were derived.
- c. using treated waste water from the water treatment plant for washing instead of fresh water. The resultant waste water can then be treated in the waste water treatment plant or re-used in the installation.

General BAT/BEP considerations in respect to air and water releases

Air emission treatment

To prevent or control the emissions mainly of dust, VOC and odours and some inorganic compounds, BAT includes restricting the use of open topped tanks, vessels and pits by:

- a. preventing direct venting or discharges to air by linking all the vents to suitable abatement systems when storing materials that can generate emissions to the air (e.g. VOCs, dust, odours).
- b. keeping waste or materials under cover or in waterproof packaging.

Correctly operate and maintain the abatement equipment, including the handling and treatment/disposal of spent scrubber media. Have a scrubber system in place for the major inorganic gaseous releases from those unit operations which have a point discharge for process emissions.

Have leak detection and repair procedures in place in installations a) handling a large number of piping components and storage and b) compounds that may leak easily and create an environmental problem (e.g. fugitive emissions, soil contamination). This may be seen as an element of the EMS.

Air emissions should be reduced at least to the levels required by the respective national legislation. Facilities are encouraged to use BAT technologies to achieve BAT emission level.

Appropriate monitoring schemes should be in place to supervise the performance and document releases.

Waste water treatment

BAT/BEP is to reduce the usage and contamination of water by:

- a. applying where necessary site waterproofing and storage retention methods
- b. carrying out regular checks of storages, bunkers, pits and tanks
- c. where appropriate applying separated water drainage according to the pollution load (roof water, road water, process water)
- d. applying a security collection basin
- e. performing regular water audits, with the aim of reducing water consumption and preventing water contamination
- f. segregating process water from rainwater

Have procedures in place to ensure that the effluent specification is suitable for the on-site effluent treatment system or discharge

Avoid the effluent by-passing the treatment plant systems

Have in place and operate an enclosure system whereby rainwater falling on the processing areas is collected along with tanker washings, occasional spillages, drum washings, etc. and returned to the processing plant or collected in a combined interceptor

Segregate the water collecting systems for potentially more contaminated waters from less contaminated water

Have a full concrete base in the critical area, which falls to internal site drainage systems which lead to storage tanks or to interceptors that can collect rainwater and any spillage.

Collect the rainwater in a special basin for checking, treatment if contaminated and further use.

Maximise the re-use of treated waste waters and use of rainwater in the installation

Identify waste waters that may contain hazardous compounds. Segregate the previously identified waste water streams on-site and specifically treat waste water on-site or off-site.

Select and carry out the appropriate treatment technique for each type of waste water.

Implement measures to increase the reliability with which the required control and abatement performance can be carried out (for example, optimising the precipitation of metals)

Identify the main chemical constituents of the treated effluent (including the make-up of the COD) and to then make an informed assessment of the fate of these chemicals in the environment

Only discharge the waste water from its storage after the conclusion of all the treatment measures and a subsequent final inspection

Achieve the water emission values required by national legislation and/or competent authority before discharge. Facilities are encouraged to use BAT technologies to achieve low releases of pollutants to water.

Prevention of soil contamination

To prevent soil contamination, BAT is:

- to provide and then maintain the surfaces of operational areas, including applying measures to prevent or quickly clear away leaks and spillages, and ensuring that maintenance of drainage systems and other subsurface structures is carried out
- to utilise an impermeable base and internal site drainage
- to reduce the installation site and minimise the use of underground vessels and pipe work
- to avoid the releases of waste water discharge to soil
- to assure that only non-contaminated sludge from waste water treatment are applied to soil

Annex 2: Generic BAT/BEP for processing technologies of plastic

A range of processing technologies are used to convert plastic from recycling (and virgin polymers) into the required shape of the final product. The processing step itself is mainly a physical transformation step using different technologies (European Commission 2011a)⁶⁸ such as:

- extrusion (for pipes, profiles, sheets and cable insulation)
- injection moulding (for products of different, often very complex shapes like machine parts, electrical plugs and medical equipment such as syringes; thermoplastics and thermosets)
- pultrusion for rods, tubes, etc.
- blown film for thermoplastics
- cast film for thermoplastics
- coating (for thin layers on different substrates)
- pressing (for resins)
- spinning (for fibres)
- transfer moulding for thermosets
- compression moulding for thermosets
- blending (generally applicable technique)

Environmental and health concerns of moulding or extruding recycled plastics are emissions of volatile/semi-volatile organic compounds including POP-PBDEs. In some cases waste waters with the potential for high loads of organic compounds, spent solvents and non-recyclable waste are generated.

Techniques to reduce VOC/SVOC emission in process design

Techniques to reduce emissions can be considered during the process design and the plant design. Process design conditions (e.g. temperature, pressure, vapour pressure of materials/chemicals) can influence the levels of VOC and SVOC emissions.

Techniques to reduce VOC and SVOC emissions resulting from process design include (European Commission 2011a):

- To optimise the reactor design and physical parameters to minimize (VOC) releases (homogeneous recycled plastic mixtures, optimum temperature, appropriate suction systems)
- Minimize the use of volatile compounds and use of materials with low vapour pressure
- To treat waste water streams which contains VOCs by stripping, rectification or extraction in order to remove solvents which could contribute to VOC emissions in further treatment operations
- To carry out solid-liquid separation in a way to minimize VOC emission (e.g. using centrifuges, keeping the system closed)

Techniques to reduce VOC/SVOC emission in plant design

The selection of plant components and the way they are configured can greatly influence the extent of fugitive emissions. These should consider (European Commission 2011a)⁶⁹:

⁶⁸ European Commission. 2011a. Best Available Techniques (BAT) Reference Document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector. Draft 2, 20 July 2011.

A) Limiting the number of potential emission points

Design piping layout appropriately by minimizing pipe length and reducing the number of connectors and valves. Also welded fittings and pipe can help to reduce emissions.

To minimize the use of pumps and to use pressure transfer

B) Maximize inherent process containment features

To enclose effluent drainage systems and tanks used for effluent storage/treatment

C) Select high quality equipment

Appropriate valves

Fitting high-integrity gaskets for critical applications

Pumps, compressors and agitators fitted with mechanical seals

D) Selecting appropriate material for equipment

The select equipment appropriate for the process

To avoid corrosion by selection of appropriate material

To prevent corrosion by lining or coating equipment

E) Facilitating monitoring and maintenance activities by good access to critical components

F) Collecting and treating emissions

Economic considerations: While the reduction of emissions might need some investment cost they also provides opportunities for saving raw materials.

Annex 3: Disposal of POP-PBDE-containing materials to landfills

The landfilling of POP-PBDE-containing materials:

The goals of waste management of POPs are threefold:

- 1) protection of human health and the environment;
- 2) conservation of resources, and
- 3) disposal and full stabilisation of wastes with elimination of POPs (and no transfer of waste related problems to the next generation as a criteria for “sustainability”).

Thus, for goal oriented waste management, landfilling of POPs-containing wastes is the least preferred option and must normally be avoided. This is consistent both with the results of several life cycle analyses of POP-PBDE disposal (Vermeulen et al. 2011⁷⁰; Boughton and Horvath 2006⁷¹; Ciacci et al. 2010⁷²; Duval et al. 2007⁷³) and with the Stockholm Convention BAT-BEP guidance (Stockholm Convention 2007)⁷⁴. That guidance recommends, for example, that car shredder residues which always contain POP-PBDEs must be disposed of in proper incinerators equipped with sophisticated air pollution control devices. Hence, the following guidelines for landfilling assume that all possibilities to establish “clean” material cycles, or to mineralise POP-PBDEs by modern incineration with advanced air pollution control or alternative equivalent treatment have been exploited.

⁶⁹ European Commission. 2011a. Best Available Techniques (BAT) Reference Document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector. Draft 2, 20 July 2011

⁷⁰ Vermeulen I, Van Caneghem J, Block C, Baeyens J, Vandecasteele C. 2011. Automotive shredder residue (ASR): reviewing its production from end-of-life vehicles (ELVs) and its recycling, energy or chemicals' valorisation. *J Hazard Mater.* 190, 8-27.

⁷¹ Boughton B, Horvath A. 2006. Environmental assessment of shredder residue management. *Resources, Conservation and Recycling* 47, 1–25.

⁷² Ciacci L, Morselli L, Passarini F, Santini A, Vassura I. 2010. A comparison among different automotive shredder residue treatment processes. *International Journal Life Cycle Assessment* 15, 896–906.

⁷³ Duval D, Maclean HL. 2007. The role of product information in automotive plastics recycling: a financial and life cycle assessment. *Journal of Cleaner Production* 15, 1158–1168.

⁷⁴ Stockholm Convention. 2007. Guidelines On Best Available Techniques And Provisional Guidance On Best Environmental Practices Relevant To Article 5 And Annex C Of The Stockholm Convention On POPs.

BAT/BEP recycling and BAT/BEP incineration are both expensive waste management technologies. While the informal recycling sector in developing countries is in some cases highly efficient at low cost it does normally not meet environmental or occupational health standards⁷⁵. BAT/BEP technologies are practiced mainly in industrial countries because of the high costs. A survey of waste management costs across different regions demonstrates that expenditures on municipal waste management amount to between 0.2% and 0.4% of Gross Domestic Product (GDP) for most countries (Brunner and Fellner, 2007⁷⁶). But as GDP ranges globally from 200 USD and to 100,000 USD per capita (The World Bank, 2011)⁷⁷, the financial resources available for waste management span a range with a factor of 500. It is evident that waste management practice must vary significantly from region to region as many countries cannot yet afford modern waste management infrastructure including incineration and other sophisticated means of waste treatment, recycling and disposal. In developing countries, therefore, a much higher proportion of wastes is still disposed of to landfills and dump sites than in industrial countries. Hence, these landfill guidelines are aimed primarily at developing countries and countries with economies in transition. These countries often rely on open dumping of waste – sometimes with open-burning - with severe negative impacts on human health and the environment. This chapter and Annex D of the guidance remains relevant to those industrial countries where the disposal of POPs-containing waste to landfill remains common in the short term – but every effort must be made to ensure that a transition is made to a more sustainable approach.

Types of wastes containing POP-PBDEs that are landfilled

Wastes containing POPs can be categorised as follows: A) wastes consisting mainly or exclusively of POPs, B) mixed wastes containing POPs as additives, C) and wastes contaminated with traces of POPs. BAT/BEP and good landfill practice should ensure that the information allowing landfill operators to identify type A wastes is available with each consignment. If type B wastes are derived from a single and known process such as a car shredder, the presence of POP-PBDEs can be assessed according to the Stockholm Convention *POP-PBDEs Inventory Guidance* (chapters 4, 5, and 6). In fact, according to the Stockholm Convention Guidance, car shredder residues always contain some POP-PBDEs. However, it is often difficult for landfill operators to identify type C wastes, or type B and C wastes when mixed with other wastes. It must also be taken into account that wastes of type B and C are likely to comprise additional hazardous substances, such as other POPs and heavy metals. Thus, decisions on the management and landfilling of POP-PBDE-containing wastes cannot be taken on the grounds of POP-PBDE content alone.

The four major application areas for POP-PBDEs, and thus the most relevant waste streams, are (see also chapter 4, 5 and 6 of this guidelines):

- electrical and electronic equipment (computers, telephone sets, office appliances, cables etc.),
- the transport sector (plastics, textiles and upholstery etc. in end-of-life vehicles),
- furniture, mattresses and others (including carpets, textiles, and the like),
- the construction sector (insulation, foils, and other polymer materials)

There are two ways to determine mass flows and concentrations of POP-PBDE-containing wastes: Either by direct analysis as described in the Stockholm Convention Inventory Guidance for POP-PBDEs, or by a mass flow analysis approach as applied e.g. by Morf et al. (2008)⁷⁸. Numeric examples of common waste flows and corresponding POP-PBDE concentrations are presented in chapter 4 and 5 of the Stockholm Convention Inventory Guidance for POP-PBDEs and HBB.

⁷⁵ The improvement of occupational health and the performance of the informal waste management sector are of crucial importance for more sustainable waste management in developing countries.

⁷⁶ Brunner PH, Fellner J. 2007. Setting priorities for waste management strategies in developing countries. *Waste Management Research* 25, 234-240.

⁷⁷ World Bank. 2011. *World Development Indicators*, Green Press Initiative, Washington D.C.

⁷⁸ Morf LS, Buser AM, Taverna R, Bader H-P, Scheidegger R. 2008. Dynamic Substance Flow Analysis as a Valuable Risk Evaluation Tool – A Case Study for Brominated Flame Retardants as an Example of Potential Endocrine Disrupters; *Chimia* 62, 424–431.

In general, the physical characteristics of POP-PBDE-containing wastes are the same as for other wastes that are landfilled: If not pre-treated, particle sizes cover a wide range from 10^{-6} to 2 m, and densities vary between 0.02 and 2 g/cm³. Thus, sampling, sample preparation and analysis of POP-PBDE-containing wastes is a difficult task and can be prohibitively expensive for individual landfill operators. There are no standard procedures yet to sample and analyse such wastes for POP-PBDEs at a given and predefined standard deviation. Support for waste sampling and characterization is given in CEN/TR 15310-1 "Characterization of waste – Sampling of waste materials – Part 1: Guidance on selecting a basic statistical approach to sampling, as applied under a variety of scenarios".

Categories of landfills to receive POP-PBDE-containing wastes

The landfill categories listed on the left hand side of Table A-1 are common in countries with advanced landfill management (see for instance Austrian Landfill Ordinance, (Deponieverordnung, 2008)⁷⁹. While some advanced nations refrain from operating hazardous landfills, above ground hazardous waste landfills are still designated in other countries and a few are using underground repositories such as salt mines or equivalent geological formations which are isolated from the hydrological cycle over very long time frames. As the capacity of this underground storage is limited and rather expensive only toxic and comparatively highly concentrated wastes are allowed to be stored. Site specific regulations apply based on the location and specification but this underground storage of wastes contaminated with POP-PBDEs is a specific topic and not covered by this Annex.

The landfill categories given in Table A-1 do not normally apply to emerging economies where it is more common to find landfills that do not meet the engineering specifications of sanitary landfill comprising liners along with landfills engineered to receive more challenging materials such as hazardous wastes and hospital wastes. In countries with a low GDP the main role of waste management is the economic collection of wastes as this is vital for sanitation and public health. This usually consumes 80 to 90% of the waste management budget. Hence, the remaining fraction does currently not allow sophisticated engineering of leachate and gas collection systems nor even site security and effective control over incoming wastes.

Delivery of wastes to landfills

Wastes must be characterised and controlled before landfilling. Characterisation includes the history of the waste (process of waste generation), type, properties and composition of the waste. Waste composition is determined according to existing landfill regulations (cf. EU landfill directive (EC 1999))⁸⁰ by sampling, sample pre-treatment and analysis. Mixing or dilution of wastes in order to meet critical concentration thresholds is prohibited and must be prevented. Modern regulations restrict individual inorganic substances and some organic sum parameters in waste inputs, but do not currently focus on individual organic substances. In emerging economies input control on the substance level is – for financial reasons - extremely challenging for both inorganic as well as organic parameters.

⁷⁹ Deponieverordnung (2008) Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über Deponien (Deponieverordnung 2008) Bundesgesetzblatt für die Republik Österreich, 30. Januar 2008. <http://www.lebensministerium.at/umwelt/abfall-ressourcen/abfall-altlastenrecht/awg-verordnungen/deponievo.html>

⁸⁰ European Commission. 1999. Council Directive 1999/31/EC of 26. April 1999 on the landfill of waste. Amended 21.11.2008.

Table A-1: Types of landfills, and corresponding constraints for disposing of wastes containing POP-PBDEs. The table serves as an example based on existing classifications in Europe (European Commission 1999)⁸¹, and may vary in different countries

	A. Landfill for inert waste	B. Landfill for non-hazardous waste		C. Landfill for hazardous waste (e.g. underground storage)
		B1. for inorganic waste (TOC<50 g/kg)	B2. for organic waste (TOC> 50 g/kg)	
General waste content (examples)	Soil, clean rubble, stones, tiles, ceramics, track ballast, etc.; no manmade organic substances	Mixed construction and demolition waste (e.g., concrete, bricks, asphalt) Inorganic residues from waste treatment (e.g., bottom ash of MSW incineration)	Untreated and pretreated MSW, organic fraction from construction wastes, residual fractions from recycling.	Hazardous wastes Criteria: TOC < 60g/kg
Content with regard to POP-PBDE wastes	None	Residues of POP-PBDEs in poorly separated polymer materials, e.g. if construction waste is not sufficiently separated Organic materials in residues from incomplete waste combustion (only if TOC < 50 g/kg; residues from pyrolysis are higher)	May contains some household hazardous wastes, WEEE, wastes from ELV, furniture and household articles, and POP-PBDE-containing residues from the construction sector (insulation, foils, and other plastic materials)	Concentrated wastes of POP-PBDEs from production or manufacturing
Barriers appropriate to retain POP-PBDEs	No	for limited time frames only	for limited time frames only	Possibly, if POP-PBDEs are safely and retrievably contained and stored in dry, stable geological

⁸¹ European Commission. 1999. Council Directive 1999/31/EC of 26. April 1999 on the landfill of waste. Amended 21.11.2008.

				formation
Leachate collection	No	yes	Yes	Depends (not necessary in geological storage)
Gas collection and treatment	No	Yes	Yes	No (Not necessary)
Regulations regarding POP-PBDEs in wastes, and in eluates derived from wastes. (POP-PBDEs are list 1 substances in the Water Framework Directive and must be prevented from reaching groundwater)	EU Landfill directive ⁸² : no limits neither for total contents nor for eluate. Austrian landfill ordinance (2008): No, but limits for eluate: EOX < 0,3 mg/kg (as Cl)	EU Landfill directive: no limits neither for total contents nor for eluate. <u>Austrian landfill ordinance:</u> Landfills for CandD waste: No, but limits for eluate: EOX < 3 mg/kg (as Cl) Landfills for residues from waste incineration: No, but limits for eluate: EOX < 30 mg/kg (as Cl)	EU Landfill directive: no limits neither for total contents nor for eluate. <u>Austrian landfill ordinance:</u> No, but limits for wastes: POX ¹⁾ (as Cl) < 1000 mg/kg (dm) for eluate: EOX < 30 mg/kg (as Cl)	EU Landfill directive: no limits neither for total contents nor for eluate.
Regulations regarding wastes that potentially may contain POP-PBDEs	EU landfill directive: TOC < 30 g/kg Austrian landfill ordinance: Plastics < 0.5% by weight (dm)	EU landfill directive: No limits Austrian landfill ordinance: TOC < 50 g/kg (for CandD waste landfills < 30 g/kg)	EU landfill directive: No limits Austrian landfill ordinance: Lower calorific values < 6,600 kJ/kg	EU landfill directive: TOC < 60 g/kg

¹⁾purgeable organic halogen compounds

⁸² European Commission. 1999. Council Directive 1999/31/EC of 26. April 1999 on the landfill of waste. Amended 21.11.2008.

Investigations of POP-PBDEs in wastes are not required by modern landfill regulation. This can be justified on the grounds that wastes to be landfilled are composed of a great number of substances, many belonging to the family of POPs and other hazardous compounds. Hence, the costs of analysis to establish concentrations of all these substances would be high. It is more effective to regulate sum parameters (Tab. A-1), and to use the results of the analysis of these sum parameters for decision-making. If landfill specifications are not met, wastes must be either pre-treated, or disposed of in another landfill class.

In developing countries, characterisation and control of incoming wastes must normally be based on local experience and good governance practice. Incoming wastes must be visually screened for those categories that are enriched with POP-PBDEs such as residues from shredding End-of-Life-Vehicles (ELV), plastics and boards from dismantling of electronic wastes, insulation materials from constructions, or wastes from removing insulation from cables. Wastes that contain POP-PBDEs, such as residues from ELV recycling, should be mixed with other non-combustible and non-reactive wastes, thus reducing the risk of producing large amounts of volatile and toxic halogenated compounds in case of landfill fires (see below).

Operation and maintenance of landfills containing POP-PBDEs

Sanitary landfills are the longest lived man-made constructions and materials buried in landfills are expected “to stay there forever”. Considering geological processes of erosion and weathering, “forever” means ten thousands of years; after this period, most landfills will be removed by geogenic processes.

Because POP-PBDEs are only very slowly degrading, the residence time of these substances will be long, too. Danon-Schaffer recently modelled the debromination of DecaBDE to lower PBDE (including POP-PBDEs) in landfills (Danon-Schaffer and Mahecha-Botero 2010)⁸³. Depending on the selected degradation rates, significant debromination occurs within 70 to several hundred years thus increasing the levels of POP-PBDEs over time. Hence, landfills represent important long-term sinks and sources for POP-PBDEs.

Ultimately containment of sanitary landfills will degrade and allow landfilled substances to escape over time. USEPA expressed concerns that the “large amounts of PCBs contained in land disposal sites present a severe hazard for the future” (USEPA 1979⁸⁴) and the risks presented by POP-PBDEs are similar. The lifetime of landfill containment systems is limited in time-scales of decades to centuries - actual experience does not yet allow more precise conclusions to be drawn (Buss et al. 1995⁸⁵, Allen 2001⁸⁶, Simon and Mueller 2004⁸⁷) - it must be expected that POP-PBDEs and other substances contained in landfills will be emitted over long time periods (centuries) (Weber et al. 2011)⁸⁸. Thus, the behaviour of landfill constituents as well as of the corresponding containment must be known in order to predict emission levels to the environment over the whole life-time of the landfill. There are many studies available assessing the first decades of open dumps as well as of sanitary landfills but studies investigating or modelling the full life cycle of PBDEs and other persistent toxic chemicals in landfills over long time periods are still rare.

Landfills in emerging economies may contain the widest range of compounds because it is not possible to (completely) control waste collection and delivery to landfills. In affluent economies, this situation has been mitigated by waste pre-treatment and by strict input regulation. However, even under these firm control measures, it is still possible that some inappropriate wastes will be disposed of in particular landfill classes. It

⁸³ Danon-Schaffer M.N, Mahecha-Botero A. 2010. Influence of chemical degradation kinetic parameters on the total debromination of PBDE in a landfill system. 30th International Symposium on Halogenated Organic Pollutants, 12-17 September 2010. San Antonio, USA.

⁸⁴ USEPA (1979). Polychlorinated Biphenyls 1929-1979 Final Report, US Environmental Protection Agency: 94

⁸⁵ Buss SE, Butler AP, Sollars CJ, Perry R, Johnston PM. 1995. Mechanisms of Leakage through Synthetic Landfill Liner Materials. *Water and Environment Journal* 9, 353-359.

⁸⁶ Allen A. 2001. Containment landfills: the myth of sustainability. *Engineering Geology* 60, 3-19.

⁸⁷ Simon F-G, Mueller W. 2004. Standard and alternative landfill capping design in Germany. *Environmental Science & Policy* 7, 277-290.

⁸⁸ Weber R, Watson A, Forter M, Oliaei F. 2011. Persistent Organic Pollutants and Landfills - A Review of Past Experiences and Future Challenges. *Waste Management and Research* 29, 107-121.

is thus essential that landfills are constructed with liners and capping systems to control water ingress and leachate escape. The costs of containment depend on the content and thus on the class of landfill. With increasing reactivity and leachability of the waste categories from landfill type A to C, the liners must fulfil more stringent requirements. Under the conditions of emerging economies with mixed waste landfills prevailing, liners should fulfil the same conditions as for type B landfill. However, this entails costs that are which are often not affordable in emerging economies.

In order to understand and control landfill behaviour and relating emissions, reactions taking place in landfills must be understood. A landfill is basically an anaerobic biochemical reactor driven by the nutrients carbon and nitrogen and controlled by the flow of water. In simplified terms, the end products of such a reactor are methane, carbon dioxide and water. Due to the many inorganic and organic constituents, some of them refractory, the products of landfilling contain a large amount of gaseous and liquid harmless as well as hazardous compounds. Thus, it is of prime importance to collect leachates and landfill gas in order to achieve waste management goals.

PBDE releases from landfills

In general, trace organic substances such as PBDEs are of little importance for the functioning of the landfill reactor. This may be different in the special case when production wastes or certain industrial wastes are landfilled (Takeda 2007)⁸⁹. However, the landfill reactor is of significance for the release of trace substances. In addition to the intrinsic properties of the trace substances (K_{ow} , Henry coefficient, vapour pressure, solubility, persistence), landfill parameters such as temperature, pressure, ionic strength, pH and redox conditions determine the fate of individual waste constituents.

When evaluating information about releases of POP-PBDEs from landfills, it is important to distinguish between state of the art landfills on one hand, and other disposal practices which include landfilling of large amounts of PBDE-containing wastes without top and bottom liners, open dumping, or illegal dumping on the other. The first practice results in very low flows of POP-PBDEs to the environment (at least in the relatively short term) whilst the latter may result in severe environmental pollution. Several authors acknowledge that semi-volatile compounds like POP-PBDEs and PCB are leaching together with heavy metals and other substances from inappropriate landfills into soil and hydrosphere (Osako et al. 2004⁹⁰, Odusanya et al. 2009⁹¹, Danon-Schaffer 2010⁹², Danon-Schaffer and Mahecha-Botero 2010⁹³, Weber et al. 2011). Leachate concentrations of PBDEs in the range of 30 to 250 ng/L have been found in a study of five different landfills in North America by Oliaei (Oliaei et al. 2002)⁹⁴. POP-PBDEs have also been detected in soils adjacent to landfills in various regions of Canada (Danon-Schaffer 2010), indicating atmospheric POP-PBDE release from landfills and subsequent deposition. Higher values have been recorded in leachates from illegally dumped shredder residues from ELV and electronic wastes that are well known sources of landfill emissions of POPs, requiring costly remediation actions (Takeda et al. 2007)⁹⁵.

⁸⁹ Takeda N 2007. Restoration project of Teshima Island stained by illegal dumping. *Organohalogen compounds* 69, 873-876. <http://www.dioxin20xx.org/pdfs/2007/07-402.pdf>

⁹⁰ Osako M, Kim Y-J, Sakai S-I. 2004. Leaching of brominated flame retardants in leachate from landfills in Japan. *Chemosphere* 57, 1571-1579.

⁹¹ Odusanya DO, Okonkwo JO, Botha B. 2009. Polybrominated diphenyl ethers (PBDE) in leachates from selected landfill sites in South Africa. *Waste Management* 29, 96-102.

⁹² Danon-Schaffer MN. 2010. Polybrominated Diphenyl Ethers in Landfills from Electronic Waste February 2010. PhD thesis. Faculty of Graduate Studies. University of British Columbia. Vancouver, Canada.

⁹³ Danon-Schaffer M.N, Mahecha-Botero A. 2010. Influence of chemical degradation kinetic parameters on the total debromination of PBDE in a landfill system. 30th International Symposium on Halogenated Organic Pollutants, 12-17 September 2010. San Antonio, USA

⁹⁴ Oliaei F, King P, Phillips L. 2002. Occurrence and concentrations of polybrominated diphenyl ethers (PBDE) in Minnesota environment. *Organohalogen Compounds* 58, 185-188.

⁹⁵ Takeda N 2007. Restoration project of Teshima Island stained by illegal dumping. *Organohalogen compounds* 69, 873-876. <http://www.dioxin20xx.org/pdfs/2007/07-402.pdf>

If state of the art landfilling with liners, leachate and gas collection and treatment and careful site management pollution by POP-PBDEs can be kept at low and environmentally tolerable levels. This is particularly the case as long as the polymers containing PBDE are not degraded and do not release the substance. An assessment of management options for c-OctaBDE commissioned by the European Commission concluded that c-OctaBDE are not expected to be leached significantly from polymers (BiPRO 2007⁹⁶). The authors consider that releases after proper disposal are negligible, a conclusion that seems applicable to the whole UNECE region (BiPRO 2007). A similar conclusion was reached in a report prepared for the New Zealand Department of the Environment for the POPRC process (Keet et al. 2010⁹⁷). By reference to three investigated landfills, the authors claim that the disposal of waste plastics containing PBDEs in controlled landfills is a well developed and safe activity resulting in very low levels of POP-PBDEs in leachates. Compared to the quantities of PBDEs stored, the quantity of these products released from the landfill was considered infinitesimal. However, the authors recommend to validate their findings more widely and in doing so it is important to consider the longer time scales over which the hazards remain but after the engineering has failed using a modelling approach.

Based on these findings, the key environmental problem – besides landfill fires (see below) - consists of the inappropriate landfilling resulting in contamination of the hydrosphere as it is most often observed in emerging economies and transition countries. This may result in the exposure of humans in the vicinity of landfills, as reported for breast milk from women living near a dump site in India (Someya et al. 2010)⁹⁸ and for juvenile scavengers living and working on a landfill in Nicaragua (Athanasiadou et al. 2008)⁹⁹.

For industrial countries with modern BAT landfilling, it needs to be established whether the debromination/transformation of PBDEs is more rapid than the degradation of containment systems - taking into account the debromination of the larger reserve of DecaBDE into POP-PBDEs within the landfill site.

For long-term considerations, climate change and extreme weather events have to be considered (Laner et al. 2009¹⁰⁰; Weber et al. 2011¹⁰¹). However, these causes are generic impacts, and not only of specific importance for POP-PBDEs. Thus, BAT landfill practice has to take these impacts, which are likely to include more rapid degradation of liners, enhanced leachate production, mobilisation of a larger waste fractions, and higher volatilisation rates into account. The situation is of particular concern for coastal areas where flooding and interaction with seawater poses a threat to environment and human health by bioaccumulation (Bebb and Kersey 2003)¹⁰².

Release of POP-PBDEs from landfill fires

Landfill fires are inevitable and are often observed - particularly in emerging economies. Indeed landfills are sometimes deliberately set on fire in order to save landfill space, to recover metals, or to improve hygienic

⁹⁶ BiPRO. 2007. Management Option Dossier for commercial octabromodiphenyl ether (c-OctaBDE) 12 June 2007. Updated version on the basis of the outcome of the Sixth Meeting of the Task Force on POPs, 4-6 June 2007, Vienna, Austria. Service Contract ENV.D.1/SER/2006/0123r DG Environment, European Commission.

⁹⁷ Keet B, Giera N, Gillett R, Verschueren K. 2010. Investigation of brominated flame retardants present in articles being used, recycled and disposed of in New Zealand, A technical report prepared for the Ministry for the Environment.

⁹⁸ Someya M, Ohtake M, Kunisue T, Subramanian A, Takahashi S, Chakraborty P, Ramesh R, Tanabe S. 2010. Persistent organic pollutants in breast milk of mothers residing around an open dumping site in Kolkata, India: Specific dioxin-like PCB levels and fish as a potential source. *Environmental International* 36, 27–35.

⁹⁹ Athanasiadou M, Cuadra SN, Marsh G, Bergman A, Jakobsson K. (2008). Polybrominated diphenyl ethers (PBDE) and bioaccumulative hydroxylated PBDE metabolites in young humans from Managua, Nicaragua. *Environ Health Perspect* 116, 400-408.

¹⁰⁰ Laner D, Fellner H and Brunner PH. 2009. Flooding of municipal solid waste landfills — An environmental hazard? *Science of the Total Environment* 407, 3674–3680.

¹⁰¹ Weber R, Watson A, Forter M, Oliaei F. 2011. Persistent Organic Pollutants and Landfills - A Review of Past Experiences and Future Challenges. *Waste Management and Research* 29, 107-121.

¹⁰² Bebb J, Kersey J. 2003. Potential Impacts of Climate Change on Waste Management R and D Technical report X1-042. Bristol, UK: Environment Agency.

conditions (rodents, birds). Even in industrial countries with modern landfilling practice, it may occasionally happen that a landfill catches fire for unknown reasons. A survey in Finland reported 0.6 fires per landfill site annually, with 25% of fires at a depth of more than 2 m (Ettala et al. 1996)¹⁰³ where thermal conditions are favourable to produce brominated dioxins and furans (PBDD/PBDF).

Landfill fires are always difficult to extinguish and release considerable quantities of hazardous volatile and pyrogenic substances into the air. They are a relevant source of PCDD/PCDF particularly for developing and transition countries (UNEP 2005)¹⁰⁴. The best practice to reduce the risk of landfill fires is a strict entrance control for burning and highly flammable wastes together with prompt compaction of freshly deposited waste and followed by daily cover using inert materials such as inorganic construction waste.

The main concern with regards to landfill fires and POP-PBDEs relates to the potential formation and release of PBDDs and PBDFs (UNEP 2010)¹⁰⁵. PBDE and PBDD/DF have been measured in intentional fires of open dumps in Mexico as part of a scientific study on emission factors of open burning in dump sites (Gullett et al. 2009)¹⁰⁶ which demonstrated that PBDE originate most likely from commercial brominated flame retardants and are not formed by thermal processes. Emissions of PBDD/PBDF were similar in magnitude to their chlorinated counterparts (PCDD/PCDF). Smouldering combustion yields larger emissions than flaming combustion. For a better understanding of PBDD/PBDF formation, the thermal debromination process needs to be investigated at varying oxygen concentrations and temperatures, in particular the thermal conversion of DecaBDE to lower POP-PBDEs which might significantly contribute to the formation of POP-PBDEs and PBDD/PBDF in thermal processes (UNEP 2010).

BAT measures to prevent short- and long-term release of POP-PBDEs from landfills

Landfilling practice:

In order to prevent illegal waste disposal, landfills must be secure and enclosed by an effective fence with a lockable entrance gate together with adequate and properly controlled receiving areas for wastes with a weighbridge. An office is also required where the type and mass/volume of waste together with the location it has been buried in the landfill are recorded. An area for intermediate storage of problematic incoming wastes must be available which allows retention and, if necessary, rejection of wastes that do not comply with regulations. If a landfill consists of different classes A to C (table A-1), separate roads must connect the entrance area with each class landfill. Care has to be taken to prevent wheels and tires of vehicles from carrying waste materials outside the landfill.

According to BAT, wastes are disposed of in compacted layers, with daily covers by inert material (e.g. construction wastes; compost is not suitable for daily covers and must be avoided). Such measures reduce the risk of fires, too. Care must be taken that fires can be quickly isolated so that they do not spread all over the landfill and that they do not damage buildings or collection and treatment systems for gas and leachate. Training of landfill personal in fire precaution and safety is crucial. Also, landfill temperatures and gas concentrations on the landfill surface must be observed. Risks due to lack of geotechnical stability can be minimised by careful selection of waste materials that are appropriate for the landfill class and the slope design, and by regular and intense compaction of landfilled wastes combined with daily covers.

Before a landfill can be closed, it must be covered by a capping liner system with the following objectives: i) Minimisation of water entering the landfill body and producing leachate; ii) prevention of uncontrolled

¹⁰³ Ettala M, Rahkonen P, Rossi E, Mangs J, Keski-Rahkonen O. 1996. Landfill fires in Finland. Waste Management and Research 14, 377-384.

¹⁰⁴ UNEP. 2005. Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases. Edition 2.1.

¹⁰⁵ UNEP. 2010. Supporting Document for the Technical review of the implications of recycling commercial penta and octabromodiphenyl ethers. Stockholm Convention document for 6th POP Reviewing Committee meeting (UNEP/POPS/POPRC.6/INF/6) Geneva 11-15. October 2010.

¹⁰⁶ Gullett BK, Wyrzykowska B, Grandesso E, Touati A, Tabor DG, Ochoa GS. 2009. PCDD/F, PBDD/F, and PBDE Emissions from Open Burning of a Residential Waste Dump. Environmental Science Technology 44, 394-399.

outflow of landfill gas; iii) protection against erosion; iv) ensuring re-cultivation. In order to achieve the first goal the site should be graded with appropriate slopes/falls together with a top liner including a water collection system or a surface layer for water management (balancing precipitation and evapotranspiration).

Collection and treatment of leachate:

Leachate collection and treatment is a major cost factor in landfilling, in particular if the very long time periods of aftercare with the need for leachate purification and monitoring are taken into account. Thus, the top priority in landfill water management is to ensure that surface and groundwater are isolated from the landfill in order to generate as little leachate as possible. Type, construction and time of installation of top and bottom liners depend on the classification of the landfill, wastes deposited, climate, landfill slope, topography and settlement of landfill body.

The waste classes summarized in Table A-1 pose different challenges in view of water management: While the concentration of pollutants in leachate from class A is low, leachate from class B1 is little and from B2 are, particularly in the early stages, very highly concentrated in organic substances and nitrogen. Class B2 thus requires sophisticated treatment for long time periods (decades to centuries), class B1 needs less efforts but still must be controlled and monitored. Because of the hazardous character of waste in Class C, it should not get in contact with water and thus relatively little leachate should be produced.

Waste materials in landfill class B2 contain water and are biodegradable, hence class B2 serves as a bioreactor. The key variable for the processes in this bioreactor is water. Thus, the control of water is crucial. Before landfilling, a concept must be elaborated with clear strategic goals: Is the bioreactor to be enhanced in order to accelerate the biochemical reactions and to focus emissions on the first decades of the landfill, or is rather a containment (“dry tomb”) strategy preferred, where the reactor is not managed with a view to achieving biological stabilisation and faces future risks of long-term emissions if water enters the waste mass.

A water balance is the key for quantitative water management, and a precondition to optimise leachate treatment. Precipitation as well as evapotranspiration has to be assessed, and the amount of leachate is recorded as fraction of net precipitation on a monthly as well as annual base.

The bottom liner system of a landfill is a manmade system that prevents pollutant transport into the sub-surface layer and groundwater. It consists of a base liner and a leachate collection system. For landfill class A, the base liner consists of a double layer of geogenic mineral material with in total 50 cm thickness. For landfills of class B, the liner consists of i) 3 geogenic mineral layers with together 75 cm, and ii) a high density polyethylene sheet of c. 2,5 mm thickness. Alternatives to these liners are possible. In order to effectively collect leachate, the surface of the base liner should have a longitudinal gradient of 2%, and a lateral gradient of 3%. Hazardous waste landfills require

Leachate collection ensures the removal of wastewater from the landfill. Due to the chemical-physical characteristics of POP-PBDEs their fraction in leachate is generally small when compared to the total content of POP-PBDEs in landfilled waste as noted above. Concentrations in leachate are even lower when standard procedures for wastewater treatment are applied.

Collection and treatment of landfill gas:

Due to the anaerobic degradation of organic waste materials, landfills of class B2 produce between 100 - 300 m³ of landfill gas per ton of waste over a period of 20 years. This is mainly methane (40-60% by volume), carbon dioxide (40-60%) (Mackie 2009)¹⁰⁷ and other volatile compounds in varying amounts. Other landfill types may also emit gases, although in much smaller quantities. Thus, class B2 landfills require gas collection systems. The main purpose of gas collection is to avert climate change by preventing emissions of CH₄ and

¹⁰⁷ Mackie KR, Cooper CD. 2009. Landfill gas emission prediction using Voronoi diagrams and importance sampling. *Environmental Modelling & Software* 24, 1223–1232.

CO₂. BAT is collection and utilisation of landfill gas for energy utilization. If energy recovery is not feasible, it is necessary to flare the gas in a controlled manner at elevated temperatures. In general, the fraction of PBDE transferred to landfill gas and atmosphere is small, and will be insignificant if gas is collected and treated properly.

BAT/BEP of landfill after care

As landfills are the longest lasting anthropogenic construction after care is a crucial issue. Rough estimations of aftercare expect that – according to the type of waste landfilled and the type of pre-treatment – the need for aftercare might be one to several centuries (Belevi and Baccini 1989¹⁰⁸, Laner et al. 2011¹⁰⁹). There are still Roman landfill sites producing polluting leachate – albeit very different from those from more recent landfills (Freeze and Cherry 1979)¹¹⁰. The goal of after care is to ensure environmental protection for the full life of a landfill. This does not mean that the landfill must be monitored for the entire life-time. But it requires that the fate of the landfill is investigated, modelled or observed until there is sufficient certainty that emissions will stay below environmental threshold levels during the remaining life-time of the landfill. POP-PBDEs may have a residence time of several hundred years before they are degraded to simpler compounds. There are other, even more persistent substances in landfills. This means, that POP-PBDEs do not need to be observed specifically in a landfill after-care strategy. It suffices to control sum parameters such as the one given in Table A-1.

Means for after care

BAT after-care actually starts during the operation phase of the landfill: Emissions such as leachate and landfill gas, and composition of ground water are monitored in order to follow their development over time. It continues with an estimation of future emissions and an assessment of the expected impact on the environment. Since the future conditions in and around landfills are only predictable with high uncertainty, it is necessary to combine a model for forecasting emissions at constant conditions with a second model taking various scenarios into account (Laner et al. 2010)¹¹¹. In any case, monitoring of e.g. leachate and gas volume and composition, settlement behaviour, and others is an essential part of landfill after care. While it is usually focusing on anions, metals, and organic sum parameters, it may include POP-PBDEs as well.

Landfill mining and impact of POP-PBDEs

The objectives of landfill mining are threefold:

- A Recovery of land
- B Recovery of materials
- C Environmental protection

From an economic point of view, the “recovery of land” is often attractive and is usually the driving force behind landfill mining. This is especially the case in rapidly developing cities and urban areas, where former landfills become surrounded by residential or office developments and land values increase. Recovery of valuable materials from landfills has not yet been proven to be economically feasible and only rarely are landfills minded for the purposes of environmental protection. Increasingly the pursuit of the three objectives together may be an attractive solution in many circumstances.

¹⁰⁸ Belevi H, Baccini P. 1989. Long-Term Behavior of Municipal Solid Waste Landfills. *Waste Management Research* 7, 43-56.

¹⁰⁹ Laner D, Fellner J, Brunner PH. 2011. Future landfill emissions and the effect of final cover installation - A case study. *Waste Management* 31, 1522-1531.

¹¹⁰ Freeze RA, Cherry J A. 1979. *Groundwater*. Englewood Cliffs, N.J.: Prentice-Hall

¹¹¹ Laner D, Fellner H, Brunner PH. 2010. Environmental compatibility of closed landfills – assessing future pollution hazards. *Waste Management Research* 29, 89-98.

From the perspective of POP-PBDEs and other POPs only the objective of environmental protection is a driving force. As for other persistent organic pollutants, excavation of landfill bodies allows physical separation and thermal treatment of waste constituents that carry hazardous organic substances for their destruction. Care must be taken to prevent POPs and other toxic chemicals from leaching and volatilization during excavation. Depending on the wastes landfilled, it may be necessary to cover the site in order to prevent release of POPs and other toxic substances (for a detailed example, see SMDK 2011)¹¹².

Besides products of complete mineralisation, landfill mining may generate other outputs such as soil fractions, metals and plastics. These fractions normally contain significant levels of contamination that may impact their marketability. In any case, it will be difficult to effectively separate POPs mechanically from such fractions (soil and plastics!), resulting in POPs contaminations of the products of separation. Thus, in view of goal oriented waste management, landfill mining practice should produce a fraction that contains most of the POPs including POP-PBDEs and other hazardous organic chemicals. This fraction must be mineralised in a BAT/BEP incinerator or other BAT/BEP destruction technology.

Summary, conclusions and outlook about landfilling of POP-PBDE-containing materials with regard to BAT/BEP

POP-PBDE emissions from landfills are a specific but secondary problem for landfilling in developing countries when compared to other issues such as hygiene and sanitation. In industrial countries with state of the art landfills, POP-PBDE emissions should be small and of relatively minor environmental significance. Exceptions include landfill fires, and possibly long term leaching of POP-PBDEs and metabolites when landfill containments fail due to damage or deterioration of engineered liners. On a global scale, state of the art landfills are still a minority; hence, contamination with POP-PBDEs and other POPs has been observed in the vicinity of landfills worldwide in both emerging and industrial countries.

If BAT is applied, POP-PBDE emissions should be controlled. BAT includes disposal of POP-PBDE-containing wastes to appropriate landfill types, strict entrance control, operation of landfilling with daily covers, state of the art bottom liners and final covers, collection and treatment of leachate and gas, and after care with monitoring for long time periods (centuries). When considering BAT, it must be kept in mind that landfill regulations do not often include individual organic substances such as POPs, rather standards for a certain group of chemicals such as extractable organic halides (EOX) and adsorbable organic halides (AOX) are set for sound management of landfills.

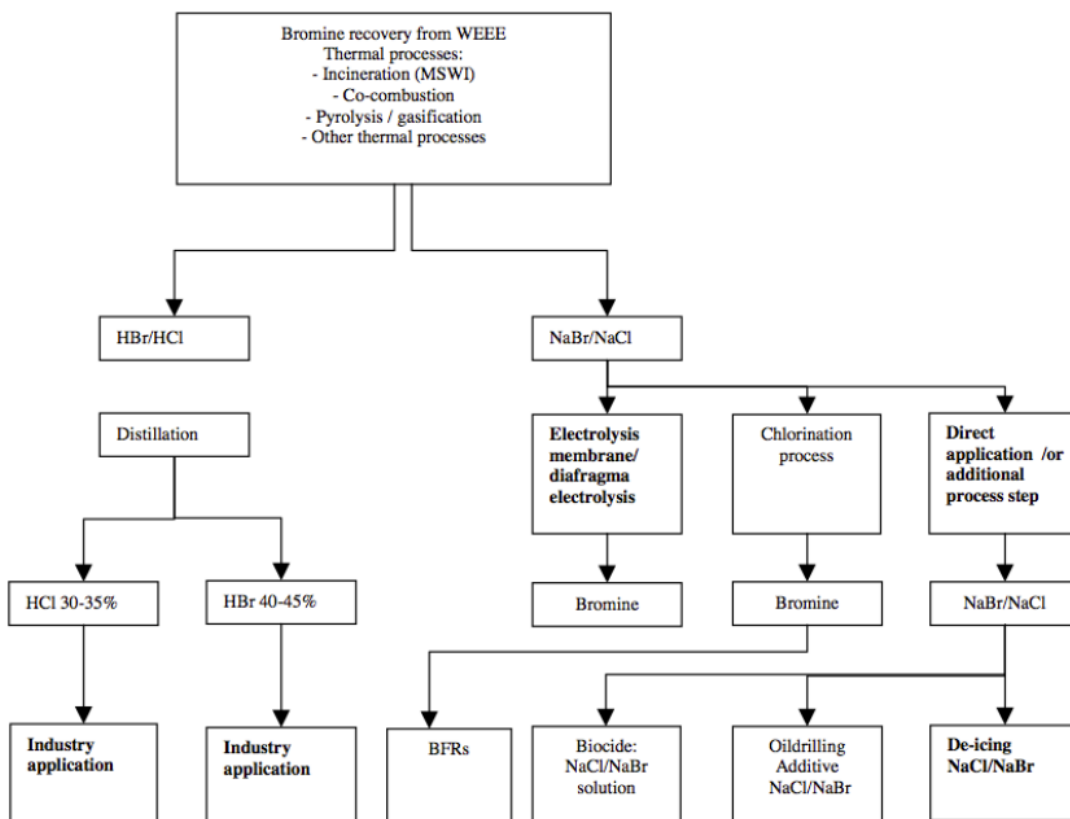
¹¹² SMDK. 2011. Sondermülldeponie Kölliken, <http://www.smdk.ch/index.cfm?andcontent=0101andpage=3>, retrieved December 8, 2011.

Annex 4: Recovery of bromine from POP-PBDE/BFR containing materials

There are a number of promising technologies in development or pilot stage capable of recovering bromine from the polymers and thus possibly allowing the safe recycling or recovery of feedstock. The recovery of bromine include techniques for recovering materials for recycling, for recycling feedstock - as either fuel or for manufacturing use, the pyrolysis of polymers with bromine recovery, recovery of bromine in incinerators, and separation of PBDE/BFR from polymer for recovery of bromine in industrial use. However, the lack of any real market incentive to remove POP-PBDEs/BFRs from end-of-life articles is possibly one reason that these technologies appear to remain at the laboratory/pilot stage. No information was available on any full-scale operation approximately 10 years after industry announced this approach as an aim (BSEF 2000)¹¹³.

Since the option of recovering bromine is increasing with full scale facilities separating bromine containing polymers, the status of these technologies although not available in full scale are shortly described here for further consideration

These technologies will, however, need further assessment before any firm recommendation can be given in respect to BAT/BEP status of these technologies. Any assessment should also address the issue of the practical level of separation of BFR/Bromine from materials containing BFR and consider the current high price of Bromine (approx. \$USD 2,500/tonne in 2010 and \$USD 4000 in 2011) together with the future markets for such bromine and the contribution relied upon from this in relation to the economics of the process



¹¹³ BSEF Bromine Science and Environment Forum. 2000. An introduction to Brominated Flame Retardants. BSEF 19 October 2000.

Figure A-1 Potential options for the bromine recovery process and closing the bromine cycle (Tange and Drohmann 2002)¹¹⁴.

Thermal recovery of Bromine

Recovery of bromine from waste incinerators

For BAT incinerators treating relatively high levels of POP-PBDE/BFR-containing wastes Vehlow suggested that bromine recovery might be possible (Vehlow et al. 2002)¹¹⁵. It was suggested that a typical MSW combustion line treats 20 tonnes of MSW per hour and that normally, to achieve suitable economies of scale, several lines operate alongside each other. On the basis that 3% of WEEE plastics containing 2.5 wt% bromine was added to three lines, (1800 kg/h WEEE plastics), this would represent 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 in theory 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 48% HBr per year. Kennedy and Donkin calculated this could contribute 7% to the income of a municipal waste incinerator (PB Kennedy and Donkin 1999).

Recovery from bromine from pyrolysis

Two thermal processes utilising pyrolysis have been developed to pilot scale where the recovery of bromine from electronic waste and waste plastic was one project feature. A main issue is to get a clear separation between the gas/liquid fuel and the HBr. If a too high concentration of halogens is left in the fuel (>50 ppm Cl or Br) it can not be further used due to a higher potential for corrosion.

The Holoclean process

The Haloclean process is a low temperature pyrolysis developed as a thermal-chemical process for the treatment of waste electrical and electronic equipment (Hornung and Seiffert 2006¹¹⁶, Koch 2007¹¹⁷). The Haloclean[®] reactor was developed with a gas-tight rotary kiln. The process tries to divide shredded electronic scrap into a valuable material stream and an energy flow. In a two-stage pyrolysis the polymer components are converted into oil and gas. A further chemical process step (called "Polypropylene Reactor") aims to strip and recover bromine and other halogens out of these products. From the remaining pyrolysis residue precious metals and other metals can be separated. To date only a demonstration plant has been developed. The process is currently used for biomass pyrolysis.

Recovery of bromine by two stage pyrolysis-gasification

In a pilot trial carried out for the bromine industry (EBFRIP) at Energy Research Centre (ECN) (Boerrigter 2001¹¹⁸, Tange and Drohmann 2005¹¹⁹) in the Netherlands it was shown that it is possible to recover bromine

¹¹⁴ Tange L, Drohmann D. 2002. Waste management concept for WEEE plastics containing brominated flame retardants, including bromine recycling and energy recovery. Flame Retardants 2002. Proceedings of a conference held in London, 5th-6th Feb. 2002.

¹¹⁵ Vehlow J, Bergfeldt B, Hunsinger H, Jay K, Mark FE, Tange L, Drohman D, Fisch H. 2002. Recycling of bromine from plastics containing brominated flame retardants in state-of- the-art combustion facilities

¹¹⁶ Hornung A, Seiffert H (2006) Rotary kiln pyrolysis of polymers containing heteroatoms. In: Feedstock Recycling and Pyrolysis of Waste Plastic. Editors Scheirs J and Kaminsky W. John Wiley & Sons, Ltd. pp. 549-567

¹¹⁷ Koch W (2007) Entwicklung eines thermisch-chemischen Prozesses zur Verwertung von Abfällen aus Elektro- und Elektronikaltgeräten - die „Haloclean“-Pyrolyse. Dissertation. Forschungszentrum Karlsruhe GmbH, Karlsruhe/Germany

¹¹⁸ Boerrigter, H. (2001). Implementation of Thermal Processes for Feedstock Recycling of Bromine, with Energy Recovery, from Plastic Waste of Electrical and Electronic Equipment (WEEE) – Phase 2: Production of Bromine Salt in Staged-gasification to Determine Technical Feasibility of Bromine Recovery. ECN-C-01-110 Report (Final version), October 2001.

via thermal processes. The process (“Pyromaat”) consisted of a staged gasification, comprising pyrolysis (550 °C) and a high temperature gasification (>1230 °C). In pilot test runs, the HBr was recovered by wet alkaline scrubbing of the syngas from treating plastic fraction of WEEE.

Technologies for separating POP-PBDEs/BFRs from the polymer matrix

Technologies of separating BFRs (including POP-PBDEs) from polymer matrix have only been established in pilot scale for a) POP-PBDE/BFR-containing polymer, and b) Printed circuit boards.

These two POP-PBDE/BFR-containing material categories have commercial market value and this has been the main driving force for the development of improved recycling technologies. Neither of the separation technologies is currently operating at an industrial scale. For POP-PBDE/BFR separation from polymer the technology now seems ready for industrial application. For printed circuit board, the POP-PBDE/BFR separation technology is still only developed and operating at a laboratory scale (see below).

Separation of BFR/bromine and polymer recovery

The common sorting approaches are based on “cherry picking” the most valuable components of the electronics/polymers from the input. Yields are generally fairly low and are normally in the range of 20% to 60% depending on input, the plant design and technologies used. The POP-PBDE/BFR and bromine load however is enriched in the residual waste fraction.

The CreaSolv® process extracts PBDE/BFRs from target polymers from polymer-rich fraction and is able to remove non-dissolved (e.g. non-target polymers and other interfering materials) and dissolved contamination (e.g. POP-PBDEs, PBB or other BFRs) from the target polymers (Schlummer et al. 2006¹²⁰) using a proprietary CreaSolv® solvent formulation. The by-product has high levels of BFR and with a market price of Bromine of approximately 4000\$/t this might be used for bromine recovery. Alternatively it could be chemically treated or incinerated. It has been developed and optimised to certain WEEE plastic fractions and is able to produce high quality RoHS compliant polymers even from BFR-rich fractions (Schlummer et al. 2006).

A UK assessment of practical and commercial applicability of the technology (WRAP 2006)¹²¹ shows that the CreaSolv® has the potential to be commercially viable with a throughput of 10,000 tonnes/year. According to Fraunhofer-Institute IVV, where the process was initially developed, the process could be developed commercially with plant capacities as low as 2000 t/year (Schlummer 2011)¹²².

The process would be able to compete with incineration (\$100+ per tonne gate fee) or landfill¹²³ disposal (cost of landfill gate fee depends strongly on region and country policy) or as treatment methods for

¹¹⁹ Tange L, Drohmann D. 2005. Waste electrical and electronic equipment plastics with brominated flame retardants - from legislation to separate treatment - thermal processes. *Polymer Degradation and Stability* 88, 35-40.

¹²⁰ Schlummer M, Maurer A, Leitner T, Spruzina W. 2006. Report: Recycling of flame-retarded plastics from waste electric and electronic equipment (WEEE). *Waste Management Research* 24, 573-583.

¹²¹ WRAP. 2006. Develop a process to separate brominated flame retardants from WEEE polymers Final Report Project code: PLA- 037 November 2006. Banbury, Waste Resources Action Program.

¹²² Schlummer M. 2011. Contributions to the Stockholm Convention guideline drafts. Vienna, Austria 23.11.2011.

¹²³ According to the convention POPs waste need to be destroyed or irreversibly transformed. Landfilling should be avoided if possible as it is not, in most circumstances, an approach which can guarantee long-term security. POPs Studies from different regions are documenting that PBDE are released from landfills and contaminate ground and surface water, the surrounding soil and for developing and transition countries contamination of humans working on or living around the landfill sites has been documented as discussed in the section on final disposal.

segregated polymer streams (WRAP 2006)¹²⁴. Creasolv will compete for BFR removal processes using spectroscopic sorting techniques, since it reaches higher yields and has high quality outputs. The WRAP assessment concluded that the process could compete with export of mixed WEEE plastic outside the EU (current sales value around \$100/tonne) if the finished high grade compounded plastic-for-recycling can be sold at about 80% of the virgin compound price.

Recovery of metals, bromine and energy from PWBs

The mechanical recycling of PWBs which also separates the BFRs from other materials in the recovery process has been developed at a laboratory scale (Kolbe 2010)¹²⁵. Within the complete material recovery strategy also the bromine is planned to be recovered (Kolbe 2011)¹²⁶. The main parts of metals are mechanically removed from PWB in a first step. In a second step the PWB resin is dissolved and the remaining metals and the glass-fibre are recovered. The metals are further recovered in metal smelters. The dissolved resin is debrominated and the bromine recovered (as NaBr). The resulting debrominated oil is planned for use in a power plant. The glass-fibre is pressed, washed and dried and can be re-used as filler material. The company also plans to recycle the residues and dust from the production of printed circuit boards.

¹²⁴ WRAP. 2006. Develop a process to separate brominated flame retardants from WEEE polymers Final Report Project code: PLA- 037 November 2006. Banbury, Waste Resources Action Program.

¹²⁵ Kolbe, P. (2010). Innovative Ansätze im Leiterplattenrecycling in "Recycling und Rohstoffe - Band 3 Karl J. Editors Thome-Kozmiensky/Daniel Goldmann Neuruppin : TK Verlag ISBN 978 3 935317 50 4.

¹²⁶ Kolbe, P. (2011). Personal Communication with R. Weber (31.10.2011).

Annex 5. Determination of POP-PBDEs in articles

Identification of POP-PBDEs by standard PBDE analysis

International Standard IEC 62321 Ed.1 (International Electrotechnical Commission, 2008) has been developed for determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, PBDEs) in electrotechnical products. The determination of PBDEs (monoBDE to decaBDE) in polymers by gas chromatography with mass spectroscopy (GC-MS) is described in Annex A to IEC 62321, including extraction, analysis and quality assurance. So far the analytical method described in IEC 62321 is only informative and seems to need improvement,¹²⁷ and the second edition is under evaluation.

The current “state-of-the-art” analytical GC-MS techniques for POP-PBDEs require appropriate extraction and clean-up. Extraction is done by solid liquid extraction (soxhlet, pressurised liquid extraction or ultrasonic assisted techniques) or by dissolution in an appropriate solvent (Schlummer et al., 2005). The organic solvents usually co-extract oligomers/polymers, and appropriate clean-up is necessary to provide an extract appropriate for sensitive GC-MS instruments.

Sample extraction and clean-up take considerable time — normally days from delivering a sample to receiving the results from the laboratory. Conventional GC-MS analysis is therefore not a practical method for the separation of POP-PBDEs in commercial recycling operations.

Rapid GC-MS analysis techniques for POP-PBDEs

To achieve a practical screening method, it is necessary to use faster extraction techniques and omit the clean-up steps. Poehlein et al. (2008) developed a rapid screening method for BFRs including polybrominated biphenyls (PBBs) and PBDEs in plastic samples using ultrasonic extraction and GC-MS analysis. The analysis time is 9 minutes (GC-MS) or 15 minutes (GC-ECD), and this method was validated for suitability to determine PBBs, PBDEs and other BFRs in styrenic industrial polymers from WEEE.

An alternative method to screen BFRs including POP-PBDEs in a selective mode without extraction and clean-up has been established. Danzer et al. (1997) used online pyrolysis of pulverised plastic and analysed with pyrolysis-GC-MS. This thermo-desorption method for plastics was optimised and used in screening of approximately 100 TVs and 80 computers (Rieß et al., 2000). Shimadzu (2010) has since developed the pyrolysis GC-MS method into a commercially available application with a 48 sample auto-sampler.

The minimum time requirement of 15 minutes (sampling, preparation, analysis) would be too long for a practical separation application in WEEE or other recycling plants (UNEP, 2010a, b). Such technologies might be used for confirmation analysis of a separation technology.

In situ monitoring of PBDEs by Raman spectroscopy

High-speed Raman spectroscopy plastic screening equipment has been developed in Japan by Saimu Corporation.¹²⁸ According to the information given by the company, the technology can screen plastics based on the POP-PBDE content (Tsuchida et al., 2009; Kawazumi et al., 2011). This equipment has been assembled in a pilot plant for separation of plastics.

¹²⁷ The inter-laboratory studies have not given very positive results to date.

¹²⁸ http://akane.saimu-net.ne.jp/plastic_en.html

In situ measurement of bromine in articles

Alternative monitoring methods have been developed to screen plastics containing bromines. Currently three technologies, which have proven bromine-screening capability in long-term trials (WRAP, 2006a) and/or are used in full-scale facilities, can be considered BAT/BEP for the screening of bromine:

- Sliding spark spectroscopy
- X-ray fluorescence (XRF)
- X-ray transmission (XRT)

The application of these technologies is described in section 4.4.

Sliding spark spectroscopy

Sliding spark spectroscopy is a surface screening method capable of rapidly detecting bromine, chlorine and inorganic additives with a detection limit of approximately 1,000 ppm. With a comparatively simple system, sliding spark spectroscopy allows direct in situ analysis of handy, compact non-conductive material without prior sample preparation.

Identification of bromine-containing materials, chlorine-containing plastics (PVC or chlorinated flame retardants), and inorganic additives (fillers, stabilisers, BFR synergists) has been described (Schlummer and Maeurer, 2006). The instrument costs approximately US\$6,000 (UNEP, 2010b).

X-ray fluorescence (XRF)

The XRF technology can be used for detection and separation of bromine-containing polymers with a detection limit of 10 ppm to 100 ppm. XRF analysis is limited to the detection of bromine in the material, without any capacity to identify the type of BFR compound. Using handheld instruments, the time requirement for a measurement is less than a minute. Precision of XRF screening measurements is limited and thus relative standard deviations could be up to 30%. This is only critical, however, when measuring levels very close to a given threshold. Therefore, the measuring threshold should be at least 30% below the threshold defined for separation. The cost of a standard instrument is approx. US\$30,000 to US\$50,000. Simpler XRF are available at lower prices.

X-ray transmission (XRT)

X-ray transmission technology uses an electric X-ray source that creates a broad-band radiation in the energy range of 80 KeV to 160 KeV. This radiation penetrates the segregation material and, when attenuated, hits an X-ray camera sensor using two independent sensor lines with different spectral sensitivity. To compensate for this technical problem, the material to be sorted is illuminated from two different directions. The resulting different transmission paths make it possible to ignore the material thickness, when applying high-speed X-ray processing.

In contrast to the handheld screening instrument (XRF and SSS) normally applied in dismantling plants, this equipment is intended to sort scrap automatically. The instrument costs approximately US\$ 400,000 (UNEP, 2010b).