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Methods of Responsibly Managing End-of-Life Foams and Plastics Containing Flame Retardants

March 2017

Berkeley
UNIVERSITY OF CALIFORNIA



GREEN SCIENCE
POLICY INSTITUTE



METHODS OF RESPONSIBLY MANAGING END-OF-LIFE FOAMS AND PLASTICS CONTAINING FLAME RETARDANTS

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Executive Summary

A workshop was held on April 12 – 13, 2016 in Berkeley, CA to identify knowledge gaps and research and innovation opportunities that could advance more responsible end-of-life management of waste consumer products that contain foam or plastic mixed with toxic or potentially toxic flame retardant chemicals.

Workshop objectives included:

- Characterizing the relative exposure to flame retardants and breakdown products;
- Establishing known health and environmental impacts and risks;
- Understanding the best available technologies;
- Identifying priority research and policy needs.

This review summarizes workshop discussions and provides background information on waste management practices and technologies, including conventional and emerging methods and technologies.

Background and Problem Formulation

Flame retardants are added to foams and plastics to comply with flammability standards for consumer products, building materials, and other products. For example, between 1975 and 2014, halogenated flame retardants were used widely in U.S. residential upholstered furniture and other foam-filled products because of a California flammability regulation called Technical Bulletin 117 (TB 117). While this requirement was specific to California, products containing TB 117-compliant fillings were sold throughout the U.S. and Canada. When TB 117 was implemented, the potential health and ecological impacts of flame retardant use were not fully recognized.

Research has shown that the adverse environmental and health impacts of flame retardants used to meet flammability regulations can outweigh potential fire safety benefits (Shaw et al. 2010). Many halogenated and other additive flame retardants are semi-volatile, and migrate out of products into humans and the environment through air/dust, soil/sediment, sewage sludge and leachate. They are released into the atmosphere during manufacturing, product use, degradation, and disposal of product. Flame retardants have an affinity for soils and sediments. Many halogenated flame retardants are persistent and bioaccumulative, and can be transported over long distances in the environment (Danon-Schaffer and Grace 2007). They are found in water surrounding landfills and sewage treatment facilities, and they also end up in sediments through atmospheric deposition (de Boer et al. 2003). Section 1.2 describes the health risks associated with certain types of flame retardants.

Depending on the product and its intended use, flame retardants may constitute as much as 5-30% of flame retarded plastics and foam by weight (Birnbaum and Staskal 2004; D'Silva, Fernandes, and Rose 2004). Section 1.3 provides an overview of consumer products that make up a significant fraction of waste material containing flame retardants.

Criteria for Evaluating Methods

This chapter describes five major criteria that were considered during the April 2016 workshop as a way to evaluate strengths, weaknesses, and research needs specific to different strategies for management of waste foams and plastics containing flame retardants: 1) environmental and health impacts; 2) technological feasibility; 3) economic feasibility; 4) policy/ regulatory considerations; and 5) societal acceptability. Criteria for regulatory guidance on waste management are discussed in much greater detail in, for instance, the United Nations Environment Programme (UNEP) guidance document (Stockholm Convention 2015c), and the International HCH and Pesticides Association (IHPA) report on the destruction of obsolete pesticides (IHPA et al. 2008).

End of Life Collection and Pretreatments

In Chapter 3, we discuss logistical considerations for collection and treatment of waste. Funding is a critical component for programs where certain types of waste (e.g., tires and mattresses) are collected and handled separately from the municipal solid waste stream. Extended producer responsibility programs or other funding mechanisms can enable the implementation of special waste collection and disposal for hazardous wastes. However, these programs usually have a narrow scope.

Given the variable and mixed composition of the waste stream, technologies for the identification and separation of products that contain flame retardants should be improved. In general, existing screening technologies are insufficient to make it economically feasible to separate materials that may or may not contain flame retardants.

Municipal Disposal: Landfilling

Currently most waste containing flame retardants in the US (as in many other countries) is disposed in landfills. While an alternative to landfilling may be beneficial for resource recovery, landfills are currently the most readily available method of disposal. Chapter 4 highlights the process of managing waste at landfill, and the risks associated with (a) the exposures to landfill workers and surrounding communities, (b) the migration of flame retardants into the environment via volatilization into landfill gas and via leachate, and (c) the potential for flame retardants to migrate into the food web from landfills. One immediate concern for flame retardant migration from landfills comes from using materials containing flame retardants, such as automobile shredder residue, as alternative daily cover.

Mechanical Recycling of Flexible Polyurethane Foam

Mechanical recycling of flexible polyurethane foam (FPF) is done by grinding scrap FPF into a fine powder. This process is primarily done using post-industrial (i.e. pre-consumer) foam, but also using post-consumer foam. This process does not currently include a step to remove or destroy added flame retardant chemicals in the foam. One significant challenge for recyclers/re-bond producers is accurately measuring concentrations and types of flame retardants in post-industrial or post-consumer foam when it is recovered for reuse. Recovered foam may come from a variety of different manufacturers and countries and content is not generally disclosed. In Chapter 5, several underlying issues have been identified that could improve management of potentially flame retardant contaminated foam waste at end-of-life.

Mechanical Recycling of Waste Electrical and Electronics Equipment (WEEE) and End of Life Vehicles (ELV)

Electronics and vehicle components, such as interior components, seats, consoles, wires and circuit boards, often contain flame retardants to meet safety standards. Recycling of these materials includes a multi-step pre-sorting and pretreatment process. Many pretreatment and processing techniques have been developed, but a significant portion of the plastic ends up not being recycled. Currently, brominated flame retardants and polyvinyl chloride (PVC) plastics are incinerated for energy recovery, but at a high cost compared to recycling. In Chapter 6, the current technologies are discussed, including shredding, automated and manual sorting, and recycling processes for WEEE and ELV.

Chemical Recycling Technologies

Chapter 7 reviews chemical recycling processes, including the de-polymerization processes for polyurethane and polystyrene foams for recycling into new products. These processes could also include a step for removal or extraction of flame retardants from the recycled content, allowing for the synthesis of a “clean” foam or plastic polymer. Several methods and technologies and associated risks are discussed, including alcoholysis, hydrolysis, hydroglycolysis, aminolysis, and extraction methods.

Destruction and energy recovery technologies

Technologies that use high temperatures to destroy toxic flame retardants by breaking chemical bonds include incineration and other oxidative processes, pyrolysis, gasification, plasma treatment, metal processing, and super critical water oxidation (SCWO). These technologies are sometimes known as incineration, thermal treatment, and waste-to-energy. Some of these methods are established in commercial applications, while others need additional research and development. Incineration continues to be an active basic research area in chemistry and fluid mechanics. There are significant issues that must be taken into consideration because of the halogen content of FR-treated wastes and the potential to create undesired byproducts such as halogenated dioxins and furans in thermal processes. Chapter 8 highlights a handful of technologies and related considerations including byproduct formation, products of incomplete combustion, greenhouse gas emissions, waste transportation, siting and environmental justice, process monitoring, and ash treatment.

Summary and Recommendations

Until responsible methods are developed for managing waste products containing flame-retarded foams and plastics, these products will continue to pose hazards to humans and ecosystems after reaching the end of their useful life. Chemicals of concern that are no longer used in manufacturing in the U.S. (e.g., polybrominated diphenyl ethers (PBDEs)) will remain an issue for human and ecological health as these “legacy” products enter the waste stream. Long-term solutions will require the destruction of the hazardous chemicals and their byproducts. Whenever possible, new products should be manufactured without hazardous flame retardant additives.

As outlined in this review, scientific, engineering, regulatory, and political challenges must be addressed to improve current waste management practices. Research should be prioritized both at the laboratory scale and larger pilot-scale to identify best practices to minimize harm to human health and the environment. This report has identified a variety of opportunities where basic science and engineering research can contribute to improved waste management for these products. These problems must be addressed soon to limit continued harm from hazardous flame retardants.

In Chapter 9, gaps in knowledge and prioritized areas of research are presented. The following are overarching areas that need further research or consideration to responsibly dispose of waste foams and plastics containing toxic flame retardants.

A need for improved policies and regulations

Below is a list of opportunities for policy changes that could support improved management of flame retarded wastes:

- Funding mechanisms that could enable separate handling and treatment of wastes containing flame retardants should be explored. Funding could initially support smaller pilot-scale programs and research and potentially be scaled-up for broader adoption. Current funding mechanisms in states and other countries should be considered.
- If new facilities are to be constructed, siting for new waste facilities must be improved. New facilities should not be located in already-disadvantaged or marginalized communities.
- Improved monitoring and disclosure must be implemented for facilities that process or treat waste products. This is an important way to both improve operation of new and existing facilities and create more trust between communities and waste management facilities. Increased transparency could also improve acceptance of existing and new technologies.
- Encourage development of manufacturer sponsored product stewardship policies and programs for FR materials.
- Hazardous additives should be limited in new products. These additives are often used in applications where they may not be needed, and represent health hazards throughout every stage of the product lifecycle (not just during the waste management stage). In some cases, product re-design,

or substitution with better alternatives based on green chemistry, can eliminate unnecessary uses of harmful chemicals. In other cases, regulations and standards may need to be improved.

- Labeling or other waste designation methods could improve separation and recycling, allowing for better diversion of hazardous materials from the waste stream. This would also provide important information to consumers.
- Designation of products that contain flame retardants as a separate waste category. This would require such waste to be handled separately from standard municipal solid waste and to be diverted from landfills.
- Increasing public awareness of product contents and how waste is processed may support improved siting and other policies.

Recommended areas of research

Responsibly disposing of household products mixed with flame retardants presents numerous challenges, and will require engagement and interaction between diverse sectors.

We identified major areas where research is needed that are non-specific to a particular technology. These, along with specific research needs identified in Chapters 3 – 8, are listed below. Each chapter includes a more exhaustive list.

1. Practical and cost-effective methods to identify, categorize, and quantify flame retardants in products.
2. Assessment of occupational exposures at all stages of handling or processing products mixed with toxic flame retardants.
3. Evaluation of exposures and hazards to human health and the environment near existing waste processing, treatment, and storage facilities.
4. Pilot scale research, to be conducted concurrently with bench-scale and basic science research, to accelerate scale-up of improved technologies and to help identify best practices.
5. Assessment of how technologies can be combined for the most effective management of high volume mixed waste with low concentrations of toxic flame retardants.

The following are suggested fundamental or priority research topics excerpted from each chapter:

Collection and Pretreatment

- Efficient ways to identify and quantify FR substances in wastes to determine the best pretreatment needs.
- Monitor the air and dust at dismantling and shredding facilities, and at transfer stations for release of toxic flame retardants.

Municipal Disposal: Landfill

- Evaluate the potential for halogenated flame retardants to volatilize with landfill gas and the extent to which they are attenuated by gas combustion. Determine if toxic byproducts, such as dioxins, form during combustion, landfill fires, and evaporation of landfill leachate using landfill flares.
- Evaluate the presence of flame retardants in MSW leachate. Some parameters that may affect leaching are the age of leachate and use of leachate recirculation. Transformation products, such as debrominated or hydroxylated flame retardants, should also be evaluated as part of this effort.

Mechanical Recycling: Flexible Polyurethane Foam

- A need for practical and cost-effective ways to identify and quantify flame retardant substances in potentially contaminated foam waste and bonded cushion products.
- Research is needed to develop a better understanding of existing PentaBDE substitute concentrations in the potential waste stream of existing carpet cushion.

Mechanical Recycling: Waste Electronics and Electrical Equipment

- More research into developing a universal method for identifying commonly used flame retardants in mixed plastics waste.
- Research is needed to develop a better understanding of existing halogenated DecaBDE substitute concentrations in the waste stream of existing products.

Chemical Recycling

- Assessment and possible development of large-scale chemical recycling projects for polyurethane, expanded polystyrene, and WEEE plastics. Similar programs to the European CloseWEEE program might prove successful in the U.S.
- There is a need for pilot scale studies on the separation of halogenated flame retardants from products using alcoholysis, glycolysis, and aminolysis methods.

Destruction and Energy Recovery Technologies

- Formation, relevance and control of mixed halogenated dioxins and polycyclic aromatic hydrocarbons. There is virtually no data on mixed halogen emissions from lab studies - almost all lab studies use chlorinated or brominated compounds alone, but real-world waste is a mixture. More complex waste streams need to be investigated in addition to model compound studies.
- Faster and more comprehensive diagnostic methods for toxic species are needed, with better real-time methods and continuous monitoring. This would allow detection/reporting of upset conditions as they occur, rather than weeks later.

Acknowledgements

This material is based upon work supported by the National Science Foundation (www.nsf.gov) under NSF award number 1500091. Research reported in this report was supported by *National Institute of Environmental Health Sciences* of the National Institutes of Health under award number R13ES025490.

Table of Contents

1	Background and Problem Formulation	9
1.1	Types of flame retardants	10
1.2	Health and Environmental Impacts	13
1.3	Major waste flows containing flame retardants	14
2	Criteria for Evaluating Methods	17
3	End of Life Collection and Pretreatments	19
3.1	Collection methods	19
3.2	Funding mechanisms	20
3.3	Pretreatments	21
3.4	Pretreatment Technologies and Methods	21
3.5	Separation Technologies	21
3.6	Examples and Case Studies	23
3.7	Recommendations	24
4	Municipal Disposal: Landfilling	26
4.1	Landfilling Methods and Process	26
4.2	Review of Potential Health and Environmental Impacts	28
4.3	Examples and Case Studies	31
4.4	Discussion	34
4.5	Analysis of Short-Term Management Options	34
5	Mechanical Recycling of Flexible Polyurethane Foam	37
5.1	Recycling Methods and Process	37
5.2	Review of Potential Health and Environmental Impacts	40
5.3	Examples and Case Studies	40
5.4	Discussion	41
5.5	Recommendations	41
6	Mechanical Recycling of Waste Electrical and Electronics Equipment (WEEE) and End of Life Vehicles (ELV)	42
6.1	Technologies and methods	42
6.2	Review of Potential Health and Environmental Impacts	43
6.3	Case studies	43
6.4	Discussion	44

6.5	Recommendations	44
7	Chemical Recycling Technologies.....	46
7.1	Technologies and Methods.....	46
7.2	Review of Potential Health and Environmental Impacts	49
7.3	Examples and Case Studies.....	50
7.4	Discussion	52
7.5	Recommendations	53
8	Destruction and energy recovery technologies	54
8.1	Technologies and Methods.....	54
8.2	Review of Potential Health and Environmental Impacts	59
8.3	Examples and Case Studies.....	62
8.4	Discussion	66
8.5	Recommendations	70
9	Summary and Recommendations.....	72
9.1	A need for improved policies and regulations	72
9.2	Recommended areas of research	73
10	References	75
11	Appendix	89
11.1	Alternative plasma methods	89
11.2	Other Alternatives	90

Abbreviations and Acronyms

ABS	Acrylonitrile Butadiene Styrene
ADC	Alternative Daily Cover
ASR	Auto Shredder Residue
BAT	Best Available Technologies
BEP	Best Environmental Practices
BFR	Brominated Flame Retardant
C&D	Construction and Demolition
CFR	Chlorinated Flame Retardant
DRE	Destruction and Removal Efficiency
EEE	Electrical and Electronic Equipment
EEPS	European Expanded Polystyrene
ELV	End-of-Life Vehicle
EPR	Extended Producer Responsibility
EPS	Expanded Polystyrene
ESR	Electronics Shredder Residue
FPF	Flexible Polyurethane Foam
FR	Flame Retardant
GM	Geomembrane
HFR	Halogenated Flame Retardant
HIPS	High-Impact Polystyrene
MC	Mechanochemical
MDI	Methylene Diphenyl Diisocyanate
MRC	Mattress Recycling Council
MSW	Municipal Solid Waste
NHANES	National Health And Nutrition Examination Survey
NIR	Near Infra-Red
NPDES	National Pollution Discharge Elimination System
OSHA	Occupational Safety and Health Administration
PBDE	Polybrominated Diphenyl Ethers
PC	Polycarbonate
PCB	Polychlorinated Biphenyls
PE	Polyethylene
POP	Persistent Organic Pollutant
PP	Polypropylene
PPE	poly(p-phenylene ether)
PS	Polystyrene
PUR	Polyurethane
PVC	Polyvinyl Chloride
RCRA	Resource Conservation and Recovery Act
RoHS	Restriction of Hazardous Substances
SCWO	Supercritical Water Oxidation
TB117	Technical Bulletin 117
TDI	Toluene Diisocyanate
TEQ	Total Equivalency
U.S. EPA	United States Environment Protection Agency
UNEP	United Nations Environmental Programme
WEEE	Electrical and electronic equipment and related waste
WTE	Waste-to-energy
XPS	Extrude Polystyrene
XRF	X-Ray Fluorescence
XRT	X-Ray Transmission

1 Background and Problem Formulation

Flame retardants are added to flexible polyurethane foam and plastics to comply with flammability standards and test requirements in products for household and industrial uses. The type of flame retardant used depends on compatibility with the product or material, costs, and the flammability standard being met. For instance, between 1975 and 2014, halogenated flame retardants (HFRs) were applied widely in U.S. residential upholstered furniture and other foam-filled products because of a California flammability regulation called Technical Bulletin 117 (or TB 117). Flame retardant chemicals were added to certain filling materials, like polyurethane foam, to meet the test requirements of TB 117. While this requirement was specific to California, products containing TB 117-compliant fillings were sold throughout the U.S. and Canada. When these regulations were implemented, the potential health and environmental impacts of flame retardant use were not recognized or fully understood.

Research has shown that the adverse environmental and health impacts of flame retardants used to meet flammability regulations can outweigh potential fire safety benefits. Exposure to halogenated flame retardants, such as those used widely in furniture foam, has been associated with and/or causally related to numerous health effects in animals and humans, including endocrine disruption, immunotoxicity, reproductive toxicity, effects on fetal/child development, and cancer (Shaw and Kannan 2009; Bellanger et al. 2015; Lyche et al. 2016; Herbstman et al. 2010; Eskenazi et al. 2013). Due in part to the mounting evidence of health harm from flame retardants, TB 117 was updated in 2013 to maintain fire safety and enable reduced use of flame retardants. Across North America, residential furniture is increasingly available without flame retardants. In Chapter 1.2, we describe the specific health risks associated with certain flame retardants.

It is estimated that an item of upholstered furniture may have several owners, with an average ownership time of 10 to 15 years per user.¹ The resale or reuse of furniture that contains flame retardants will result in continued household exposures, especially in low-income and student communities. At the end of useful life, most furniture in the U.S. is deposited in landfills, where flame retardants can leach into soil, water, and the environment (Abbasi et al. 2015; R. Liu et al. 2016). Other potential routes of disposal, such as recycling, can also prolong exposures to flame retardants since there is no viable technology for the removal of these chemicals during processing (DiGangi 2012). Therefore, furniture and other products containing flame retardants will continue to pose health and environmental risks after they are discarded.

The Circular Economy is a concept that aims to reduce waste and avoid pollution by design. It differs from the linear process (Take, Make, Dispose) that depletes finite resources and produces products or waste that end up in landfills or in incinerators (see the report by Ellen MacArthur Foundation 2013). Recycling and recovery of products that contain hazardous substances, such as certain flame retardants and other persistent organic pollutants, can contaminate the entire cycle (Wright 2015). While eliminating the hazardous substances allows for better and more complete reuse and recycling, products that contain these hazardous materials need to be removed from the circular economy, since long-term, low-level exposure of humans to these chemicals continue to cause problems – for example, a recent study determined that the annual cost to society from impacts of PBDE flame retardants in the US is 266 billion dollars (Attina et al. 2016).

In order to minimize continued human and environmental exposures to hazardous flame retardant chemicals from discarded products, waste management technologies and processes must be improved. Research is needed in the areas of responsible collection, pretreatment, processing, and management of wastes containing toxic flame retardants. A workshop was hosted during April 12 – 13, 2016 in Berkeley, CA to identify knowledge gaps and research and innovation opportunities for more responsible end-of-life management of waste consumer products that contain foam or plastic mixed with flame retardant chemicals.

Workshop objectives included:

¹ See Appendix 1 for a case study of a second-hand household goods service in the Portland, Oregon area. “Community Warehouse, 2014 Annual Report” Community Warehouse <https://www.communitywarehouse.org>

- Characterizing the relative exposure to flame retardants and breakdown products;
- Establishing known health and environmental impacts and risks;
- Understanding the best available technologies (BAT);
- Identifying priority research and policy needs.

This report summarizes workshop discussions and provides background information on waste management practices and technologies, including conventional and alternative approaches. The focus is on U.S. practices, but there are references to practices and policies primarily used outside of the U.S. that may provide insight.

This report considers the following end-of-life materials containing flame retardant chemicals:

- Polyurethane (PUR) foam in furniture;
- Plastic from electronics and electrical equipment (EEE);
- Polymers from end of life vehicles;
- Polymer insulation from construction.

For the purposes of this report, we have identified four methods of disposal which reflect the discussions during the April 12-13, 2016 Symposium in Berkeley, CA. These methods are:

- Municipal Disposal: Landfilling (Chapter 4);
- Mechanical recycling (Chapter 5-6);
- Chemical recycling (Chapter 7);
- Destruction technologies (Chapter 8).

We attempt to identify the multi-disciplinary issues, as well as some priorities for fundamental scientific research for each.

1.1 Types of flame retardants

Flame retardants are used in electronics and electrical devices, building and construction materials, furnishings, transportation, and other sectors in order to meet regulatory or performance requirements. This report focuses on those most widely used: PUR foam, EEE, polymers from vehicles, and building insulation. Table 1-1 summarizes typical products in which four different halogenated flame retardants have been widely used.

Additive flame retardants are mixed into the polymer formulation and are not chemically bound to the polymer. Consequently, these flame retardants escape more easily from the materials to which they are added, and end up in air and dust. Some of the most prominent additive halogenated flame retardants include commercial grades of pentabromodiphenyl ether (c-PentaBDE, or “Penta”), octabromodiphenyl ether (c-Octa-BDE), decabromodiphenyl ether (c-DecaBDE), and hexabromocyclododecane (c-HBCD). Commercial formulations (e.g., c-PentaBDE, c-Octa, etc.) are a mixture of PBDE congeners. For example, c-PentaBDE is primarily a mixture of PBDE congeners (U.S. Department of Health and Human Services 2004). In one recent study, the total North American consumption of c-Penta-, c-Octa-, and c-DecaBDE from 1970 to 2020 in products has been estimated at approximately 46,000 tonnes, 25,000 tonnes, and 380,000 tonnes, respectively (Abbasi et al. 2015).

Reactive FRs are chemically bonded to the base material. Reactive FRs and brominated polymers are not expected to escape as readily into air and dust, because they are chemically bonded to the polymer. One example is tetrabromobisphenol A (TBBPA), used as a reactive FR in printed circuit boards of electronics to prevent internal fires. TBBPA is the highest-volume flame retardant in use (Shaw et al. 2010). Despite a lower release rate of TBBPA from its reactive uses, the large volume used results in measurable environmental levels (Kajiwara, Noma, and Takigami 2011). Reactive or chemically-bound brominated FRs can degrade to other toxic species (Koch et al. 2016).

Table 1-1 Types of flame retardants

Flame Retardant	Products	Quantities	Reference
Pentabromodiphenyl ether (Penta-BDE, PBDE, or Penta)	Polyurethane foam (PUF): mattresses, seat cushions, furniture, and packaging. Also: carpet padding, imitation wood, paints, sound insulation panels, small electronic parts, fabric coatings, epoxy resins, conveyor belts	46,000 tonnes (US/ Canada 1970-2020) 119,000 tonnes (Global 2001)	Abbasi et al. (2015) Shaw et al. (2010) Birnbaum & Staskal (2004)
Octabromodiphenyl ether (Octa-BDE, OBDE, or Octa)	Acrylonitrile-butadiene-styrene (ABS) plastic: housings for fax machines, computers and other electronics. Also: automobile trim, telephone handsets, kitchen appliance casings, small electronics parts, audio/video equipment, remote control products	25,000 tonnes (US/ Canada 1970-2020) 3,790 tonnes (Global 2001)	Abbasi et al. (2015) Shaw et al. (2010) Birnbaum & Staskal (2004)
Decabromodiphenyl ether (Deca-BDE, or Deca)	High impact polystyrene (HIPS): electronics, wire and cable, public buildings, construction materials, automotive, aviation, storage and distribution products, textiles, waterborne emulsions & coatings	380,000 tonnes (US/ Canada 1970-2020) 56,150 tonnes (Global 2001)	Abbasi et al. (2015) Shaw et al. (2010) Birnbaum & Staskal (2004)
Chlorinated Tris (TDCPP, or Tris)	Polyurethane foams: baby mattresses, furniture cushions. Also: plastics, resins, textiles, and polyisocyanurate foams	43.3 mg/g [see sofa foam study by Stapleton et al. (2012)]	Stapleton et al. (2012) Shaw et al. (2010) Janssen (2005)
Tetrabromobisphenol A (TBBPA)	Reactive and additive flame retardant: epoxy and polycarbonate resins, ABS. Also: printed circuit boards in electronics (96%), office equipment housings, housings of computers, monitors, TV, office equipment, adhesive coatings in paper and textiles Additive flame retardant: various plastics, paper and textiles.	1-10 g/kg [see household electronics study by Wager et al. (2012)] 119,600 tonnes (Global 2001)	Wager et al. (2012) Shaw et al. (2010) Birnbaum & Staskal (2004)
Hexabromocyclododecane (HBCD)	Various plastics: Polystyrene (EPS, XPS, HIPS), polypropylene. Also: textiles and carpet backing, television and computer housings, textiles in automobiles, building materials (insulation panels, construction blocks, thermal insulation, roofs), upholstered foam, latex binders	31,000 tonnes (Global production in 2011)	Stockholm Convention (2015) Janssen (2005)

In the U.S., manufacturers voluntarily phased-out the production of c-PentaBDE and c-OctaBDE by 2004, and c-decaBDE was phased-out after 2013. In 2004, brominated FRs stopped being used in flexible polyurethane foam (FPF); c-PentaBDE was largely replaced by TDCPP and the Firemaster 550 (a mixture which is mainly 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB) and bis(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH), and other compounds were replaced with chlorinated and non-halogenated organophosphates, which may pose similar health hazards (Stapleton et al. 2012; Cooper et al. 2016). The substitution of one harmful chemical with another (Fantke, Weber, and Scheringer 2015) further complicates disposal methods, since those who handle the products must assume it contains a mixed FR content.

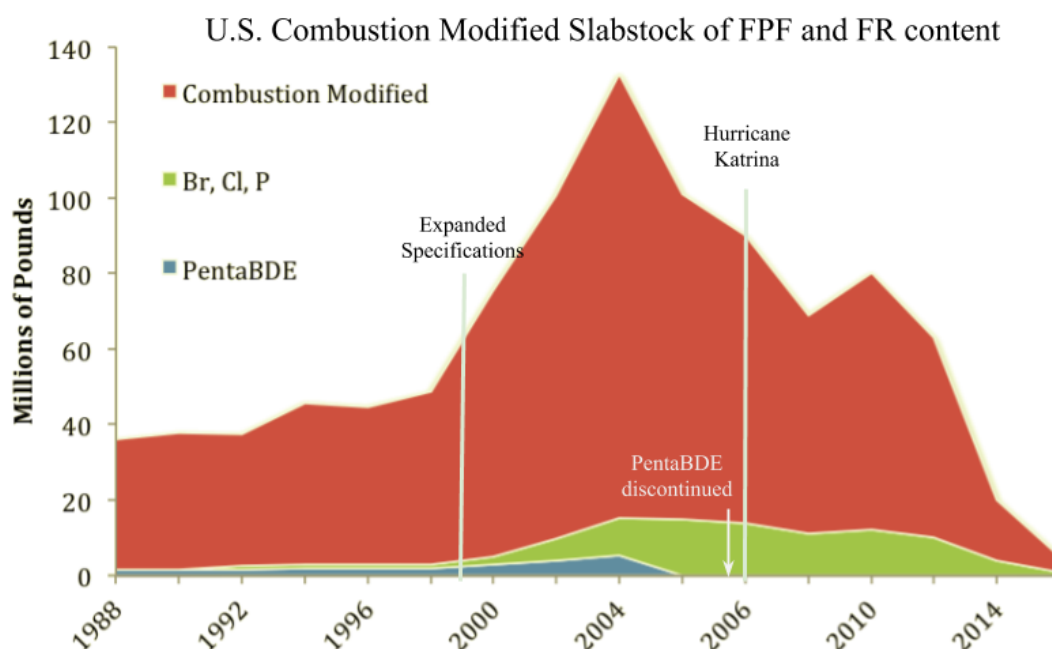


Figure 1-1 The amount of slabstock flexible polyurethane foam (FPF) containing flame retardants from 1988 to 2016 (red) is shown along with the content of PentaBDE (blue), and replacement flame retardants (green). Source: Polyurethane Foam Association.

Regrettable substitution of flame retardants in FPF

Figure 1-1 shows the amount of flexible polyurethane foam manufactured with flame retardants in the United States. Shortly after the phase-out in 2004 of PentaBDE, the use of other Br-, Cl- and P-based flame retardants increased. Before being phased out, PentaBDEs averaged about 4% of the weight of FPF. When they were replaced, the substitute flame retardant comprised about three times the amount. The figure also shows how specifications can influence the amount of flame retardant added to FPF. In 1999, broader use of TB 117-compliant foam led to the use of more flame retardants. After Hurricane Katrina, furniture was manufactured without foam on the backs, leading to a decline in the amount of FPF manufactured. However, due to a number of years of expanded use of FR foam in the U.S., the amount of FRs did not show a related decline.

Next generation flame retardants in the Great Lakes Region

Without disclosure from the manufacturers of flame retardants, the quantities and types of flame retardants being used as replacements are largely unknown. A comprehensive effort is being made to understand the trends of legacy and next generation flame retardant transport behavior in the Great Lakes Region. The analysis includes measurements of concentrations in air and water at several sites (R. Liu et al. 2016; Venier et al. 2014). Concentrations of organophosphate esters have been detected, including tris(2-chloroethyl) phosphate (TCEP), triphenyl phosphate (TPhP), tris(butoxyethyl)-phosphate (TBEP), tris(1-chloro-2-propyl) phosphate (TCPP), tri-n-butyl phosphate (TnBP) (Venier et al. 2014). Organophosphate esters measured in urban air (Toronto, Canada) had a median concentration of 2650 pg/m³ which was mostly TCPP, TCEP and TPhP (Abdollahi et al. 2017). Over time the concentration of PBDEs has declined, while concentrations of these next generation flame retardants have just started to be monitored. The highest levels were of TBEP at 75 ± 39 ng/L in Lake Erie (Venier et al. 2014). Truong (2016) measured concentrations of organophosphate ester FRs in streams located in Toronto, Canada, that discharge into Lake Ontario. The highest concentrations measured were for TCPP (average 1600, range 100-5000 ng/L), TBEP (average 1070, range 40-5200 ng/L) and TCEP (average 260, range 40-700 ng/L). These concentrations are likely within the range capable of causing adverse effects to aquatic biota.

1.2 Health and Environmental Impacts

As previously mentioned, many halogenated and other additive flame retardants are semi-volatile, and migrate out of products into humans and the environment through air/dust, soil/sediment, sewage sludge and leachate. They are released over time mainly into the air during manufacturing, product use, and disposal of products (Rauert and Harrad 2015). As semi-volatile organic compounds, most flame retardants tend to accumulate in solid phases such as indoor dust, outdoor soils and lake sediments. Many halogenated flame retardants are persistent and bioaccumulative, and can be transported over long distances in the environment (X. Zhang et al. 2016). They are found in water surrounding landfills and sewage treatment facilities, and they also end up in sediments through atmospheric deposition (de Boer et al. 2003).

Indoor air is the primary method of PBDE exposure for humans, and electronics are likely the main source (X. Zhang et al. 2011; Abbasi et al. 2015). PBDEs have been linked to neurotoxicity, thyroid hormone dysregulation, endocrine disruption, and poor semen quality (Buttke et al. 2013). Because PBDEs pass the placental barrier, maternal exposures can result in fetal exposures. Toxicological data show that PBDEs pose serious health risks such as thyrogenic, estrogenic, and dioxin-like behaviors, affecting the nervous, endocrine and immune systems (Cowell et al. 2015; Herbstman et al. 2010; Birnbaum and Staskal 2004; Legler 2008; Darnerud et al. 2001). They can mimic the biological action of thyroid hormones because of structural similarities. PBDEs are neurotoxins and endocrine disruptors, causing thyroid and neurodevelopmental dysfunctions (Darnerud et al. 2001; Jacobson et al. 2016). PBDE concentrations in children were associated with attention problems and decrements in processing speed, perceptual reasoning, verbal comprehension, and full-scale IQ. These associations were not altered by adjustment for birth weight, gestational age, or maternal thyroid hormone (Erkin-Cakmak et al. 2015). Latino children living in California have much higher PBDE serum levels than their Mexican counterparts (Eskenazi et al. 2011). Given the growing evidence documenting potential health effects of PBDE exposure, this presents a major public health challenge (Eskenazi et al. 2013).

The potential cognitive risks in children have been documented in several studies. Children with prenatal exposures to high levels of pentaBDEs were more likely to show motor, cognitive and behavioral difficulties (Shaw et al. 2010). Even low levels of BFRs appear to affect motor skills, and are associated with lower thyroid levels in adolescent children (Kiciński et al. 2012; Jacobson et al. 2016). In a recent study, increased levels of PBDEs in prenatal serum was associated with cognitive effects in children, including reduced reading comprehension, and externalizing behavior problems (H. Zhang et al. 2016).

Similar concerns are listed for TBBPA, which is structurally related to bisphenol A (BPA), a known endocrine disruptor. TBBPA is associated with thyroid hormone activity, and produces effects on neurotransmitter uptake at similar concentrations as for polychlorinated biphenyls (PCBs) (Legler 2008).

HBCD is present in dust, having migrated from building insulation to indoor dust. Children and adults are exposed to HBCD through dust (Harrad et al. 2010). HBCD crosses the placenta and has been found globally in human breast milk (Marvin et al. 2011), placing a higher risk on developing children. In one study, higher HBCD concentrations in prenatal serum were associated with negative effects on cognitive levels in children (Kiciński et al. 2012).

HBCD and certain PBDEs have been listed under Annex A of the Stockholm Convention, meaning that the 181 countries that are parties to the Convention have banned them, and manage and control products containing them.² Limited exemptions were granted for the use of HBCD in insulation in construction and recycling of c-OctaBDE containing plastic. Chemicals used as replacements for banned or phased-out flame retardants may pose similar risks. Replacements for PBDEs, sometimes called novel brominated flame retardants (NBFRs) have been detected in household dust, the environment, and breast milk (Covaci et al. 2011; Brown et al. 2014). This is of concern, since little is known about the toxicology or potential impacts of these replacements, yet they are being detected at higher amounts in indoor dust (Brown et al. 2014). The majority of environmental and health studies concerning flame retardants have focused on brominated and chlorinated flame retardants, so a limited amount of information exists on other types of flame retardants.

² The Stockholm Convention list of POPs: <http://chm.pops.int/TheConvention/ThePOPs/ListingofPOPs>

1.3 Major waste flows containing flame retardants

Depending on the product and its intended use, flame retardants may constitute 5-30% of flame retarded plastics and foam by weight (Birnbaum and Staskal 2004; D'Silva, Fernandes, and Rose 2004). It is difficult to estimate the flow of flame retarded foams and plastics entering the waste stream over time, since there is limited data on exact use levels and product content. Abbasi et al. (2015) estimated the flow of the major products containing PBDEs from the use to waste phase in North America. They estimated an annual flow of ~10,000 tonnes of PBDEs in the major product categories, excluding vehicles, between 2005 and 2008. Further, based on the single use of products (i.e., no re-use), they estimated that PBDE-containing products entering the waste stream would decrease at 4-12% annually after 2013.

Table 1-2 provides a summary of products that commonly contain flame retardants (Abbasi et al. 2015; Janssen 2005; Birnbaum and Staskal 2004). The following is an overview of consumer products that make up a significant fraction of waste material containing flame retardants.

Table 1-2 Primary uses for flame retardants (Abbasi et al. 2015; Birnbaum and Staskal 2004).

Electronics and Electrical Devices	Building and Construction Materials
<ul style="list-style-type: none"> • Television and other electronic device casings • Computers and laptops, including monitors, keyboards and portable digital devices • Telephones and cell phones • Refrigerators • Washers and dryers • Vacuum cleaners • Electronic circuit boards • Electrical and optical wires and cables • Small household appliances • Battery chargers 	<ul style="list-style-type: none"> • Electrical wires and cables, including those behind walls • Insulation materials (e.g., polystyrene and polyurethane insulation foams) • Paints and coatings which are applied to a variety of building materials, including steel structures, metal sheets, wood, plaster and concrete • Structural and decorative wood products • Roofing components • Composite panels • Decorative fixtures
Furnishings	Transportation (Airplanes, Trains, Automobiles, Marine Vessels)
<ul style="list-style-type: none"> • Natural and synthetic filling materials and textile fibers • Foam upholstery • Other upholstery (e.g., cotton and fiber) • Curtains and fabric blinds • Carpets 	<ul style="list-style-type: none"> • Overhead compartments • Seat covers and fillings • Seats, headrests and armrests • Roof liners • Textile carpets • Mattresses for bunks and berths • Curtains • Sidewall and ceiling panels • Internal structures, including dashboards and instrument panels • Insulation panels • Electrical and electronic cable coverings • Electrical and electronic equipment • Battery cases and trays • Car bumpers • Stereo components • GPS and other computer systems

1.3.1 Flexible polyurethane foam in furniture and mattresses

For decades, a large share of polyurethane foam in furniture in the US was treated with Penta-BDE. The primary furniture use was in seating and sofas. According Polyurethane Foam Association, more than 1.2 billion pounds of foam are produced and used every year in the U.S. The amount of foam production for furniture applications in 2015 is estimated at 226 million pounds (Luedeka 2016). The amount of furniture and furnishings in municipal solid waste (MSW) has increased from 2.2 million tons in 1960 to 11.6 million tons in 2013, which constitutes 4.6% of total MSW (USEPA 2015). Most post-consumer furniture is not recycled, with the exception of mattresses in certain parts of the U.S. However, pre-consumer scrap FPUF is recycled into rebond (open cell polyurethane foam, manufactured by compressing scrap & shredded foam).

1.3.2 Electrical and electronic equipment (EEE) and related waste (WEEE):

Flame retardants are added to EEE casings, cables and printed circuit boards. Household EEE products, such as TVs and monitors, laptops, and desktop computers that contain PBDEs have lifespans that range from ~5-10 years. In a screening of more than 1000 products (Abbasi et al. 2015), 26% of laptops and desktop computers were treated with PBDEs. The percentage of flat-screen TVs and monitors treated with PBDEs was much higher at 54% and 40%, respectively. Between 1970 and 2020 the total mass of PBDEs used in electronics casings of Penta-, Octa-, and DecaBDE is estimated at 0.5-1.5, 1-10, and 25-225 kt, respectively (Abbasi et al. 2015). In one study, TBBPA was detected in most household electronics at levels of 1,000-10,000 ppm (Wäger et al. 2012). Kajiwar et al. (2011) analyzed several electronic products for a range of flame retardants. The highest concentrations were found in the power board of LCD TVs (for example, one LCD TV had 0.7% TPHP and 0.5% of TCP in addition to lower concentrations of brominated flame retardants).

1.3.3 Vehicles

BFRs and CFRs have been and continue to be added to polymers and textiles used for the transport sector (cars, busses, trucks, airplanes, ships). In particular, it is estimated that the U.S used 40% of PentaBDE for PUR slabstock foams in seats, head rest, ceiling and acoustic systems (Alcock et al. 2003; Stockholm Convention 2015c; Stockholm Convention 2015b). In a recent study on BFR contamination of cars in Japan, it was found that other parts such as textile seat covering, and floor mats also contain BFRs (Kajiwar et al. 2015). Flexible polyurethane foam is estimated to represent about 30-40 pounds per passenger vehicle.³ From 1970-2020 the total mass used in automobiles and light weight trucks of Penta-, Octa-, and DecaBDE is estimated to be 2.5-25, 3-35, and 25-225 kt, respectively (Abbasi et al. 2015), but these values may not be accurate due to limitations of using PBDEs in molded foams.

Foams and textiles treated with HBCDs have also been found in vehicles (Stockholm Convention 2015a). The highest level of HBCD exposure in the United Kingdom has been linked to cabin dust in cars (Harrad and Abdallah 2011; Kajiwar et al. 2015; Stockholm Convention 2015a). The highest concentrations were found in floor coverings for two end of life vehicle (ELVs) samples at 3,000 and 13,000 mg kg⁻¹ (Kajiwar et al. 2015).

The majority of plastics and foams found in ELVs end-up in the auto-shredder residue (ASR) after dismantling and shredding. Quantifying the amount of flame retardants in ASR is difficult. There are no standards for classifying ASR, which can be based on particle size, or fraction generated during different shredding stages. Foam and plastics generally comprise 20-49% of ASR (Vermeulen et al. 2011). However, this number is highly dependent on the shredding processes, and nearly 27 types of plastics are found in ASR. Besides flame retardants that have been mixed into the PUR foam, ASR contains high concentrations of chlorine from PVC and heavy metals.

1.3.4 Construction

A considerable share of BFRs is used in polymer building insulation such as expanded polystyrene (EPS), extruded polystyrene (XPS) or rigid polyurethane foam. More energy efficient buildings commonly use EPS and XPS insulation are common and affordable insulation materials. The main additive flame retardant for polystyrene insulation foams is HBCD, accounting for 80-90% of its global use (Babrauskas et al. 2012). HBCD content in EPS ranges from 0.5-0.7%, and for XPS 0.8-2.5%. A common flame retardant for spray and rigid polyurethane foam is TCPP. Babrauskas et al. (2012) reported that TCPP is commonly added at levels of 2-25%. Truong (2016) confirmed this with analyses of several samples of polyurethane foam insulation with concentrations range from 2-26%. Chamber studies have measured the release of TCPP from newly-sprayed and older previously-installed SPF insulation (Poppendieck et al. 2014; Kemmlein, Hahn, and Jann 2003; Salthammer, Fuhrmann, and Uhde 2003). Truong (2016) found strong evidence for the migration of TCPP from polyurethane foam insulation into the interior air and dust of a highly insulated home.

³ Estimate provided by The Woodbridge Group, a global manufacturer of foam and interior parts for vehicles.

1.3.5 Textiles

Textiles accounted for 10% of global use of HBCD, and has largely been phased out with listing of HBCD in the Convention (Stockholm Convention 2015a). HBCD was applied with a polymer dispersion on cotton, cotton blends, or synthetics on a back coating with concentrations ranging from 2.2-4.3%. According to U.S. EPA (U.S. EPA 2014), 20-25% of the total global decaBDE production of approximately 300,000 tonnes was applied to textiles from 1970 to 2013.

1.3.6 Recycled products

In the last 30 years, plastics and foams mixed with halogenated flame retardants have been recycled into new products. These flame retardants are not removed from the original material, and remain in the recycled product at detectable levels. Samsonek and Puype (2013) reported TBBPA and decaBDE from recycled WEEE in thermal cup lids with a measured content as high as 1294 mg kg⁻¹. Ionas et al. (2014) found low levels of PBDEs in 106 toys available in the European market with a maximum concentration of 0.14 mg/g. However, 50% of the toys had organophosphate esters with concentrations of TPhP as high as 1.3%. They concluded that the flame retardants were in the toys as contaminants likely carried over from recycled materials (Ionas et al. 2014; S. J. Chen et al. 2009).

In the U.S., bonded foam carpet cushion represents approximately 90% of all carpet cushion products sold. PentaBDE was used in FPF from 1980-2004. Once pentaBDE was phased out, old foam scrap continued to be recycled into rebonded carpet padding and detected at levels of 0.1% by weight (see [Chapter 5.1](#)). Chapters 5, 6 and 7 include more detail on the current processes for recycling of FR containing products.

2 Criteria for Evaluating Methods

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During the April 2016 workshop, we discussed a number of criteria that should be considered when prioritizing research, technologies, and policy. These criteria are summarized briefly in Table 2-1.

Criteria for regulatory guidance on waste management are discussed in much greater detail in, for instance, the UNEP guidance document (Stockholm Convention 2015c), and the IHPA report on the destruction of obsolete pesticides (IHPA et al. 2008).

Table 2-1 Criteria to consider when managing waste foam and plastic mixed with flame retardants.⁴

Criteria	Description	Examples of Considerations
Environmental & health impacts	Goal: to minimize detrimental human and ecosystem impacts	<p>Toxic byproducts – identify residue streams that may be toxic, including off-gas treatment systems (e.g., incinerators, landfill off-gas collection)</p> <p>Uncontrolled releases - any releases that are potentially uncontrolled are identified along with measures that are taken to ensure that such releases do not occur.</p> <p>Wastes/ Residuals – includes secondary waste stream volumes/masses – e.g., residual ash, slag, or other residue.</p> <p>Worker exposure – considers occupational exposure of workers involved with waste disposal and recycling to harmful products.</p> <p>Environmental impact assessment – discharges will need to be monitored and residues appropriately and safely handled and disposed.</p> <p>Risks – includes risks that are inherent to use of the disposal method as well as operational risks.</p>
Technological feasibility	Scalability of technology, and capacity and ability to treat toxics by reduction, removal or destruction of the flame retardants should be examined.	<p>Toxic byproducts – identify residue streams that may be toxic, including off-gas treatment systems (e.g., incinerators, landfill off-gas collection)</p> <p>Uncontrolled releases - any releases that are potentially uncontrolled are identified along with measures that are taken to ensure that such releases do not occur.</p> <p>Wastes/ Residuals – includes secondary waste stream volumes/masses – e.g., residual ash, slag, or other residue.</p> <p>Worker exposure – considers occupational exposure of workers involved with waste disposal and recycling of harmful products.</p> <p>Environmental impact assessment – discharges will need to be monitored and residues appropriately and safely handled and disposed.</p> <p>Risks – includes risks that are inherent to use of the disposal method as well as operational risks.</p>

⁴ Some of the criteria and the sub-criteria below include sections from “Obsolete Pesticides –a Burning Question” Chapter 2: Criteria for Locally Applicable (On Site) Methodologies. Available here: <http://www.iHPA.info/docs/library/reports/burningq/obsolete-pesticides-a-burning-question.pdf>

Economic feasibility	Ideally includes cost of avoiding negative outcomes.	<p>Resource needs – measures the annual outlay of financial resources for use of disposal method. What advancements or changes are needed to bring costs down? What is the cost for monitoring to ensure proper function?</p> <p>Funding Sources – includes sources of funding, as well as any conditions for use of funds. Are there feasible funding mechanisms for the technology or practice? Is there any marketability for waste components or residuals after treatment?</p> <p>Costs – estimation of incurred costs, which may include the cost of installation and commissioning of the disposal method, site preparation, monitoring costs, reporting costs, compliance costs, running costs with and without waste, and decommissioning costs. What is the current cost of use and implementation of the technology or practice? Is there any marketability for waste components or residuals after treatment?</p>
Policy/regulatory considerations	What kind of regulatory or legal framework is needed to ensure implementation with minimal health and environmental impact?	<p>U.S. Regulations – includes federal regulations governing the use of disposal method. What U.S. regulations currently apply to the technology or practice? Are these sufficient? Are there any legal impediments to its effective use? Can international regulations produce better U.S. policies?</p> <p>State and Local Regulations – includes regulations imposed by state and local authorities.</p> <p>Transparency – pertains to peer sampling and external audit/review conducted by trained personnel or an independent organization. In their absence, specialists outside the country can undertake sampling and audit.</p>
Societal acceptability	Has there been a history of opposition? How can these concerns be addressed? What is the societal context?	<p>Previous instances of opposition – considers instances of previous opposition and whether there could be buy-in from the general population that is affected by the use of the disposal method. Is there a history of opposition to the disposal method, and what are the reasons? Can they be addressed?</p> <p>Demographic considerations – examines exposure to harmful emanating from the site and from the use of the disposal method.</p>

3 End of Life Collection and Pretreatments

Author Contributions for Collection: Jamie Rhodes and Gretta Goldenman

Author Contributions for Pre-treatments: Roland Weber and Brian Riise

In United States, there has been a steady development and maturation of a multitude of programs designed to collect items, material and other “waste” when it is no longer in use by commercial and residential consumers. In general, the default programs are provided at taxpayer expense by local governments. Specific programs have been developed on a state-by-state basis to meet particular needs where local governments have not developed programs for safety and/or financial reasons. Below, end of life collection is broken down into two components based on funding mechanisms and collection methods.

3.1 Collection methods

In general, there are three types of collection methods for waste materials: pick-up programs, drop-off locations, and retail return locations. Pick-up programs can be done by the waste collection agency, or by the retailer. Drop-off locations can be used as a method of collection to reduce transportation costs or avoid potential workplace safety hazards for collection employees. Retail returns are a market solution, which encourages the consumer to bring back the used item to a retailer at the end of its useful life.

3.1.1 Pick-up programs

Bulky units that are too large to fit into curbside garbage or recycling collection bins/bags (e.g., furniture) may be collected through pickup programs like curbside collection at the place of product use. Collection can happen at varying frequency – from weekly to a semi-annual basis. Demand service, where the consumer calls either a private waste hauler or municipal government office, also exists. The cost of these programs is typically borne by municipal or state governments and is administered either by public employees engaged in waste collection or as part of a service contract if waste collection is provided by private vendor.

3.1.2 Drop-off locations

Drop-off locations are often municipally owned and operated transfer stations, where residents can bring their recyclable material and sort it according to commodity type. Bulky items are collected separately, and transported to processing facilities or for disposal. This model reduces transportation costs for local governments, because residents transport all of their own materials. If the transfer station is staffed, as most but not all are, it can also be used for quality control to ensure that materials are properly sorted and that non-recyclable items are not intermingled. The mattress programs in place in California and Connecticut primarily use this method.⁵ A financial incentive for drop-off can be built into the program to encourage participation.

3.1.3 Retail return locations

Consumers can be encouraged to bring their used furniture, or other products containing flame retardants, to a retailer. Giving financial benefits for returning the old furniture encourages participation. Tires provide an example of a successful retail return program: consumers are charged a recycling fee upon purchase of new tires, which goes toward disposal programs. Retailers take-back old tires. See Chapter 3.2.1 for description of the California Tire Recycling Act.

Take-back programs are often regarded as the best solution for managing expensive or bulky waste items to divert them from landfills. They have been successful with appropriately funded initiatives, such as recycling fees at purchase and manufacturer’s product stewardship programs.

⁵ Mattress Recycling Council. “Bye Bye Mattress.” <http://byebyemattress.com/>.

3.2 Funding mechanisms

3.2.1 State or local governments

As management of waste is considered a public interest, it has been funded traditionally by taxpayers. Municipal waste disposal programs, which were initially designed to meet public health goals and deal primarily with waste streams comprising of inorganic waste, have come to deal with materials such as aluminum, glass, plastic, durable goods and organics. Local governments, by necessity, responded by meeting these needs. The downside to this response mechanism is that it created a mindset in the general public that local governments are best positioned to manage the ever-changing type of materials of which households and businesses dispose. However, local governments are often challenged to optimize the collection systems to deal with the ever-changing composition of waste streams, thus creating inefficiencies. This is certainly the case with flame retarded foams and plastics. Local governments do not necessarily have the ability to manage these hazardous chemicals through their localized systems.

3.2.2 Extended Producer Responsibility

A consideration here is whether placing the onus of waste disposal on the state and local governments shifts the onus away from manufacturers of products, goods and packaging. The manufacturers then do not pay for the burden of these materials on waste disposal. In the absence of requiring producers to be responsible for managing disposal of their own products, manufacturers can avoid developing a safe means of waste management to protect the public from any health or environmental impacts of their products. To fix this imbalance, a policy shift is needed to require producers of products to create, fund, and implement material collection programs for end of life products. Such programs can be funded by advanced disposal fee (currently used for paints and mattresses in some states) which is an up-front fee paid by consumers at the time of product purchase. Alternatively, there could be cost internalization which is an Extended Producer Responsibility (EPR)⁶ model (used in electronics and e-waste) whereby individual producers are required to pay for the collection, transport, and processing systems associated with their products out of the product revenue that they receive. This cost is usually borne by the consumers at the time of product purchase.

3.2.3 Examples of Policies to Regulate Collection and Funding

Designating a specific product as universal hazardous waste under a regulation can help reduce the requirements of hazardous waste collection and transportation. Universal waste (u-waste) mandates could provide an opportunity to require separation of the waste either through establishment of dedicated collection sites, or by mandatory removal from general waste streams. Designation as a universal hazardous waste would require additional expense to consumers or local governments since universal hazardous wastes can only be handled in specially permitted facilities. In California and certain other states, items listed as u-waste are banned from being discarded with non-hazardous solid waste streams. It is unlikely that foams and plastics containing flame retardants could easily be designated as u-waste: flame retardant use is rarely disclosed for specific products, and a wide variety or mixture of flame retardants may be used.

The California Used Mattress Recovery and Recycling Act (passed in 2013; Cal. Public Resources Code § 42985) is an extended producer responsibility program, mandating that manufacturers create a statewide recycling program for mattresses discarded in the state. A recycling fee of \$11 is collected with each purchase of a new mattress to fund the program. The mattress industry created the Mattress Recycling Council to comply with the law.⁷ Currently, they use the fee to support municipal collection, drop-off sites, and retail take-back programs. Once the mattresses are collected, they are transported to recycling centers for dismantling and processing.

The California Tire Recycling Act (1989) is an example of a collection program that utilizes a recycling fee at purchase and a retail take-back model to divert waste from landfills. The framework is provided by CalRecycle, which allocates funds annually from the sale fee. While practical technologies and methods for

⁶ CalRecycle EPR, Available here: <http://www.calrecycle.ca.gov/EPR/>

⁷ Mattress Recycling Council, Available here: <http://mattressrecyclingcouncil.org/>

recycling tire waste exist, there are still significant amounts in stockpiles, posing risks, and 8.5 million tires were landfilled in the state in 2015.⁸

EPR policy must be properly enforced. If a fee is imposed on sales of new products to support handling regulated waste, and it isn't being enforced, the policy fails. For example, a problematic loophole in Texas led to stockpiles of 1.2 billion pounds of shredded tires. The policy did not specify that, in order for processors to receive reimbursement for processing tires (e.g., shredding, etc.), the product must be sold to a handler for recycling (SAIC Energy Environment & Infrastructure and CalRecycle 2012). Changing the policy language, requiring documentation for any sale of the processed tires, insured that the funding went to proper processing and reuse of the tires instead of stockpiling.

3.3 Pretreatments

Once items are collected, they are often stored and may require some pretreatment before ultimately being recycled, destroyed, or landfilled. Sofas, automobiles, and electronics are comprised of many different materials that need to be separated and dismantled, and sometimes reduced in size. This chapter summarizes the types of separation methods in use and in development and highlights areas for further research.

3.4 Pretreatment Technologies and Methods

3.4.1 Dismantling

A product often consists of multiple components, which may or may not contain flame retardants or other hazardous additives. For efficient and effective management of such wastes, it is necessary to separate materials that contain FRs from materials that do not contain FRs. This could be achieved through manual disassembly or with automated equipment.

Product components may or may not be dismantled prior to further treatment. In some cases, products undergo shredding or another pre-treatment, and the shredded material is separated into various material streams based on chemical composition, density, or other attribute. In terms of mitigating hazards of flame retardants in wastes, it may be economically or technologically advantageous to separate certain components of the waste stream before treatment.

For example, in some furniture, the PUR foam is readily removable from the other materials. Sofa cushions may be opened using zippers or cut open to manually remove the PUR foam. This can create a highly concentrated stream of PUR foam, though additional foam may also be present in furniture backing and elsewhere. However, such manual disassembly would involve worker exposure to the furniture components, so shredding may be a preferable approach.

Another example relates to waste electrical and electronic equipment (WEEE). WEEE is manually disassembled in some North American facilities with workers potentially exposed through inhalation of, for example, the interior dust with high flame retardant concentrations.

3.5 Separation Technologies

The related guidance developed for the Stockholm Convention (Stockholm Convention 2015c) implementation addresses the identification and separation of brominated and non-brominated polymers for PBDE-containing material flows, such as FPF foam and WEEE plastics, which we summarize below.

3.5.1 Sliding spark spectroscopy

A sliding spark spectrometer is usually a hand-held device, and the instrument operates in the optical to ultraviolet range, making it appropriate for detecting PVC and halogenated materials (Seidel et al. 1993). The lowest detection limit for bromine with this technology is 0.1%. For practical reasons the recyclers set

⁸ CalRecycle Tire Management, Available here: <http://www.calrecycle.ca.gov/Tires/default.htm>

the system at 1% bromine to screen out FR-containing plastics, which can contain between 3% and 20% BFR (Seidel, Golloch, Beerwald, & Böhm, 1993). Therefore, operators can distinguish between halogen-containing and low-halogen components. The scanning time takes only a few seconds, the instrument needs a direct contact to the material surface, and coated materials need to be scratched.

The handheld sliding spark equipment is available with additional detectors (near infrared; NIR) for determination of the polymer type, and could be used for producing clean polymer fractions with associated higher market values. 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. NIR has difficulties with recognizing black plastic (Stockholm Convention 2015c).

3.5.2 X-ray fluorescence technology

The X-ray fluorescence (XRF) technology can be used for detection and separation of BFR-containing plastic with a bromine detection limit of 10 to 100 ppm. These detection limits allow even the separation of WEEE rigid plastic containing BFRs from previous recycling of BFR-containing polymers. These may contain mixtures of different BFRs, but exhibit bromine levels in the range of 100-1000 ppm (Bantelmann and Ammann 2010). XRF is sensitive enough to trace these materials, detecting the total bromine content.

The time requirement for a measurement when applying handheld items is a few seconds. Since the handheld XRF instrument needs a direct contact with 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 handled by scratching the coating. XRF technology is applied by Austrian dismantlers to abide by the Austrian Waste Treatment Obligation Ordinance, which requires the monitoring of plastics from WEEE (Aldrian, Ledersteger, and Pomberger 2015). According to the Austrian study, handheld XRF was proven as an effective and fast tool on large volumes of waste plastics. With a cost of approximately U.S. \$20,000-50,000, its use in small size enterprises may be limited (Stockholm Convention 2015b).

3.5.3 X-ray transmission technology

X-ray transmission (XRT) has been developed to separate materials with different optical densities. In contrast to the handheld screening instruments described previously, XRT is designed to automatically sort scrap. Industrial machines sort up to 1 tonne of scrap per hour. The technology is used to separate BFR-containing plastics from BFR-free types in Switzerland. It can play a role in WEEE plastic recycling plants, particularly if combined with NIR. XRT is not a stand-alone technique as the produced bromine-reduced fractions require further treatment in order to make marketable recycled polymer (Stockholm Convention 2015c).

One of the companies claims its system is able to clean and separate alumina fractions, cathode ray tube glass fractions (Pb vs. non-Pb), and refuse-derived fuel fractions from metals, glass and PVC, and to remove halogen-containing materials. Limited information, however, exists on the separation success with mixed WEEE plastic scrap (Stockholm Convention 2015c).

3.5.4 Raman spectroscopy

Raman spectroscopy equipment in combination with sorting to separate BFR/PBDE-containing polymers has been developed in Japan in pilot scale (Kawazumi et al. 2014). The pilot equipment sorted 400 kg of plastic shredder/hour.

3.5.5 Separation of plastic 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. Flame retardant additives increase the density of the ABS and HIPS materials at typical concentrations. For example, using 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 Mäurer 2006).

A simple two-stage separation has recently been tested in a German collaborative project called SpectroDense (Arends, Schlummer, Maurer, Markowski, & Wagenknecht, 2015). The mixture is treated in a liquid with a density of $\sim 1,100 \text{ kg/m}^3$. The float fraction consists mostly of polypropylene, polyethylene and BFR free polystyrene, and ABS. The sink fraction will mostly consist of those containing BFRs and HIPs. The float fraction is further treated with water (density $1,000 \text{ kg/m}^3$) to separate HIPs and ABS from PP and PE. 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, and approximately 30% of the casings in Europe contain BFRs. For these products, sink and float (S/F) is an efficient separation technique (Stockholm Convention 2015c). Sink and float has also been reported to effectively separate BFR containing materials from non-BFR types of ABS and/or HIPs (Schlummer and Mäurer 2006). Additionally, sink and float methods have been successful in Sweden for separating BFR rich fractions of TV/PC (Retegan, Felix, and Schyllander 2010).

With respect to plastics from small electronic equipment and mixed WEEE plastic from recycling of mixed WEEE, sink and float techniques can efficiently separate 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. Currently, the small yield of these techniques does not support the economic recovery of polymers. Therefore, unless the bromine-free fraction can be converted into valuable plastic for recycling, sink and float is unlikely to be widely used. Operators are unwilling to use a separation technique to produce what might be, in effect, two new waste streams without adding value to the output (Stockholm Convention 2015c).

3.5.6 Combinations of technologies for producing marketable product

None of these techniques can individually separate the complex mixture of WEEE plastics into marketable polymer fractions, and FR-containing plastics. In addition, no technique achieves a 100% separation, leading to residual FR levels in the intended bromine-free fraction. In the case of handheld sorting, this is due to errors by the operators. For automated systems, the sorting efficiency with blowing bars has its limits and the purity of sorted fractions is normally below 95%. Some combination of separation technologies are described in the Stockholm Convention BAT/BEP guidance (Stockholm Convention 2015c).

3.6 Examples and Case Studies

Use of the separation technologies for other polymers (PUR foam; XPS/EPS)

The XRF and sliding spark technologies can likely also be used for manual separation of PUR foam and XPS/EPS as well as for BFR containing polymers, textiles or other materials. The use of other technologies needs to be assessed for a practical use of separation for the individual waste/recycling materials.

E-waste is commonly collected in take-back programs. A 2014 global study by the United Nations University reported that the U.S. generated 7.1 Mt of e-waste, 15% of which was collected in a take-back program (Baldé, C.P., Wang, F., Kuehr, R., Huisman 2015). Take-back amounts were 40% in the EU and 28% in China. The primary collection methods in the U.S. differ by region, but include a mix of municipality, retailer and commercial pick-up programs.

Collection of WEEE in California

California enacted the Electronic Waste Recycling Act of 2003, which established a fee at retail to fund the program. The fee depends on the screen size of the device. Figure 3.1 shows CalRecycle fee revenues by fiscal year since 2004. Despite the increase in electronics waste, the waste fee revenue has declined, leading to a request for a new fee structure, which is projected in the 2016/17 fiscal year amounts. The fee is used for diversion of waste at landfills. Over 40 million pounds were diverted in 2014/15 (see Chapter 4.3.2).

Consumers can drop-off their waste electronics at designated sites.

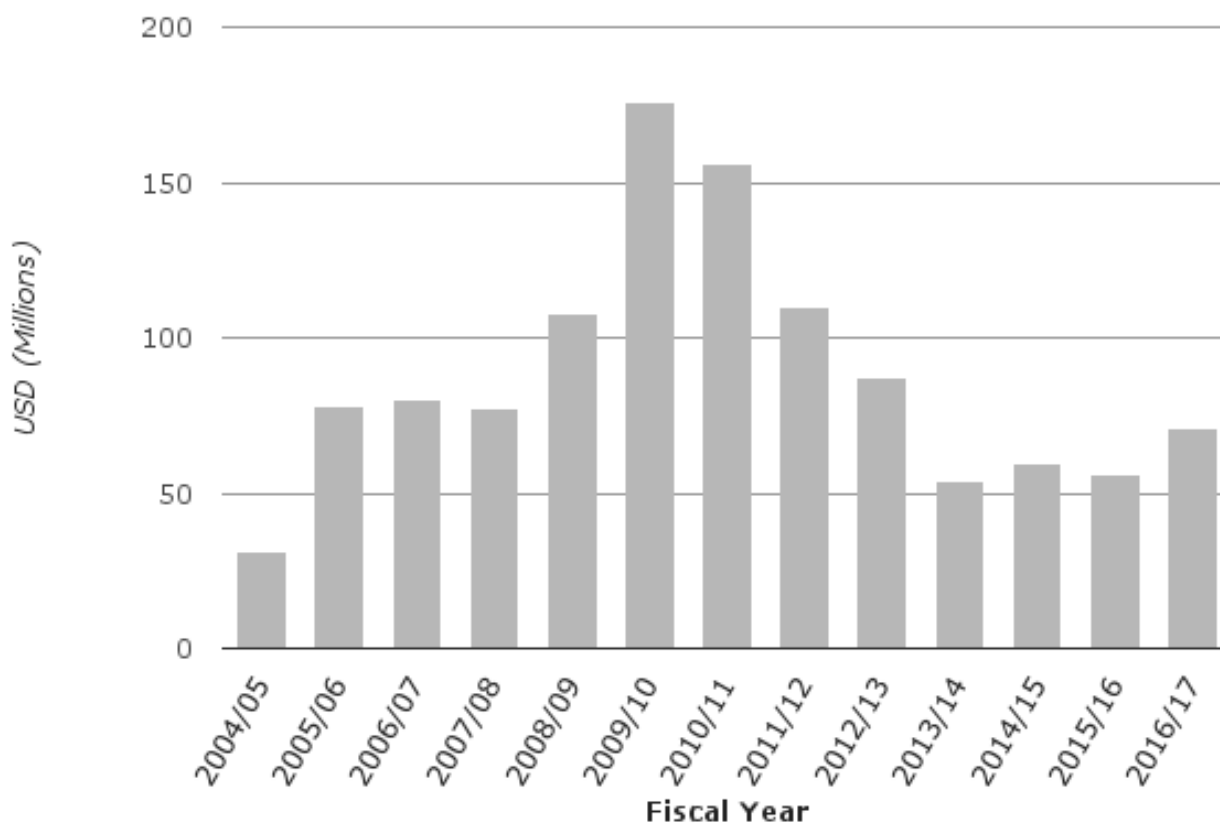


Figure 3-1 CalRecycle revenues for the covered electronic waste recycling program. Note that 2015/16, and 2016/17 show projected amounts.

Separation of BFRs from polymers by solvent technology (CreaSolv®)

The CreaSolv® process extracts 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 and Mäurer 2006) using a proprietary CreaSolv® solvent formulation. It has been developed and optimized to certain WEEE plastic fractions and is able to produce high quality RoHS⁹ compliant polymers even from BFR-rich fractions. This process is described in more detail in Chapter 7.

3.7 Recommendations

Designing a system for safe collection, centralization and transportation of household waste is difficult without the input of those producers, retailers and municipal officials who are either engaged in existing programs or would be responsible for particular pieces of a new system. However, recognizing the absence of such a dialogue, there are some core considerations for the standardization and implementation of an aggressive collection system with the primary goal of removing hazardous flame retarded foams and plastics from homes in an efficient manner.

Screening technologies 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 (Freegard et al. 2006), and therefore appear appropriate. 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 (Stockholm Convention

⁹ Restriction of Hazardous Substances, Directive 2002/95/EC. Available here: <http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32002L0095>

2015c). These technologies need to be further assessed for their practicability.¹⁰ Alternatively, such equipment could be used for confirmation of other separation techniques (e.g., sink and float or manual separation based on experience) (UNEP 2010).

Fundamental areas of research, include:

- Efficient ways to identify and quantify FR substances in wastes to determine the best pretreatment needs.
- Monitor the air and dust at dismantling and shredding facilities, and at transfer stations for release of toxic flame retardants.
- Monitor collection programs for gaps in service or accessibility to marginalized communities.
- Monitor occupational exposure to FRs during waste collection, handling and dismantling.
- Explore willingness of FR manufacturers to dialogue regarding product stewardship programs.

¹⁰ 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.

4 Municipal Disposal: Landfilling

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Currently most waste containing flame retardants in the U.S. (as in many other countries) is disposed in landfills. The U.S. EPA estimates that 41.7% of selected electronic were recycled in 2015.¹¹ While an alternative to landfilling may be beneficial for resource recovery, landfills are currently the most economical and efficient method of disposal. The Stockholm Convention BAT/BEP guidance for managing PBDE has included an Annex on requirements for landfilling PBDE containing waste (Stockholm Convention 2015c).

Landfilling waste with flame retardants does come with a range of risks even in state-of-the-art facilities. The risks discussed in this chapter are those associated with (a) the exposure of landfill workers and surrounding communities, (b) the migration of flame retardants into the environment via volatilization into landfill gas (followed by atmospheric deposition) and via leachate (both accidental seepage and purposeful disposal), and (c) the potential for flame retardants to migrate into the food web from landfills.

4.1 Landfilling Methods and Process

Furniture reaches a solid waste transfer station either through self-haul where customers or providers of hauling services bring the furniture, or a garbage collection crew brings it in as part of provided bulk collection services. In some cases, furniture is also illegally dumped, and then collected and brought to a transfer station. There is an underlying assumption here that if the furniture is reusable, then customers will sell or donate it themselves. Furniture that enters the waste stream is considered non-reusable and is not separated from other MSW for recycling or reuse. At a transfer station, MSW is compacted into larger long-distance trucks for delivery to the landfill. Larger items, such as mattresses or furniture, are commonly broken down for ease of compaction. In some cases, furniture may be brought to the landfill directly.

With the implementation of Subtitle D of the Resource Conservation and Recovery Act (U.S. EPA 2014) and related state regulations, landfills have become highly engineered facilities designed to contain waste and separate it from the environment, capture leachate and control gas migration. A landfill site is typically excavated and lined with a system of layers to (1) minimize the migration of leachate to the groundwater and (2) collect leachate for treatment. A common system used to restrict leachate migration consists of a 0.67- to 1-m-thick clay layer with a hydraulic conductivity of no more than 10^{-7} cm/sec overlain with a geomembrane (GM). The GM is typically 1.5-mm-thick polyethylene with an equivalent hydraulic conductivity (based on vapor diffusion) of about 10^{-12} cm/sec (see Fig. 5-1). A drainage layer designed to collect leachate is placed above the liner. A protective barrier is then installed above the leachate collection system to shield it from the equipment used to place and compact the refuse. Waste may then be placed above the protective barrier, compacted and covered daily to minimize wind-blown refuse, odors, and the attraction of disease vectors. The cover material used at the end of each operating day is traditionally 15 cm of soil or other materials known as alternative daily cover (ADC).¹² Materials that comprise ADC differ from state to state. In California, ADC includes the following 11 material types: ash and cement kiln dust, treated auto shredder waste, construction and demolition waste, compost, green waste, contaminated sediment, sludge (including wastewater treatment biosolids), shredded tires, geosynthetic fabric or panel products (blankets), spray-foam and spray-applied cement. The ADC is again topped with compacted MSW and this process continues until the landfill is filled. Once refuse has reached the design elevation, a final cover is applied. The final cover will include, at a minimum, a layer of low permeability soil designed to minimize storm water infiltration, overlain by a layer of soil that will support vegetative growth. The final cover invariably includes a drainage layer and a GM beneath the vegetative layer. Vegetation serves to minimize erosion of the soil cover and to promote evapotranspiration.

¹¹ U.S. EPA Advancing Sustainable Materials Management. Available here: <https://www.epa.gov/smm/advancing-sustainable-materials-management-facts-and-figures>

¹² Alternative daily cover (ADC) means cover material other than earthen material placed on the surface of the active face of a municipal solid waste landfill at the end of each operating day to control vectors, fires, odors, blowing litter, and scavenging. "Alternative Daily Cover (ADC)." Alternative Daily Cover (ADC): Local Govt. Basics. Accessed March 30, 2016. <http://www.calrecycle.ca.gov/lgcentral/basics/adcbasic.htm>.

Conceptual Landfill Liner System

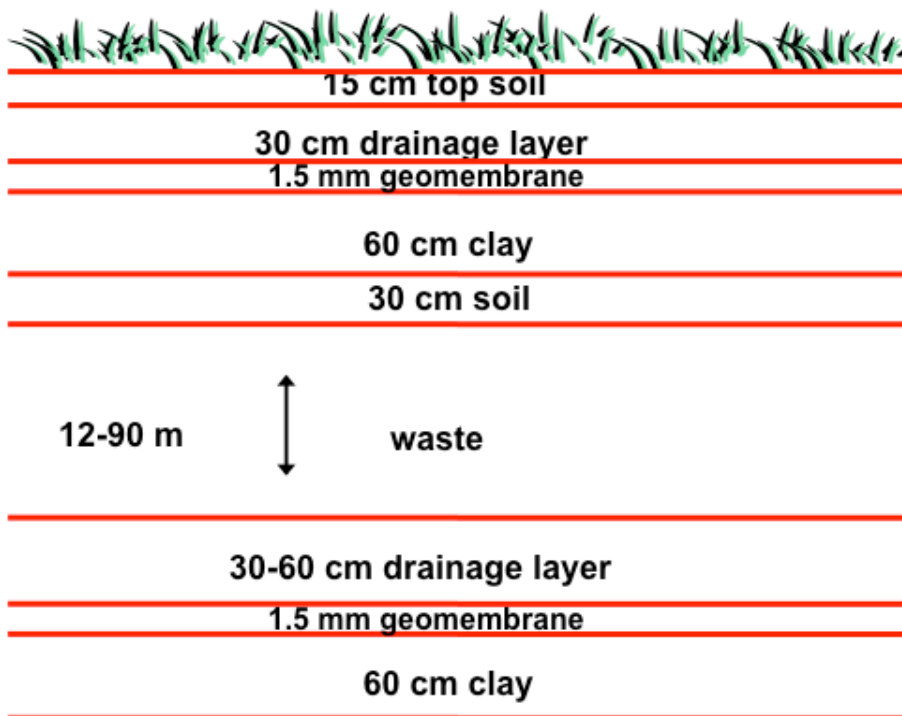


Figure 4-1 Illustration of typical landfill liner system to contain leachate.

The landfill owner (private or government) manages gas and liquid (leachate) generated by the waste decomposition processes throughout the landfill operation and for a post-closure period (Laner et al. 2012). Federal regulations specify 30 years unless this period is extended by the governing regulatory agency to protect human health and the environment. Both landfill gas and leachate can be potential routes of migration for flame retardants into the environment as discussed below. The gas can have a high fraction of methane (~50%), and is typically burned in a flare or used for energy generation. However, gas collection efficiency varies from essentially zero in freshly buried waste to about 90% once a final cover is installed.

In the United States, there are several management options for leachate:

- I. Disposal
 - a. The landfill can obtain its own National Pollution Discharge Elimination System (NPDES) permit under the U.S. EPA Clean Water Act. This allows the landfill to treat leachate to applicable Federal and State standards and discharge treated leachate into the environment.
 - b. The landfill can discharge leachate into a sewer after necessary pretreatment in agreement with the wastewater treatment facility receiving the leachate. The level of pretreatment is based on the needs of the wastewater treatment facility to protect its workers and processes and to stay in compliance with its own NPDES permit.
 - c. Occasionally, for landfills that do not classify as Significant Industrial Users, leachate can be disposed into a sewer without pretreatment. This would be applicable only when certain standards outlined in NPDES Pretreatment Program are met.
- II. On-site management
 - a. One of the most common ways to manage leachate on-site is to recirculate it back into the landfill. This is a popular practice as it enhances waste decomposition and minimizes leachate treatment costs. This method may involve some issues with leachate building up in the landfill and exerting hydraulic head on the landfill liner, although many landfills recirculate leachate without problems (Bareither et al. 2010). Even at landfills that recirculate leachate, some may still require disposal.
 - b. Leachate may also be evaporated. In arid regions, leachate may be stored in ponds from which it will evaporate. In regions where natural evaporation does not occur at a sufficient

rate, the leachate may be evaporated in equipment designed for this purpose. Landfill gas is often used as the energy source to operate evaporators. Leachate may also be sprayed directly into a flare to promote its evaporation. As above, the landfill should always have a contingency plan to treat leachate off-site if needed.

- c. Some leachate may be used for dust control on haul roads internal to the landfill. This is functionally equivalent to recirculation onto the waste and is likely a small outlet.

4.2 Review of Potential Health and Environmental Impacts

Some of the potential migration routes for PBDEs from landfills are (1) as particulate matter released during compaction of the disposed items, (2) volatilization into landfill gas or dissolution into landfill leachate during landfill operation and post-closure, and (3) uptake into the food chain by organisms foraging in waste. Each route of migration has the potential for occupational exposure or environmental contamination. These routes of migration and the risks associated with each are discussed in the sections below.

PBDEs have been detected in leachate and there is evidence that they have been released to landfill gas based on their presence in adjacent soil. While PBDEs are present in the environment surrounding landfills, mechanistic interpretation of field data is often not appropriate. Several processes are likely acting concurrently on transport of PBDEs, including leaching, which is influenced by infiltration rates and liquid flow paths, sorption, volatilization, association with humic matter in leachate, and possibly biotransformation. In addition, landfills contain heterogeneous waste of multiple ages, and the measured concentrations in leachate and gas typically represent composite samples collected over broad areas or the entire landfill, making it difficult to draw conclusive relationships between PBDE detection in the environment surrounding landfills and factors that influence it.

4.2.1 Risk of flame retardant release from landfills by air

Particles of disposed solid waste containing flame retardants can be picked up by air currents and deposited in the surrounding areas. This is particularly relevant for foam products that can be carried long distances due to their low density. Several studies investigated the soils surrounding landfills. For example, one study found substantial concentrations of PBDEs in the soil adjacent to all landfills and dumpsites in various regions of Canada (Danon-Schaffer 2010), indicating atmospheric PBDE release and deposition from landfills. Another study in China also found elevated PBDE concentrations in soils in the vicinity of landfills compared to other land use sites (Tang et al. 2015). Similar results were found in a survey of soils around open disposal sites in five developing countries in Asia (Eguchi et al. 2013). Weinberg et al. (2011) studied landfills as sources of several compounds, including PBDEs.

According to several studies, releases of PBDEs from landfills also reach human communities living near the landfills. Elevated levels of persistent organic pollutants similar to PBDEs have been reported in breast milk from women living near an open dump site in India (Kunisue et al. 2006) although there would be no attempt to control leachate or gas from an open dump so the applicability of this to a well-operated engineered landfill is low. Additionally, waste composition and the level of contact between waste and neighboring community differ by landfill (e.g., locals may be allowed to scavenge through open dump sites for reusable materials). Another study in China showed higher blood serum concentrations of PBDEs in populations who worked/scavenged at the dumpsites compared to those who lived in the vicinity (50 km radius) (Qu et al. 2007). Both populations had PBDE levels much higher than the rural control group living outside the 50 km radius. The same trend for some of the congeners of PBDE was demonstrated by Athanasiadou et al. (2008) in a study of populations in Nicaragua that either worked/scavenged at dump sites, or lived nearby, compared to the rural control group. It must be noted that all of the studies cited above were conducted in populations affected by open dumpsites in developing countries. Limited studies exist in developed countries. One such study evaluated the association between residential proximity to solid-waste facilities (MSW landfills and transfer stations) and blood serum levels of PBDEs among a sample of 923 California adult women in the same occupation (R. Liu et al. 2016). The study participants living < 2 km from a landfill had significantly higher levels of BDE-47 and BDE-100 (used mainly in flexible PUR foams) than those who lived > 10 km from a landfill. The relationship between the time of exposure, landfill operational practices, types of waste accepted, and cover materials has not been studied.

Vapor pressures of PBDEs are estimated to be in the range of 10^{-7} - 10^{-8} mm Hg (U.S. EPA 2010), so volatilization will be relatively slow. However, volatilization is still a potential route of PBDEs migrating into the environment, especially as some loss of bromine (debromination) is possible in the oxygen-deprived reducing environment of a landfill. Debromination will make the molecule lighter and more volatile. Studies conducted with BFR-containing materials and products in enclosed chambers reported volatilization of BFRs (Kemmllein, Hahn, and Jann 2003; Kajiwarra and Takigami 2013). High temperatures often found in landfills (37-40 °C) can further increase the volatilization. Considering that the gas generated in the MSW breakdown process is typically burned, the PBDEs volatilized with gas will be destroyed at least partially by combustion. Incomplete combustion products of PBDEs in landfill gas (e.g., PBDD/PBDFs) may pose an environmental concern, and have not been thoroughly investigated. Collection rates of landfill gas range from zero prior to the installation of a gas collection system to greater than 90% once a final cover is installed (Barlaz, Chanton, and Green 2009). Therefore, capture of volatilized BFRs will vary based on the landfill stage of operation.

While open burning of solid waste is often practiced in developing countries, it is not practiced in engineered landfills. Nonetheless, there are occasionally fires at landfills. Such fires can facilitate the release of semivolatile persistent substances like BFRs, and incomplete combustion releases of dioxins and furans, depending on the quantity of waste that burns and the duration of the fire. In an assessment of persistent organic pollutants (POPs) released from landfill fires in Mexico, high levels of PBDE were detected (Gullett et al. 2010). Another study evaluated costs of human health impacts due to various methods of disposal of TV cabinet back covers treated with DecaBDE (Hirai, Sato, and Sakai 2008) and found that landfilling with open fires was the largest source of DecaBDE and PBDD/PBDF emissions compared to mechanical recycling, thermal recovery, feedstock recycling, and landfilling without open fires. In the U.S., landfill fires do occur and represent an upset condition as occurs with many processes. While not quantified, such fires may represent a source of BFR emissions.

Another potential source of airborne BFRs is from the use of auto-shredder residue (ASR) as ADC. Typically, ASR that is used for ADC is called “fluff”, which means that the metal and plastic parts have been recovered for recycling. The fluff mainly consists of seats, floor mats, and other miscellaneous non-recyclable material. Sometimes it may include everything but metal parts of the vehicle. Kajiwarra et al. (2015) analyzed BFRs in end-of-life vehicles in Japan and found that seat fabric and filler had the highest BFR content, up to 5% by weight, compared to other parts of a car. ASR fluff is to the large extent seat material, and having been shredded, it will contain many particles small enough to travel long distances if picked up by wind. ASR’s exposure to ultraviolet radiation from the sun can lead to photodebromination of BFRs (Söderström et al. 2004), and will make them more volatile and soluble, increasing their mobility in the environment. ASR is used as a daily cover at some landfills.

ASR is not the only type of ADC that may contain BFRs. Other potential sources are electronics shredder residue (ESR) and small pieces left after sorting construction and demolition debris (called C&D fines). ESR has BFRs incorporated into plastic casing, and C&D fines may have pieces of insulation and carpet padding containing BFRs (Gavilán-García et al. 2016).

Most of the air emission studies focused on landfills, and little attention has been devoted to transfer stations, or processing facilities where some of the bulk items containing FRs may be broken down and compacted potentially creating elevated concentrations of BFR-containing particulates in the air. Multiple studies focused on the exposure of the workers of electronics dismantling industry in the developing countries (Qu et al. 2007; Athanasiadou et al. 2008), as most electronics contain materials with flame retardants. However, the potential exposure of solid waste workers in developed countries has been largely overlooked.

4.2.2 Risk of flame retardant release from landfills by water

As most of the flame-retardants-containing consumer products went into circulation in 1970s, they can be expected to be found in a limited number of unlined landfills that were in existence prior to RCRA (enacted in 1976). However, landfill liners in non-hazardous waste municipal landfills did not become a common practice until the 1990s. In the U.S., there is a certain degree of protection from groundwater contamination by leachate seeping from a landfill as described above, although some risk of liner failure or leakage still exists. In countries that have less stringent leachate containment regulations, contamination of surrounding

groundwater has a higher likelihood. PBDE-contaminated groundwater near South African landfills has been reported (Odusanya, Okonkwo, and Botha 2009). Other studies also reported BFRs and phosphorous flame retardants in landfill leachate and groundwater pollution plumes from unlined landfills (Eggen, Moeder, and Arukwe 2010; Barnes et al. 2004).

Chemical and biological transformation of PBDEs in a landfill can also affect their fate and transport. The debromination of PBDEs (removal of bromine from its molecular structure) increases the risk for environmental contamination as it makes the molecule more soluble and therefore more mobile in the water. A basic model that estimates debromination rates in landfills for e-waste was developed by Danon-Schaffer and Mahecha-Botero (2010). The authors of the study conclude that the time horizon of centuries for deposited waste in landfills is sufficient for the debromination process. The risk of debrominated compounds being released from a landfill increases with time if the containment systems designed to protect the environment leachate releases fail over extended timescales. However, leachate generation over long periods of time is insignificant if the closed landfill is properly covered with a very low permeability cover system designed to eliminate infiltration (Bareither et al. 2010; Laner et al. 2012). Furthermore, hydroxylation and methylation are important degradation pathways for PBDEs (Ueno et al. 2008). Hydroxylated PBDE have higher solubility and subsequently higher potential to leach from landfills. Hydroxylated PBDEs can have higher toxicity compared to their parent PBDE (Su et al. 2014), and some of them exhibit dioxin-like toxicity (Su et al. 2012).

Apart from the accidental environmental release of leachate into the immediate surrounding of the landfill, leachate discharged by approved means also poses a concern. The presence of BFRs in landfill leachates has been demonstrated in multiple studies across the world. A study of seven landfills in Japan found PBDEs at relatively low concentrations, but showed high levels of TBBPA (Osako, Kim, and Sakai 2004). A study of landfills in Europe also found BFRs in leachate, some of them in $\mu\text{g/L}$ (ppb) levels (Öman and Junestedt 2008). In Canada, 27 landfill leachates were surveyed, all containing BFRs, mainly at ng/L (ppt) levels (B. Li et al. 2012). BFRs were also detected in leachates in the U.S. (Oliaei, Weber, and Watson 2010). In general, the range of values reported by various studies is broad ($<1\text{--}133,000 \text{ ng/L}$), and the waste disposal practices of the country where the study was conducted should be taken into consideration (Stubbings and Harrad 2014). In the U.S, collected leachate is sent to a wastewater treatment facility so release to the environment is largely governed by treatment plant removal efficiencies.

A majority of landfills do not have their own NPDES leachate discharge permit and dispose of leachate to a wastewater treatment plant. The receiving wastewater treatment plants are not equipped to remove contaminants such as PBDEs. At the wastewater treatment plants, flame retardants have been shown to concentrate in the biosolids (sludge consisting mainly of microbial cells that grow during biological wastewater treatment) (Kim et al. 2014). The biosolids typically go through two main disposal routes: (a) they are sent to a landfill as solid waste essentially returning a portion of the flame retardants back to the landfill; or (b) are applied to specifically designated land areas. Land-applied biosolids can leach flame retardants with runoff and infiltration into surface water and groundwater. Flame retardants have also been shown to bioaccumulate in organisms such as earthworms collected at biosolids application sites (Kinney et al. 2008; Navarro et al. 2016).

Occasionally, a landfill may have an NPDES permit and manage treatment and disposal of leachate. The leachate treatment processes typically used at landfills in the U.S. that have an NPDES permit may not be effective at attenuating flame retardants. Common treatment processes include metals precipitation and biological treatment to decrease organic loads and sometimes to oxidize ammonia. The extent of flame retardant removal from landfill leachate in those processes is largely unstudied. A study in Japan demonstrated good removal of BFRs in leachate treatment systems (Osako, Kim, and Sakai 2004). However, those systems were advanced by comparison to the U.S. leachate treatment practices and included activated carbon adsorption – a process highly effective for removal of hydrophobic organics from water. One plant also included Fenton's advanced oxidation process, which is also effective for treatment of a wide range of organic compounds.

While many studies have detected the presence of flame retardants in treated wastewater and in biosolids, no study has investigated the role of leachate (e.g., comparing wastewater treatment plants that receive leachate

to those that do not). Some of the flame retardants detected at wastewater treatment plants could result from the disposal of water used to launder items that contain flame retardants, from washing off household dust that originated from flame-retardant-containing household objects, and through a variety of other pathways (Schreder and La Guardia 2014; Saini et al. 2016). Therefore the role of landfill disposal of flame retardants on eventual release of these chemicals into the environment via wastewater effluent and biosolids disposal is yet to be established.

Conditions inside the landfill, such as moisture and high temperatures, may speed up leaching of PBDEs. Additionally, leachate has a high content of dissolved humic material, which was shown to increase leaching of PBDEs from plastics in a bench-scale study with humic acid standards (Choi, Lee, and Osako 2009). A separate full-scale study (Osako, Kim, and Sakai 2004) also showed that landfills that receive higher organic content waste leached higher concentrations of BFRs, and the authors suggested that dissolved organic matter enhanced the mobilization. The ability of organic matter to improve dissolution of hydrophobic organic chemicals is a recognized phenomenon. Other factors that were shown to influence leaching of PBDEs from landfilled waste are precipitation and the quantity and degree of compaction of waste materials being received, as reported for a Cape Town, South Africa landfill (Daso et al. 2013). Osako et al. (2004) also found that the concentrations of BFRs at Japanese landfills were higher in leachate from active landfills and those within a year of closure than in older landfills.

4.2.3 Risk of flame retardant uptake from landfills into the food web

Several studies suggest that PBDEs can be taken up by organisms that forage for food at landfills and can migrate further into the food web.

A Canada-based study evaluated the concentrations of PBDEs in the eggs of European starlings (*Sturnus vulgaris*) that nested in proximity to landfills and compared the results to the eggs collected in urban industrialized areas and rural areas (D. Chen et al. 2013). The eggs collected in the vicinity of the landfills contained orders of magnitude higher concentrations of PBDEs than the eggs collected in other areas. The authors hypothesize that omnivorous/insectivorous starlings may be exposed to PBDEs by either feeding on insects collected at the landfill or directly foraging for food among the refuse. The worms and other insects collected by starlings can have PBDEs on the surface from direct contact with PBDE-containing materials or from ingesting food materials contaminated with PBDE dust. The study posits that the presence of organic wastes in landfill sites attracts animals that facilitate bio transport of FRs from landfills to local ecosystems.

Gentes et al. (2015) found clear evidence that particular ring-billed gulls (*Larus delawarensis*) nesting in the Montreal area (Quebec, Canada) routinely visited landfill sites. Subsequent analysis of those birds found elevated levels of a range of BFRs compared to individuals that did not forage at the landfill.

Another study in Shanghai found that muscle tissue collected from 37 Eurasian tree sparrows showed higher concentrations of PBDEs in the samples collected near landfill sites, followed by those collected at urban and industrial sites (Tang et al. 2015). The study also showed a correlation between the concentration of PBDEs in sparrow tissue and in the soil at the site where the sparrow was collected. These studies expose the potential role of waste disposal sites as a source of PBDEs in the food web.

4.3 Examples and Case Studies

4.3.1 Mattress diversion program, Yolo County Landfill

Products containing halogenated FRs are currently not treated any differently than other MSW during disposal in landfills. However, if separate handling becomes necessary, there are some examples of diverting specific waste streams from bulk waste, so that they can be managed differently. Examples include mattresses, tires, electronics and other specialty wastes.¹³

¹³ CalRecycle Mattress Recycling Program, Available here: <http://www.calrecycle.ca.gov/Mattresses/>; CalRecycle Tire Recycling Program, Available here: <http://www.calrecycle.ca.gov/Tires/>; CalRecycle Electronics Waste Recycling Program, Available here: <http://www.calrecycle.ca.gov/Electronics/>

One such example is the mattress diversion program at the Yolo County, CA landfill. In February 2016, the state-mandated mattress recycling program took effect. In the February-August period of 2016, Yolo County landfill diverted over 4100 mattresses. In the previous year (before the program implementation) it is estimated that 8000-9000 mattresses were landfilled, indicating that the statistics from 2016 are consistent with the year before and that most mattresses are being successfully separated from bulk MSW through this program.

The success of this program largely rests on the built-in financing mechanism for such operations. California has Extended Producer Responsibility laws that require that recycling fees be collected on consumer products that need special handling for disposal. The state organization, California Product Stewardship Council, works with the solid waste industry to pass bills that mandate fees for the end-of-life handling for specific products. The fee is paid by the consumer at the time of purchase. A vendor must keep separate accounting for fees collected for specific products (e.g., mattress fees have to be managed separately from electronics fees by a vendor that sells both types of products). The fees provide a funding mechanism for landfills to process the specialty wastes. In California, CalRecycle is the entity that manages the fund for electronics recycling. The mattress recycling fund is managed by Mattress Recycling Council (MRC). MRC worked to determine an appropriate value for a mattress recycling fee that was substantiated by the actual cost of the process. The process involves collection, disassembly of the mattresses, sterilization of the mattress fabric, transport to a recycling facility and handling at the recycling facility. The recycling fee that was established for mattresses is \$11. The fee is established in collaboration with all entities involved in handling the specialty waste. Only a portion of the overall process is handled at the landfill, so the landfill can claim a small portion of the fee that covers the cost of handling. That portion has to be substantiated by the standard worker salary rates, fork-lift hourly operation rate, number of mattresses that can be handled by a fork lift in an hour, etc. Depending on the area cost-of-living, it may be more expensive for some landfills to comply with the program than for others (due to difference in worker compensation, fuel costs, etc.). The amount determined by MRC is an average value, so each landfill is compensated according to the expenses. Any surplus that remains in the fund collected by MRC goes towards public education programs on the subject. One of the important messages of the public education program is that once the program is established, the disposal of the items under the program is free even if the mattress was purchased prior to the program enactment and the consumer did not pay the recycling fee at the time of the purchase.

4.3.2 Electronics recycling program

State of Washington

In 2006 the Washington State legislature created an electronics recycling program (E-Cycle Washington) that has been used as a model by many other states.¹⁴ Instead of landfilling electronic waste the legislature determined that a convenient, safe, and environmentally sound system for the collection, transportation, and recycling of electronic products must be established. The legislation was enacted to encourage the design of electronic products that are less toxic and more recyclable. Although the responsibility for the electronics management system is shared among various stakeholders, manufacturers are responsible for financing and contracting for the collection, transportation, and recycling.

The Washington Materials Management and Financing Authority (WMMFA) was created by statute as a business management organization to collection funds, manage the finances, and operations of the E-Cycle Washington program. Its membership is made up of participating electronics manufacturers. Fees are paid by manufacturers to operate the program and no fees are collected from consumers at the end of life management phase.

Manufacturers selling covered electronic products in Washington are required to participate in the E-Cycle program through the WMMFA plan.¹⁵ The WMMFA works with retailers, solid waste management firms,

¹⁴ Revised Code of Washington (RCW) Chapter 70.95N. See also the implementing rule, Washington Administrative Code Chapter 173-900, Electronic Products Recycling Program.

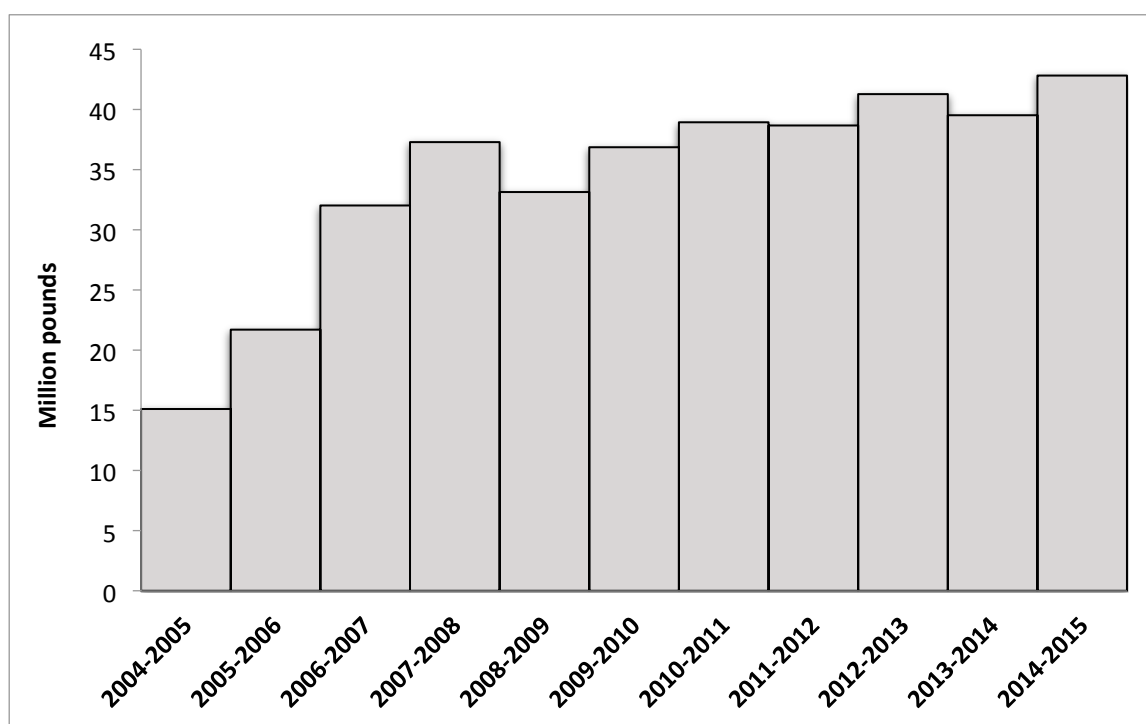
¹⁵ RCW 70.95N.170 and RCW 70.95N.050

non-profit organizations, and local solid waste authorities in implementing the statewide collection and recycling system.

In the first five years the E-Cycle Washington program diverted over 200 million pounds of electronics from landfill disposal, with 98% of that material being recycled or reused. 330 collection sites provided over 90% of residents access within 10 miles of their homes. An estimated 13 million pounds of lead was recycled, 125 jobs were created, and no materials were sent to developing nations in the first five years. In 2016 approximately 37 million pounds of electronics were collected consisting of 83.1% televisions, 9.5% monitors, and 7.4% computers.¹⁶ In 2015 the WMMFA reported the cost of running this program in Washington was \$11.2 million and cost 26.3 cents per pound of material collected and processed.¹⁷ The preferred environmental standards that all processors contracted with the WMMFA must subscribe to require that any materials of concern (materials that present potential risk to humans or the environment) exported to a NON OECD (Organization for Economic Co-operation and Development) member country have approval from the destination country and confirmation from the US Environmental Protection Agency.¹⁸

State of California

The electronics recycling program in the State of California operates in a similar manner. Yolo County landfill conducts weekly load checks in which a load of discarded items is thoroughly sorted to look for any illegal items. Some electronics can still be found among general refuse during such spot checks. While landfill customers have been generally diligent with proper disposal of larger electronics, such as TVs and monitors (both cathode-ray tube and flat screen), some of the more obscure electronic are still found in bulk waste (e.g., projectors, chargers, etc.). A public communication program is essential to improve the diversion of less obvious household hazardous wastes, such as electronic waste items¹⁹. Figure 4-2 shows the amount of electronics waste diverted from landfills in California, which has been increasing over the last decade.



¹⁶ <http://www.ecy.wa.gov/programs/swfa/eproductrecycle/docs/2016TotalCEPPoundsWA.pdf>

¹⁷ <http://www.ecy.wa.gov/programs/swfa/eproductrecycle/docs/2015WMMFAAnnualReport.pdf>, page 40.

¹⁸ *Ibid.* page 29.

¹⁹ In the State of California, e-waste is considered a household hazardous waste, and therefore must be diverted from the landfill. See <http://www.calrecycle.ca.gov/HomeHazWaste/>

Figure 4-2 Amount of electronics waste diverted from landfill in California. Source: CalRecycle
<http://www.calrecycle.ca.gov/HomeHazWaste/Reporting/Data/Collection/Data.aspx>

4.4 Discussion

Disposal of BFRs-containing consumer products into municipal solid waste has a potential for environmental release of BFRs into the air and leachate. As a result, solid waste workers and surrounding communities may be exposed to elevated levels of BFRs from air emissions. Leachate is treated by methods that typically do not remove BFRs. Treated leachate is ultimately released into the environment. Upsets in the managed process of landfilling (fires, leachate containment failure) can exacerbate the potential for environmental contamination by landfilled BFRs.

Understanding the mechanisms by which BFRs are released from solid waste management operations is important for finding ways to minimize the environmental impacts. Furthermore, the disposal of hazardous FRs are a risk for future landfill mining which is gaining popularity in recent years (Krook, Svensson, and Eklund 2012), but has already resulted in food contamination with POPs (Torres et al. 2013).

4.5 Analysis of Short-Term Management Options

While a long-term solution could be completely phasing out HFRs from consumer products, this section will focus on short-term goals of (a) sustainably managing the disposal of the consumer products currently in circulation, and (b) containing the release of HFRs from waste disposed over the past few decades. The recommendations in this section are based on the assumption that landfilling of products containing HFRs will continue. It does not consider alternative options of disposal, such as recycling or incineration. There are several alternative approaches to handling MSW containing FRs that are discussed in greater detail below:

1. Designate it as a hazardous waste
2. Separate wastes at MSW landfills and keep HFR contaminated materials completely dry to reduce releases.
3. Continue disposing with MSW but adjust current landfilling practices to reduce the release to the environment

4.5.1 Designate as hazardous waste

Hazardous waste landfills have more rigorous requirements for leachate containment. However, maintenance of hazardous waste landfills is costlier than conventional landfills to the waste management industry, which in turn charges the public (waste generator). Considering the large volumes of consumer products in circulation that may eventually become BFR-containing hazardous waste, solid waste collection entities may need to impose fees for collection of furniture and electronics containing BFRs if they have to be taken to a hazardous waste landfill.

This alternative will require consumer participation in proper disposal and will likely require a massive public education campaign. Proper disposal of household hazardous waste is at the discretion of the consumer and is a challenge to enforce. The imposition of additional fees would further discourage proper disposal.

4.5.2 Keep separate at MSW landfill

One of the recommendations to prevent migration of HFRs into the food chain would be to dispose of HFR-containing materials into landfills that do not contain organics that attract insects, rodents and birds. Despite the daily cover that prevents nocturnal animal foraging, animal exposure cannot be fully eliminated during the day. For example, birds often forage for food at landfill sites. Separating HFR-containing items to a separate area at a landfill would prevent them from coming in contact with leachate high in dissolved organics that helps mobilize HFRs. In California, SB 1383 was passed in 2016 to reduce the organic waste landfilled to 50% of tonnage produced in 2014 by year 2020 and to 75% by 2030. This may reduce the transport of HFRs by leachate that is high in dissolved organic waste. This practice might also reduce microbial debromination, hydroxylation, and methylation of HFRs that in theory would slow or even stop the environmental release of HFRs from landfilled products due to debromination. Separation of these products

may be achieved with reasonable effort at the transfer station as most of the items are fairly bulky (furniture, appliances) and do not easily blend with other waste. However, many smaller items (e.g., some electronics, sofa cushions) can still be easily disposed by consumers with mixed MSW. Additionally, the use of ASR as ADC would have to be discontinued, or evaluated for HFR content, where its use would need to be limited to the dry portions of the landfill if available.

Construction and demolition (C&D) debris would also need to be separated into two streams depending on whether the item contains HFRs (insulation, carpeting, etc.) or not (drywall, wood products, etc.). Additional labor will be necessary to accomplish the separation. Some C&D waste generation and hauling is performed by contractors rather than solid waste managing entities. Therefore, contractors would require additional training in handling specialty wastes.

Additional handling costs associated with separate sections of a landfill could lead to resistance from landfills unless there is additional funding provided or the costs are transferred to the consumers. The funding could be provided by disposal fees built into the price of the HFR-containing objects. The fees could be imposed on the product manufacturers as an end-of-life disposal fee and would likely be passed on to the consumer. It may be a challenge to determine whether the fee is to be assessed from the raw material manufacturer (e.g., PUR) or from the finished product manufacturer (e.g., sofa filled with PUR). Exported and imported consumer materials create an additional complexity in fee assessments.

4.5.3 Dispose with MSW but adjust landfilling practices

Examples of adjusting landfilling practices to prevent the release to air or water are understanding the effects of gas emissions, additional leachate treatment, reevaluation of and changes to current compaction practices (e.g., to minimize worker exposure to dust).

While there are new approaches to waste management that can be implemented going forward for newly collected items, there are thousands of closed and active landfills across the U.S. that currently contain HFRs and will be producing gas and leachate for decades. Their maintenance may also need to be adjusted as more information becomes available.

Overall, the best immediate approach is to improve the safety of the current landfilling practices while seeking long-term disposal rules. Any short-term or long-term solution to release of BFRs from landfills would require new, evidence-based regulations for the disposal of materials containing flame retardants on a state or national level. While flame retardants in the environment are a national and international phenomenon, initial steps in regulatory action may be more easily achieved at the state level. Some states have regulatory agencies that specifically deal with generation and disposal of substances such as flame retardants, for example California Department of Toxic Substances Control. However, it is essential to involve the EPA and to create national regulations based on research on safe disposal of BFRs-containing materials.

Any approach would require training and education programs for the general public and the waste handling personnel. If materials containing flame retardants are determined to be hazardous waste, then a public information campaign will be necessary to assure proper disposal by consumers. Additionally, MSW staff will need to be trained on the new collection, processing and disposal practices as well. Worker exposure at landfills will need to be evaluated by national or state-level Occupational Safety and Health Administration (OSHA) to develop best practices for waste management workers handling items that contain flame retardants.

Sustainable management of BFRs in solid waste will require cooperation from stakeholders, such as the solid waste industry, BFR manufacturing industry, and federal and state agencies to develop a solution. Further research is needed to address many unanswered questions to inform better short-term and long-term policy. The benefits and costs of the various short-term options must be thoroughly evaluated.

Research is recommended in the following areas:

- a. Evaluate the potential for halogenated flame retardants to volatilize with landfill gas and the extent to which they are attenuated by gas combustion. Determine if toxic byproducts, such as dioxins, form during combustion, landfill fires, and evaporation of landfill leachate using landfill flare, and evaluate the presence of flame retardants in MSW leachate. Transformation products, such as debrominated or hydroxylated flame retardants, should also be evaluated as part of this effort.
- b. Evaluate the use of shredder residue (ASR, ESR) and C&D fines for their ability to leach BFRs if used as ADC.
- c. Measure the presence of flame retardants in groundwater surrounding older landfills with higher risk of leaking (in operation earlier than the 70s and the 80s) and compare to modern landfills to evaluate the effectiveness of the current landfilling practices in containing flame retardants.
- d. Evaluate whether flame retardants can be contained effectively when they are landfilled separately from the rest of MSW.
- e. Evaluate occupational exposure to flame retardants for solid waste workers, e.g., in dust particles at transfer stations and facilities, especially during compaction of furniture and other items containing flame retardants. Occupational exposure of C&D waste facilities workers should also be evaluated, especially if waste is sorted and recycled. This should include workers at C&D waste generation sites, not only waste disposal sites.
- f. Perform risk assessment to evaluate whether the exposure to BFRs from landfills poses a considerable risk to humans and the environment that would require mitigation.
- g. Evaluate leachate treatment methods that could reduce the transfer of flame retardants from landfill to the environment. This may involve the evaluation of the current leachate treatment practices as well as development of novel methods. Research on chemical and biological treatment methods should involve evaluation of byproduct formation.
- h. Conduct life-cycle analyses and evaluate the CO₂ footprint of proposed mitigation strategies.

5 Mechanical Recycling of Flexible Polyurethane Foam

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Co-authors: Bob Clark and Lynn Knudtson

Mechanical recycling of urethane foam is done by grinding scrap foam into a fine powder, using post-industrial foam and post-consumer foam.

5.1 Recycling Methods and Process

Flexible polyurethane foam (FPF) waste is generated from manufacturing trim scrap as a byproduct of industrial fabrication and at end-of-life for a number of consumer and industrial products such as upholstered furniture, mattresses and mattress pads, automotive interior parts, packaging, and healthcare items. End-of-life carpet cushion also may be recovered and recycled for use in producing new bonded foam carpet cushion.

Flexible foams mixed with flame retardants historically have been used in the production of upholstered furniture and interior parts for vehicles.

While there have been several attempts to commercialize foam scrap recovery from vehicles at end-of-life, these efforts have not proved to be economically or technologically viable. Vehicle residue after metal shredding tends to be very finely ground particulate (fluff) and is of limited value as an additive to chemical raw materials used in foam production or for use in the production of bonded polyurethane foam products. On the other hand, use of recovered and recycled foam in the production of carpet cushion has been very successful.

Since the introduction of polyurethane foam carpet cushion in the late 1960's, the market share for bonded carpet cushion has grown to achieve significant consumer acceptance. Among available carpet pad options, which may include bonded carpet cushion, fiber pad, latex and synthetic foam rubber, virgin polyurethane foam (prime), and froth polyurethane cushion, more than 85% of the market belongs to bonded polyurethane cushion products.

Bonded cushion products are manufactured by blending varying portions of recovered post-industrial and post-consumer scrap with a polymeric binder. Under pressure and steam, a composite bonded product results, made up of countless individual pieces of scrap that may have originated from many points on the globe, having various colors and physical properties, including FR and non-FR mixed types. In 2015, from U.S. sources, approximately 800 million pounds of FPF waste (combined post-industrial and end-of-life post-consumer scrap) was recovered and about 200 million more pounds of scrap were imported mainly from Europe. This volume of collected scrap was mechanically processed and used as a raw material feedstock in the manufacture of bonded foam products.

The recovery of foam trim scrap from various end-use industries typically involves a pick-up or delivery logistic. Recovery of post-consumer foam waste is currently focused on recovery of used foam carpet cushion during the installation of new carpet. Known as "take up," the used foam pad is typically removed by the new cushion installer and taken to a collection point, where "take up" scrap gathered from a number of different new carpet installations is combined until the collection container is ready for pick up by a recycler or scrap foam broker. Foam scrap from a number of containers may be combined and baled for over-the-road shipment to another consolidation point, or filled trailers may be taken directly to a bonded foam manufacturing site.

Post-consumer scrap is utilized in bonded carpet cushion production for two main reasons: 1) there is not adequate supply of suitable post-industrial scrap to meet the total U.S. scrap feedstock requirement, and 2) post-consumer scrap is necessary to produce higher density grades of bonded cushion.

Once delivered to a bonded foam producer, scrap may be stored, or baled foam opened and inspected for immediate use. Pre-processing includes opening bales for a visual inspection and/or magnetic screening to

prevent foreign objects from entering the shredding and grinding process. Post-industrial scrap may be graded by estimating density and hardness, and checking for excessive moisture. Bales of foam scrap typically contain foam products of differing color, scrap size, density and hardness. With the exception of bonded carpet cushion “take up,” there may be little consistency from lot-to-lot and, with such variation, there is no feasible way to perform more than a simple grading assessment. Therefore, the inspection and separation process is based almost exclusively on experienced knowhow, rather than quantifying properties. There is no known way to effectively screen foam scrap for FR content.

Bales of post-industrial trim scrap are more likely to be identifiable by end use. Trim scrap gathered from a foam fabricating distributor typically contains pieces of outside foam top skins, side and bottom materials, and usually will be visually different from scrap generated from upholstered furniture manufacturing, automotive, packaging fabrication, or mattress production. Post-industrial scrap is also graded and segregated based on density.

Mechanical processing includes shredding and grinding the scrap into small chunks with sizes large enough to retain the foam support and resilience, and small enough for an adequate surface area to bond together. Effective sizes are between 0.5 and 1.5 inches in diameter. The chunks are then blended together based on a “recipe” for the type of cushion being manufactured. A polymer binder is added to the blend, and the mixture is bonded and cured under high-pressure steam into blocks or “logs,” before being sliced or peeled. FRs are not added to carpet cushion; however, FR substances may be present in post-industrial scrap resulting from the fabrication of foam parts for some automotive, transportation and aviation applications, furnishings for use in high risk settings, and in much of the post-consumer bonded carpet cushion collected as “take up” by carpet installers. Scrap obtained from these sources is often visually distinguishable and may be segregated for “blend down” bonded foam formulations reducing the content of FR contamination.

Blend down formulations began in the early 2000’s as carpet cushion manufacturers became aware of the possibility of PentaBDE contamination, mainly found in California TB117-2000 compliant post-industrial foam used for upholstered furniture, and in some of post-consumer “take up” collected around the country. Using blend down formulations, bonded foam manufacturers were able to combine amounts of scrap having suspected PentaBDE content, with known “clean” scrap without PentaBDE content to produce new bonded products having minimal PentaBDE impurities. As blend down processing continued, and furniture foams were modified to remove PentaBDE content, bonded foam manufacturers were able to produce products that complied with PBDE content restrictions as imposed in a number of states. In states having PBDE content restrictions, 0.1% by weight PentaBDE was typically allowed for unintended impurities. Through random inventory sampling and third-party GS/MS testing, the U.S. carpet cushion industry demonstrates an ability to achieve this target level for maximum PentaBDE impurities.

In 2004, the U.S. foam industry discontinued use of PentaBDE in flexible polyurethane foam production, but California TB 117-2000 still mandated that foam and other resilient materials used in upholstered furniture pass a small open flame qualification test. This regulation essentially created a requirement for combustion-modified foams for use in upholstered furniture. While use of PentaBDE FR additives ended, until 2014 FR additives were still needed to satisfy the long-standing California TB 117-2000 furniture flammability standard. When TB 117-2000 was updated, FRs were no longer required, creating a supply of “clean” (lower or no FRs) post-industrial trim scrap from the U.S. upholstered furniture industry for use in bonded foam cushion manufacturing. However, there is a 10-year legacy of post-industrial and post-consumer scrap that may contain larger concentrations of PentaBDE-substitute FRs than the original products containing PentaBDE FR additives. Because of this, the Healthy Building Network suggests more frequent testing for a wide range of flame retardants in recycled FPF feedstocks, and until the feedstock is free of flame retardants, post-consumer recycled content foams are not recommended in building products where their use potentially exposes workers, installers, children, and other vulnerable populations (Stamm 2016).²⁰

²⁰ Healthy Building Network report is available here: <http://healthybuilding.net/uploads/files/optimize-recycling-fpf-report.pdf>

To manage concentrations of these replacement FRs (typically TDCPP), blend down formulations are still applied, but more time is necessary to reach optimal (0.1% by weight). Measurement of non-PentaBDE FR additives in “take up” scrap is not yet technically feasible, or cost-effective. Assumptions are therefore made that the scrap in question contains a maximum FR concentration. Without a practical means to test for FR content, it must be assumed that “take up” scrap contains a maximum amount of TDCPP content. Although very unlikely, “take up” may contain 100% FR foam that originated as TB-117-2000 compliant furniture trim scrap. If this is assumed, the maximum FR content would be about 12% for blend down purposes. If 0.1% is the target concentration for FR impurities, a few years may be needed for new bonded foam products to uniformly reach this target level. In the meantime, where restrictions on FR impurities have been imposed, and when there is not sufficient “clean” scrap for blending, scrap suspected of having high FR content may need to be disposed of rather than mechanically recycled as bonded carpet cushion. Unfortunately, current disposal options are very limited and, in many cases, landfill may be the only available disposal option.

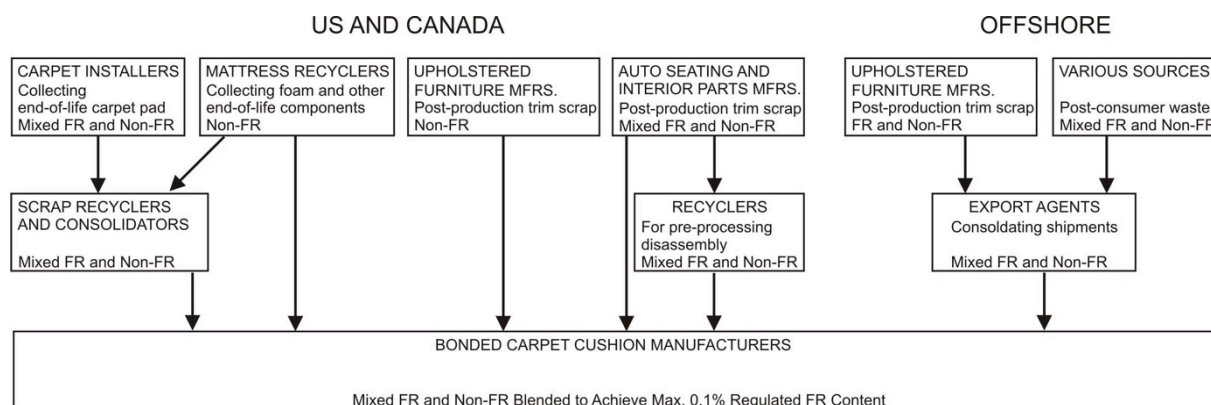


Figure 5-1 Stocks and flows of U.S. and Canada foam recycled into bonded carpet cushion. Source: Used with permission from the [Polyurethane Foam Association](#).

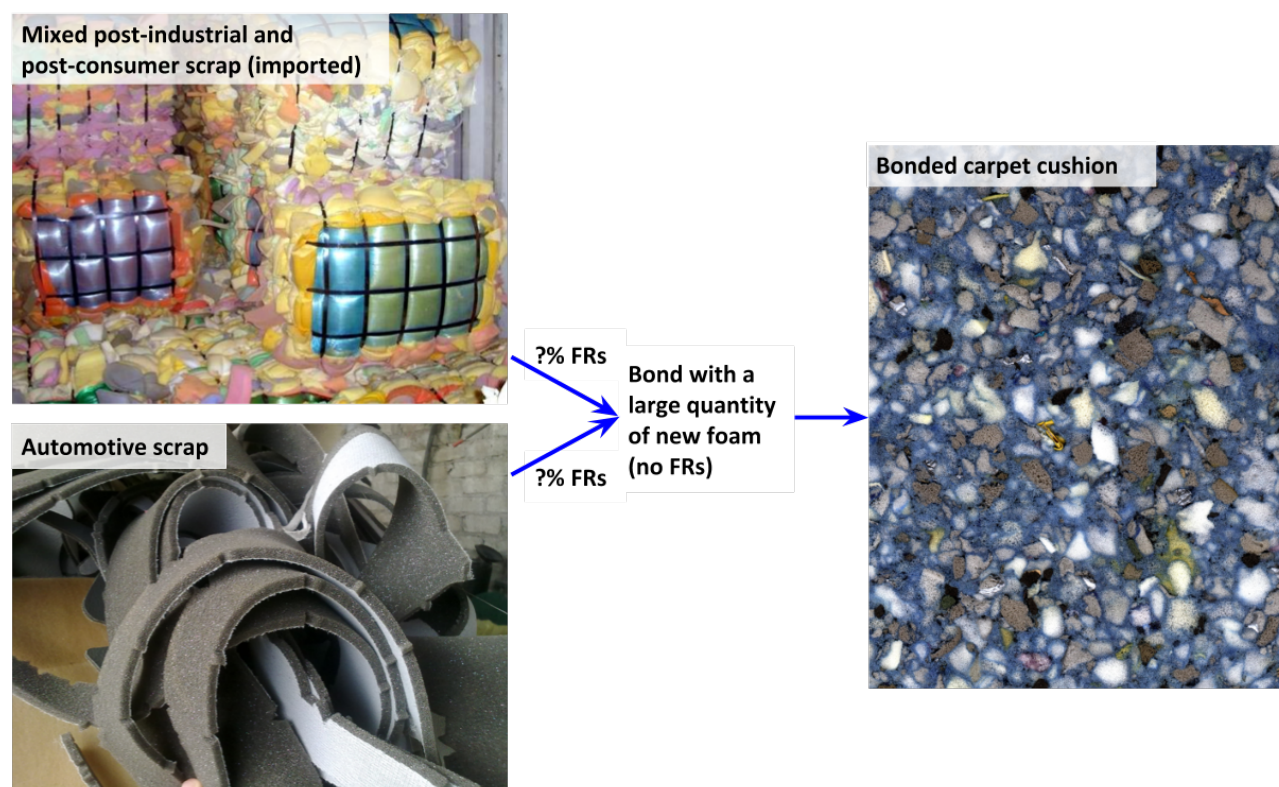


Figure 5-2 Scrap from multiple sources is bonded with new “clean” FPF to create the bonded carpet cushion (right). Source: Used with permission from the [Polyurethane Foam Association](#).

5.2 Review of Potential Health and Environmental Impacts

There are a few studies that evaluate potential FR exposure among carpet cushion installers and bonded cushion production workers. As a result, the exposure and consequential health effects for workers are unknown. In 2004 researchers measured emissions on a selection of bonded carpet cushion.²¹ The test, ISO16000²² was performed in an emissions test chamber over 72 hours at 23°C/50% RH, applying an air exchange rate n of 0.5 per hour and a chamber loading L of 0.4 m²/m³. Air samples collected from the chamber were analyzed and there was no detection PentaBDE.

One study by Stapleton et al. (2008), measured serum concentrations of PBDEs for foam workers ($n=12$), carpet layers ($n=3$), and a control group ($n=5$). Total PBDE concentration were 160, 178 and 19 ng/g lipid for the foam workers, carpet layers, and control group, respectively. Of the congeners detected, BDE-47, 99, 100, and 153 made up 90% of the total PBDE. While the sample numbers are low, comparisons with the national health and nutrition examination survey (NHANES) data set on the general U.S. population show that the PBDE levels for the foam workers and carpet layers had levels nearly a magnitude higher.

Since PentaBDE is no longer used in U.S. foam production, these results are only helpful as guidance that larger sample sizes are needed for meaningful comparisons. There are no studies available that evaluate possible foam worker exposure to PentaBDE substitutes.

California has identified TDCPP as a substance known in the State to cause cancer in humans. A Maximum Allowable Dose Level (MADL) of 5.4 µg/day has been established, representing 1000x the known dosage known to cause cancer in animals. Exposure doses associated with the removal or production of TDCPP contaminated carpet cushion are unknown. The volatility characteristics of possible TDCPP impurities in bonded carpet cushion have not been determined.

5.3 Examples and Case Studies

5.3.1 The Case in California

Although there were no specific flammability performance requirements for carpet cushion, manufacture of bonded cushion products from available scrap sources involved use of California TB 117-2000 compliant foam containing PentaBDE (BDE congeners with a phosphate carrier). Projections were made regarding the possibility of reducing the estimated PentaBDE congener concentration of 0.25% - 1% by weight (2004) for medium density bonded cushion, and 2.0 – 2.8% by weight for higher density bonded cushion to no more than 0.1% by weight. A rather long timeline in excess of 10 years was provided and the concept of blending PentaBDE contaminated scrap with non-PentaBDE scrap was validated through commercial trials and spot testing. Noticeable results took several years, and by 2009, the average PentaBDE concentration had been reduced to less than 0.3 % by weight.²³ In 2011, spot tests showed the average had dropped to less than 0.1% by weight. By 2012, PentaBDE concentrations were reaching detection limits. Industry believes similar results can be achieved for management of PentaBDE substitute contaminations through mechanical recycling. However, with the case of PentaBDE substitute contaminations, higher concentrations are likely, and a longer timeline may be needed to achieve desired concentrations. The timeline may be further delayed if limited supplies of “clean” FR-free scrap must be allocated for production of bonded foam products for sale in states where concentrations of PentaBDE substitute impurities could be limited.

5.3.2 Estimates of PentaBDE Substitute Contamination Concentrations

Management of PentaBDE substitute content through mechanical recycling requires an understanding of potential contaminant concentrations. Blending ratios of potentially contaminated scrap with FR-free scrap must be based on estimates, models and supply chain assurances. There is no known practical way to perform field testing to measure potential FR content when the content does not contain brominated components. Even when there is possible bromine detection (XRF spot checks), such detection does not

²¹ “Volatility of Penta Bromodiphenylether (PentaBDE),” Carpet Cushion Council, the proceedings of the Polyurethane Foam Association Technical Conference, October, 2004

²² ISO 16000-Parts 3, 6, 9, & 11

²³ Source: Polyurethane Foam Association

reveal the possibility of other FR contamination or actual concentrations. With suspected contaminated post-consumer “take up” or post-industrial trim scrap that originates from industries that may still require foam products with flame resistant performance, without definitive information, bonded foam manufacturers must assume there are maximum concentrations of FR impurities and blend accordingly with “clean” foam to achieve desired end product concentrations. This does not contribute to efficient use of “clean” scrap.

As discussed, PentaBDE substitute concentrations may be much higher in the waste stream now that PentaBDE has been eliminated from domestic manufacturing. The commercial PentaBDE product was a blend of PentaBDE components and a phosphate carrier. The commercial PentaBDE product could have been used in low density furniture foams in concentrations as high as 15% by weight, but the active PentaBDE component content represented only a small portion of the total PentaBDE FR additive product. So, from the late 1970’s through 2004, the actual concentration of PentaBDE components in California TB 117-compliant foam was relatively low. PentaBDE concentrations varied with foam densities, but the active PentaBDE components probably averaged about 4% by weight across the spectrum of densities used in California TB 117-2000 compliant foams. PentaBDE substitutes did not necessarily have the same flame retardant performance efficiency as PentaBDE. Nor, did the substitutes all have significant carrier component content. In some cases, such as with TDCPP, the commercial product was mainly all TDCPP. Instead of an average of about 4% active PentaBDE content, the average TDCPP content across the spectrum of California TB 117-2000 compliant foam densities was likely closer to about 12% by weight. This created a significant inventory of legacy foam products that contain comparatively large concentrations of PentaBDE substitute FRs, beginning with foam produced from around 2000 and carrying through until the California furniture flammability standard was updated in 2013. Because upholstered furniture may have a useable life of as long as 20 years, a large volume of legacy products containing non-PentaBDE FR content will need to be managed for several years to come. Success managing PentaBDE-contaminated foam at end-of-life through blend down techniques and mechanical recycling provides guidance for the current and future waste management challenge.

5.4 Discussion

Mechanical recycling options are limited when it comes to FPF (PUR includes rigid foam and there are many recycling options). Many challenges exist for accurately measuring the concentrations and types of FRs in post-industrial or post-consumer foam when it is recovered for reuse. Since the 1960s, the bonded carpet cushion industry has diverted billions of pounds of foam scrap from landfills. Bonded carpet cushion represents a component that is important to the economic performance of the carpet industry and to foam manufacturers. Without an outlet for scrap, a number of industries would turn to landfill or otherwise dispose of the material. The carpet cushion industry developed methods for managing possible PentaBDE content in its products and achieved concentration objectives in advance of its own forecasts. Based on this experience, several underlying issues have been identified that could assist future efficient management of potentially FR contaminated foam waste at end-of-life.

5.5 Recommendations

Recommended areas for research and improved technologies:

- A need for practical and cost-effective ways to identify and quantify FR substances in potentially contaminated foam waste and bonded cushion products.
- There is a growing need for “clean” scrap as a bonded foam blending feedstock. Domestic sources of “clean” trim scrap are declining due to a trend toward use of offshore upholstered furniture manufacturing resources.
- Bonded foam production technology innovations are needed to support use of a growing supply of post-consumer scrap generated by mattress recycling. The amount of “clean” mattress foam that can be used in a “recipe” is currently limited.
- Testing is needed to develop a better understanding of existing PentaBDE substitute concentrations in the potential waste stream of existing carpet cushion. This will support future blend down “recipes.”
- There is a separate need for technologies and logistical support to help manage the future recovery and recycling of current “in use” upholstered furniture that may contain FR additives.

6 Mechanical Recycling of Waste Electrical and Electronics Equipment (WEEE) and End of Life Vehicles (ELV)

Primary Author: Brian Riise

Co-author: Roland Weber

Electronics and vehicle components, such as seats, consoles, wires and circuit boards, often contain flame retardants to meet safety standards. Recycling of these materials includes a multi-step pre-sorting and pretreatment process. The current technologies include shredding, as well as automated and manual sorting; these processes for WEEE and ELV are described in this chapter.

6.1 Technologies and methods

WEEE recycling process

Each year, 40-60 million tonnes of electrical and electronics equipment reaches the end of life globally (Baldé, C.P., Wang, F., Kuehr, R., Huisman 2015); a significant fraction of WEEE is plastic (Haig et al. 2012), possibly providing hundreds of millions of tonnes of plastic for recovery.

One method includes dismantling WEEE by hand. Plastics from TV's and monitors are often removed in this way. Ideally, this provides a more pure ABS and HIPS polymer fraction to be recycled. The polymers are often sorted by color and type before compaction into bales. In the U.S., much of this compacted material is exported to Asia.

Another method to recycle plastics from WEEE involves shredding mixed materials after removing cords and batteries. Metal is recovered from the shredded mixture, and the remaining material that is rich in plastics is known as electronics shredder residue (ESR).

The ESR material is sent to processors who separate and purify the plastics. The purified plastics may be compounded and pelletized so that they can be sold to manufacturers of new products. Mixtures containing BFR and PVC plastics are incinerated, which is costly and comes with potential health and environmental risks if not done properly. Mixtures of plastics, rubber and wood with low levels of BFR and PVC may be processed for energy recovery in cement kilns as a replacement for coal. This outlet is less expensive and more environmentally favorable than incineration, though strict limits on halogens and heavy metals must be met (Stockholm Convention 2015c). Small amounts of metals can also be enriched and sold for a positive value.

End of Life Vehicles (ELV)

In the U.S., nearly 13 million cars are recycled per year.²⁴ The cars contain nearly 150 kg of plastic, equating to ~2 million tonnes of plastic per year. One study suggests that 1.6 million metric tons per year could be recovered from ASR in the U.S., leading to a number of environmental and economic benefits (Damuth 2010).

The recycling process for ELVs is significantly more complicated than the WEEE process, because of the multiple components and materials. Much of the plastic, composites, and polyurethane foam end up in the final stages of ASR sorting. Dismantling, depollution, and shredding are the main stages for recovering and processing ELVs. ASR is often defined as the remaining 15-25% of the ELV's mass after the last shredding process when metals have been removed (Vermeulen et al. 2011).

Depending on the material being recovered for recycling, different post-shredder techniques in multiple steps are used to separate materials from ASR. Most plastics will be recovered in the secondary recovery processes. Recovering techniques include air classification, magnetic separation, optical sorting, manual sorting, drying, float/ sink separation (e.g., Vermeulen et al. 2011, Table 8). ASR plastic is generally not

²⁴ World Auto Steel <http://www.worldautosteel.org/life-cycle-thinking/recycling/>

recycled into other products that require a specific type of plastic. In few cases, the ASR itself may be incorporated into composites, asphalt, or concrete, where flame retardants would remain in the final product. The shredder residue is a fine power fluff that does not have value for foam production.

A small number of companies do separate and recover plastics from ASR, including MBA Polymers in the United Kingdom and Galloo Plastics in France. Other metal recyclers are also making progress into recycling these plastics, especially in Europe where the ELV Directive require 95% reuse and recovery from ELV (European Parliament and Council Directive 2000/53/EC) and high landfill costs encourage minimization of materials that are incinerated or sent to landfill. In the U.S., restrictions on PCB levels in products had prevented the processing of ASR until recently, but the low cost of landfill and a decline in the price of plastics (beginning in 2015) has discouraged companies from building such recycling operations in the U.S.

6.2 Review of Potential Health and Environmental Impacts

WEEE and ASR wastes include a wide diversity of plastics, including some plastics containing flame retardants (Shaw et al. 2014; Samsonek and Puype 2013; Abbasi et al. 2016). Analyzing plastics for the amounts and types of flame retardants is costly and inefficient for manufacturers of new products. This has increased the likelihood of products containing toxic flame retardants, where it is unsafe for them to be present. A study on black plastic food contact items found that thermal cup lids contained TBBPA and decaBDE with levels as high as 1294 mg kg⁻¹ (Samsonek and Puype 2013); the types of FRs associate them with WEEE recovered plastics.

In a study of 21 toy products, OctaBDE and DecaBDE were detected in 17 (DiGangi and Strakova 2015). Three of the products contained OctaBDE, and six contained DecaBDE at levels greater than 50 ppm. The Basel Convention COP12 sets two POPs content levels: 50 ppm and 1000 ppm. In a study of plastic toys in South China BFRs were detected in all monitored toys (Chen et al. 2009). In a study of plastic toys in Belgium PBDEs were detected in plastic toys but 10000 times higher levels of PFRs (and phthalates) were also detected (Ionas et al. 2014).

Despite the presence of various flame retardants and the fact that these flame retardants can end up at low levels in products manufactured from recycled WEEE plastics, a number of studies have shown environmental benefits of recycling plastics from WEEE in terms of reduced energy use, CO₂ emissions and various other environmental impacts (Wäger and Hischier 2015; Huysman et al. 2015; Shonfield 2008).

6.3 Case studies

WEEE Plastics Recycling in Japan

The Japanese Industrial Standard (JIS) for marking plastics for electronics and electronic equipment (JIS-C991221 was established to identify recycling plastics for electric home appliances, and includes marking the parts that contain flame retardants, and recycled plastics. These labels make transparent the flow of the material and any additives, such that a closed-loop recycling is efficient (Stockholm Convention 2015c).

In Japan, legislation covering the recycling of home appliances was implemented beginning in 2001²⁵. This legislation required the collection and recycling of refrigerators and freezers, televisions, air conditioners, washing machines and driers. Manufacturers of such equipment, including Sony, Panasonic, Mitsubishi and others, established separate companies to handle the recycling of these products. The legislation also encouraged design changes and marking of plastics to better enable recycling of these products in the future.

MBA Polymers

MBA Polymers has built and operates (along with its joint venture partners) plastic recycling facilities in China, Austria and the United Kingdom. The factories in China and Austria process plastics from shredded WEEE, and the factory in the United Kingdom processes plastics primarily from shredded ELVs. Products

²⁵ Ministry of the Environment, Japan, Available: <https://www.env.go.jp/en/focus/docs/files/20151112-96.pdf>

from these facilities are sold to manufacturers of plastic parts for the construction, electronics, automobile, office supplies, packaging and horticultural industries.²⁶

Dell

Dell has been using recycled plastics from WEEE for several years as part of a closed loop recycling program.²⁷ They have received a number of awards for their use of these recycled plastics in new products.²⁸ Their program includes collection of WEEE by Goodwill and hand sorting the plastics so they can be re-used.²⁹ The program is not without controversy, though, as some of the e-waste collected in the program was found to be exported illegally to China and other countries (Puckett, Hopson, and Huang 2016).

6.4 Discussion

The UNEP BAT/BEP Guidance document (Stockholm Convention 2015b) lists four main difficulties for recycling of WEEE plastics. 1) The first is industry tight specifications for types of plastic (purity); 2) There are 15 or more types of plastics mixed in WEEE; 3) Waste could contain POP-BDEs, which will remain in the recycled product, placing consumers at risk; 4) Manufacturers require larger quantities of plastic, which suggests that recycling should be encouraged more.

The largest costs associated with WEEE recycling are the separation of the plastics, and compounding. Many techniques have been developed, but a significant portion of the plastic ends up not being recycled. Currently, BFR and PVC plastics are often incinerated for energy recovery, but at a high cost compared to recycling.

6.5 Recommendations

- More research into developing a universal method for identifying commonly used flame retardants in mixed plastics waste.
- Testing is needed to develop a better understanding of existing halogenated DecaBDE substitute concentrations in the waste stream of existing products.
- Research into compositions of e-waste in the U.S., and recommendations for how to segregate so that FR streams may be isolated from non-FR plastics.³⁰
- Incentives for using recycled plastics in new products, such as the Electronics Products Environmental Assessment Tool (EPEAT).
- Regulations should be fairly stable, as changes to regulations lead to economic uncertainties that discourage investment in increasing capacity for legitimate recycling.
- Regulations should be harmonised supported by the Stockholm and Basel Convention process, ensuring safe recycling of plastic and polymers.
- It needs to be assured that toxic BFRs and PFRs and other toxic chemicals are not recycled into sensitive products such as toys, food contact materials, and other sensitive uses (Stockholm Convention 2015c).
- Regulations should encourage complete recycling locally to minimize transport costs, better control hazardous emissions and to create green jobs. Currently, regulations and economics incentivize exporting of WEEE plastics.

²⁶ MBA Polymers, Available: <http://www.mbapolymers.com>

²⁷ Dell, Closed Loop Recycling, Available: <http://www.dell.com/learn/us/en/uscorp1/corp-comm/closed-loop-recycled-content>

²⁸ PRW. "Dell honored for use of post-consumer recycled plastics" *Plastics News*, September 28, 2015. Available: <http://www.plasticsnews.com/article/20150928/NEWS/150929911/dell-honored-for-use-of-post-consumer-recycled-plastics>.

²⁹ Dell, Reconnect Program, Available: <http://www.dell.com/learn/us/en/uscorp1/corp-comm/us-goodwill-reconnect?c=us&l=en&s=corp>

³⁰ MBA Polymers Austria is successful because there are large and consistent feed streams containing its "target plastics". The consistency is because the EU defines what types of E&EE products go into the mixtures. In the U.S., on the other hand, there is no standard approach to handling e-waste. Some recyclers include a broad mix. Others segregate by product type or color as this gives them the best price when exporting the plastics. Others only process E&EE for which they get a processing fee (e.g., CRTs in California).

- Investigate occupational exposure to FRs and other hazardous substances during dismantling and recycling handling.

7 Chemical Recycling Technologies

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This chapter addresses chemical recycling processes for end-of-life foams and plastics containing brominated flame retardants (BFR). Polymers of concern are polyurethane (PUR) foams from furniture, mattresses, upholstery and building applications, expanded and extruded polystyrene (EPS and XPS) employed as insulation material of buildings as well as polymers like acrylonitrile-butadiene-styrene (ABS) or high impact polystyrene (HIPS) used in electric and electronic equipment.

In contrast to above discussed mechanical treatment processes, this chapter reviews chemical recycling processes including depolymerisation processes for polyurethane foams, which produces oligomers and monomers from polymeric PUR foams. These can be applied to synthesis of recycled PU. Other approaches like the CreaSolv® process apply chemicals to dissolve a polymer without affecting the chain length of the macromolecule. As the polymer does not react with the applied solvents, these dissolution based processes may be handled as mechanical processes. However, in this report we treat them as chemical processes due the application of chemicals and the fact that these processes require equipment significantly different from mechanical processes.

In addition, dehalogenation processes and extractive technologies are discussed, which eliminate halogens from BFR contained in the matrix or separates brominated flame retardants from the polymer matrix. Thus, the aim of the chosen chemical recycling processes differs significantly.

7.1 Technologies and Methods

7.1.1 Pre-Treatment

Pre-treatment of waste streams for chemical recycling may include shredding and sorting processes, whereas shredding is applied to enable feeding of waste as bulk material into treatment vessels and not considered as disintegration method. In order to reduce total treatment cost, coarse shredding is preferred.

7.1.2 Chemical recycling of PUR foams

PUR is produced by the reaction of di- or polyisocyanate with a polyol. Chemical treatment of PUR reverses these reactions and produces oligomers of the polyols and isocyanates. The names for these processes depend on the applied chemicals and catalysts.

Alcohololysis

Alcohololysis is a process where foam reacts with alcohol like methanol at an elevated temperature. If boiling points of applied alcohols are lower than the required reaction temperature, processes occur under pressure. Given the correct reagent and degradation conditions, this process delivers a high quality polyol, not only with low reaction temperature and short reaction time, but also with higher degradation efficiency. If bivalent alcohols (diols or glycols) are used, the term **glycolysis** is applied for this special kind of alcohololysis.

Degradation of a PUR foam has been reported by Asahi et al. (2004) by application of methanol in a temperature range from 160 to 300°C and at pressures up to 15 MPa, partly in the supercritical state of methanol. Decomposition percentages were over 90% at temperatures above 200°C. Reactions with 1,2-propanediol have been tested by Feng et al. (2004) and produced polyols and amines. Other glycolysis processes using grinded PUR foams reacted with diols above 200°C showing efficient production recycled polyols well comparable to virgin polyols (Aguado et al. 2011; Molero et al. 2010).

Most alcohololysis processes apply catalysts in order to reduce reaction temperatures and to achieve high degradation rates. Typical catalysts are diethanolamine or bases like NaOH or KOH. Depending on the

material, the reaction takes place in a single-phase or split-phase reaction medium. The latter is appropriate for flexible foam and produces rather pure polyols in the upper phase (Aguado et al. 2011).

However, the fate of BFR and especially hydrophobic PBDE in glycolyses processes has not been studied in detail yet. A treatment of PCBs with KOH and polyethylene glycol led to substantial dehalogenation (Velazco et al. 2015).

Hydrolysis

Hydrolysis is a steam (200°C) process of heating PU in an oxygen-free environment producing polyols and intermediate products that can be potentially recovered for reuse. These processes apply alkali metal hydroxides as catalysts (Wang and Chen 2003) or amines like diaminotoluene (Dai et al. 2002).

Hydroglycolysis

A hydroglycolysis process applies superheated water, catalysts and glycols. As reported by Nikje and Tavassoli (2012) good results were achieved by addition of PUR to water, diethylene glycol, water/sorbitol and include KOH or NaOH catalysts.

Aminolysis

Aminolysis is a depolymerization process using a degrading agent (i.e., diethylenetriamine) and NaOH as both a reactant and catalyst at around 200°C (Chuayjuljit, Norakankorn, and Pimpan 2002).

Extraction

In contrast to the above discussed processes, solid-liquid or supercritical fluid extractions of PU foams have been performed in order to remove additives like foaming agents or flame retardants from the solid PU matrix. Filardo et al. (1996) applied liquid and supercritical CO₂ as well as CO₂/propane supercritical mixtures to extract chlorofluoroalkanes (CFC) from rigid PU foams.

Solvent extraction of PU foam is a routinely processed in analysis of air samples for BFR, when PU foams are used a sampling trap. Extraction protocols vary extensively and make use of solvents like hexane, toluene or dichloromethane (Hazrati and Harrad 2007; Fromme et al. 2009; Chaemfa et al. 2008). It is highly effective as proved by recovery experiments with standards focused on PUF foams. However, technical scale applications of extraction processes are not in place for industrial scale removal of BFR from waste PU.

7.1.3 Chemical recycling of polymers from WEEE

A variety of studies have revealed the presence of brominated flame retardants in the casings of WEEE products (Schlummer et al. 2007; Morf et al. 2005; Wäger et al. 2012; Herat 2008). Polybrominated diphenyl ethers (PBDE), tetrabromobisphenol A (TBBP A) and 1,2-(2,4,6-bis-tribromophenoxy)ethan (TBPE) are the most common FR additives in thermoplastics from recent WEEE, whereas the presence of significant amounts of polybrominated biphenyls (PBB) has not been stated since 2000 (Riess et al. 2000). Each of these has a potential to build polybrominated dioxins and furans (PBDD/F) during the processing of the plastics. This includes compounding of BFR into plastics, injection moulding of BFR equipped granules, and recompounding of shred of BFR containing casings. The highest potential is reported for PBB, followed by octaBDE and decaBDE. TBPE and TBBP A may produce PBDD/F but not the highly toxic 2,3,7,8 substituted congeners (Weber and Kuch 2003). Therefore, PBB and PBDE have been regulated by the European RoHS directive and comparable acts throughout the world.³¹

Whereas the mentioned brominated flame retardants are mainly used in ABS and PS, phosphorous based FRs are applied in blends of ABS and PS, namely PC/ABS and PPO/PS (Roth et al. 2012).

Solvent-based plastic recycling processes make use of selective organic solvents, which are able to dissolve a target polymer, while not interacting with any non-target polymers. Such approaches enable efficient separation of dissolved target polymers from undissolved polymers, foreign materials and even co-dissolved

³¹ European Commission Directive, 2002/95/EG, Directive 2011/65/EU, Health and Safety Code sections 25214.9-25214.10.2

contaminants. After the polymer purification, the solvent is evaporated from the polymer solution again, and reused within the process.

Solvent based processes have been installed in industrial scale for PVC (Vinyloop, Italy), alumina coated PE films (APK GmbH, Germany) and BFR-free styrenics (Wietek, Germany). However, a general process concept has been developed and optimized at the Fraunhofer Institute IVV, in Germany, namely the CreaSolv® process (Figure 7-1). In this process, tailor-made CreaSolv® solvents target and extract polymers such as (E)PS, ABS, PP, PE, PET, PC, PBT or PA. After mechanical and extractive cleaning processes, the polymer is precipitated and dried. The entire process has low energy demand, and performs well in environmental impact assessment studies (Freegard et al. 2006).

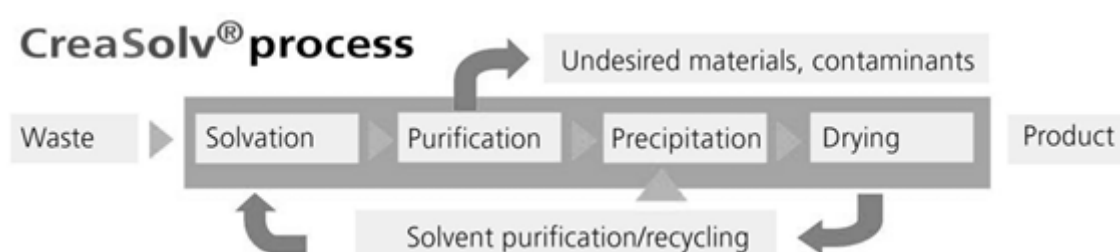


Figure 7-1 Principle scheme of the CreaSolv® Process a solvent based polymer recycling technique.

The purification step is rather effective in removing brominated flame retardant additives, which are extracted from the polymer solution and stored separately from the polymers upon the solvent recovery (Freegard et al. 2006). This allows reuse of recycled polymers in new products in compliance with the RoHS standard. Separated BFR fractions have to be disposed of separately, which is performed by high temperature incineration in standard practice.

Mechanochemical processes

Mechanochemical (MC) reactions have been reported as non-combustion technologies for the disposal of solid waste containing chlorinated persistent organic pollutants (POP) (Rowlands et al. 2004; Tanaka, Zhang, and Saito 2004). Compared with the traditional combustion technology, MC destruction does not require heating or off-gas treatment, consumes less energy, emits less carbon dioxide, and can avoid the unintentional formation and release of POPs such as PCDD/PCDFs (Rowlands et al. 2004). This process has been successfully applied to halogenated organic pollutants, such as DDT (A. K. Hall et al. 1996), hexabromo benzene (Q. Zhang et al. 2002), and PCBs (Aresta, Dibenedetto, and Pastore 2005). A more recent study tested tetrabromobisphenol A (TBBPA) in a ball mill using CaO or a mixture of SiO₂ and Fe as reactants (K. Zhang et al. 2012). This reaction resulted in a complete degradation of TBBPA within a 5 hour treatment, and suggests a better reaction yield of the Fe/SiO₂ approach compared to the reaction with CaO. Another study eliminated HBCD from contaminated soil by treatment in a planetary ball mill with Fe-SiO₂ as a reactant (K. Zhang et al. 2014). Using HBCD as a model for organobromine compounds, the study indicates the efficient destruction potential of mechanochemical treatment since HBCD was completely destroyed and transformed into inorganic bromide.

7.1.4 Chemical recycling of insulation foam made of expanded polystyrene (EPS)

For the last 50 years, HBCD has been added to expanded polystyrene (EPS) to comply with fire safety requirements. The Stockholm Convention has listed HBCD as a POP in 2013 with the exemption of use in building insulation and related continued production, leaving a legacy disposal issue (L. Li et al. 2016). During demolition or refurbishment of buildings, the EPS waste requires special handling due to the likely presence of HBCD and the volume of EPS foams.

One chemical recycling approach dissolves EPS in a limonene solution (Noguchi et al. 1998). Undissolved material is filtered, and polystyrene is recovered from the limonene solution by evaporation of the solvent. However, this approach does not remove HBCD from EPS.

The CreaSolv® Process has successfully separated HBCD in a laboratory and small technical scale trial (Schlummer et al. 2016). The process is a polystyrene specific solvent formulation that selectively dissolves the polymers from the waste EPS. Any undissolved matter can then be mechanically separated (i.e., inorganics, foreign polymers, glue), leaving a polymer solution. For the case of HBCD, it is co-dissolved in the first step, meaning that the undissolved matter is HBCD-free. In a separate extractive, purification step, a polystyrene gel is extracted from the co-dissolved solution, isolating the HBCD in a single phase. Once the polystyrene gel is dried, the polystyrene is ready for reuse. A demonstration industrial plant has been constructed in The Netherlands (Tange et al. 2016).

7.2 Review of Potential Health and Environmental Impacts

7.2.1 Fate and impact of BFR in PUR recycling

Alcoholysis and glycolysis can recover a polyol from polyurethane (PU). However, these processes do not separate the flame retardants from the polyol. The extracted polyol may be restricted or would require specific certification before reuse. Purification is technically feasible, but it is expensive and not state of the art.

Mechanical treatment of PU is a preferred end-of life option. A mechanochemical approach may be used for PU foam mixed with BFRs. Steps include: a) size-reduction into small particles, b) eliminate the bromine by adding CaO or Fe/SiO₂ and c) produce a bromine free PU feedstock. However, there are no reports on the purity of recycled PU, and the downstream use of eliminated bromine or related processing costs.

The following chemical treatment option would debrominate PU treated with BFRs, but is not at a scale to be economical.

During chemical recycling (alcoholysis/glycolysis) gaseous emissions into the environment can be minimized by proper condensation and trapping of glycolysis products, including brominated flame retardants and related degradation products, which may exhibit increased vapor pressures. The byproducts of chemical recycling include the dissolved polyols in a solution, and any other undissolved materials that are filtered out. If the flame retardants are not further separated from the polyol, then the solution will contain a co-mixture of the polyols and flame retardant. Extractions of flame retardants, because they are separated, enable a separate and safe disposal of the toxic chemicals. Chemical treatment options would debrominate PU treated with BFRs, but not at a scale to be economical.

If particle-bound or gaseous emissions of flame retardants are not well controlled at recycling sites, the exposure of workers cannot be excluded, necessitating strict monitoring. Worker exposure to emissions from these recycling processes has not been studied.

7.2.2 Fate and impact of BFR in chemical recycling of WEEE recycling

Mechanochemical ball milling may create by-products containing FRs, and/or their degradation products (Cagnetta et al. 2016). Especially in the case of highly brominated species like DecaBDE, the ball mill will dehalogenate BFRs successively and may lead to the production of more toxic lower brominated PBDE like tetra- to heptaBDE. This can be overcome by optimized treatment possibly resulting in useful products (Cagnetta et al. 2016). Other health and environmental impacts of such processes have not been studied, since this is not an industrial scale process.

Recycling of WEEE plastics by the solvent based CreaSolv® Process separates more than 98% of BFR from the polymer phase. However, the small amount of BFR that remains in the recycled polymers should be monitored for safety to comply with RoHS or POP legislation –a required certificate for users of recycled plastics.

Via this treatment route, human exposure to BFR from recycled plastics may still occur. Even if BFR migration from rigid plastics is a very slow process, these recycled polymers should not be used in sensitive applications like food contact materials or toys.

The CreaSolv® process was subjected to the evaluation of environmental impacts in a competitive analysis of treatment options for BFR containing plastic waste (Freegard et al. 2006). The study shows significantly lower environmental impacts compared to incineration processes or even simple mechanical recycling.

7.2.3 Fate and impact of BFR in EPS recycling

Transport of EPS should be properly monitored. Due to its low density, the materials can escape more readily, leading to a direct emission into the environment. The major share of EPS used for packaging is assumed to not contain FRs, and can be recycled by classical compression and remolding processes. In a study in Asian country HBCD was found in some packaging products (Rani et al. 2013). However, recent measurements of recycled PS from packaging EPS in Germany have revealed HBCD levels higher than 100 ppm if the collection is contaminated by EPS from building application.³²

Treatment of BFR containing EPS with the CreaSolv® process will result in: a) <100 ppm levels of residual HBCD in recycled product, which may exclude recycled plastics from repurposing into certain products; b) safe disposal of a HBCD fraction via thermal destruction with or without bromine recovery; c) low exposure via product levels.

Other available techniques and practices for EPS treatment include re-granulation of EPS into resin compounders without elimination of BFR. This is not allowed in Europe, and additional restrictions will follow due to the listing of HBCD as a POP in the Stockholm Convention. Selecting and sorting the EPS containing FRs using automated spectroscopic sorting is currently not available for EPS foams.

7.3 Examples and Case Studies

7.3.1 Recycling of EPS from insulations

In a recent pilot project, Schlummer et al. (2016) showed that EPS with up to 1.5 wt% HBCD was processed into solid polystyrene beads with HBCD levels <100ppm, using the CreaSolv® process. The beads were recycled by Sunpor into new Lambdapor EPS, meeting all specifications for application, such as for External Thermal Insulation Composite System (ETICS) applications. The removal efficiency of HBCD in the CreaSolv® process was higher than 99.7%.

Due to the global phase out of HBCD, there is an immediate need for a large-scale program. Based on the results of CreaSolv®, a representative group from various sectors of the European Expanded PolyStyrene (EPPS) industry and authorities met in late 2015. They supported the creation of a demonstration plant for recycling polystyrene (PS) building and construction waste, using the “CreaSolv® Process” concept. The decision was made in order to properly deal with the growing volumes of construction waste expected from the demolition of buildings in the coming decades (> 400,000 tonnes per year in Europe). The purpose of the foundation is to prepare the groundwork for a demonstration plant, whereas the plant itself will be operated by a separately funded entity.

As explained above, the proprietary solvent-based CreaSolv® Process dissolves PS coming from EPS and XPS waste while maintaining the polymer chain. The demonstration plant will only recycle end-of-life building and construction PS foam. A full bromine recovery will occur at the bromine recovery installation (BRU) at ICL-IP in Terneuzen. The bromine recovered from HBCD, will be re-used to make a polymeric flame retardant.

At the BRU in Terneuzen, a destruction efficiency greater than 99.999% for the HBCDD has been documented, bringing the destruction efficiency in line with BASEL-POP guidelines. The process recovers PS containing residual levels of HBCDD < 100 ppm.

³² Jörg Vogelsang and Martin Schlummer, Private Communication

The Creasolv® process can be described according to the text of the General Technical Guidelines on the Environmentally Sound Management of POP containing waste³³ in a series of steps. The first one is the dissolution of the polymer followed by the removal of the additives including HBCDD/wastes. This initial step should be characterized as D9 (Physicochemical treatment), as explained in Annex IV A of the Basel Convention. After this first step, there are two material streams: 1) the bromine containing stream, and 2) the polystyrene stream. Each stream undergoes a second treatment. The bromine containing stream is fed into a hazardous waste incinerator, leading to destruction of HBCDD followed by the recovery of bromine. These steps should be classified as D10 (Incineration on land) followed by R5 (Reclamation of other inorganic materials). The polystyrene stream is recycled in the production of new PS foam. This step would classify as R3 (Recycling of organic substances not used as solvents). The incorporation of the D9-D10/R5 treatment in the main body text of the General Guidelines will allow the factory in Terneuzen to operate within an agreed legal framework.

7.3.2 Recycling of ABS and HIPS from WEEE

The CreaSolv® process has also been applied to WEEE plastics in several trials. Pre-sorted plastic shred from small WEEE appliances had BFR amounts reduced by 98% (Schlummer et al. 2006). The approach was positively evaluated in terms of technological, economic and environmental performance in a global study on recycling options for BFR-containing waste.

After a trial period, the PolyResource Project (Schlummer, Mäurer, and Altnau 2012) optimized the process for economic efficiency, which did not reduce the cleaning efficiency. With only three consecutive cleaning steps, BFRs were eliminated by 98.4%.

Currently, the CreaSolv® approach is part of the European CloseWEEE project.³⁴ The plastics are first presorted by density. Then, an industrial scale XRT tool sorts bromine and chlorine containing plastics. This project recovers the ABS, PS, bromine and the BFR synergist antimony trioxide from the bromine positive fraction. The project is still running a trial, however, separation of these four fractions works well at a small technical scale.

Once BFRs are separated from the polymer matrix and the CreaSolv® solvent, they are destroyed at thermal destruction facilities built for handling these types of chemicals to avoid de novo formation of PBDD/F and PXDD/F. Alternatively, the BRU process may be discussed as a treatment option. This technology is globally available at two bromine industry sites, which uses the off-gas of thermal destruction to recover chlorine and bromine. The chlorine and bromine may then be used for new and safer polymeric brominated flame retardants. However, this process cannot be used if the bromine rich feed contains too high levels of catalytically active metals (e.g., copper), which may increase formation of PBDD/F.

7.3.3 PUR recycling

Troy Polymers, Inc., holds a patent for recycling of polyurethane foam scrap from shredder residue into polyols (Sendjarevic 2004). This process is best suited for PU foam scrap from shredder residue, which is a mixture of PUF different polyether and polyester polyols, and isocyanates, TDI and MDI. In addition, such shredder residues contain other types of cellular foam and fluff of non-PU materials.

The process starts with subjecting PU foam to glycolysis, followed by filtration of the liquid glycolyzed product. In stage two, the glycolyzed products are used as initiators in a propylene oxide reaction to prepare new PU polyols.

Sendjarevic (2007) describes several successful laboratory glycolyses with two different types of PU foams recovered from SR. At its highest efficiency, laboratory trials reached an 80% conversion into initiator liquid. At its lowest efficiency, 50% of mixed PU materials separated by an automated separation process from ELV shredder residue were converted into the initiator liquid. In both cases, glycolysis was performed

³³ BASEL Technical Guidelines on Environmentally Sound Management of POP Containing Waste are available here: <http://www.basel.int/Implementation/POPsWastes/TechnicalGuidelinesarchives/tabid/2381/Default.aspx>

³⁴ More information on the CloseWEEE Approach is available here: <http://closeweee.eu/closeweee-approach/>

with dipropylene glycol using KOH as a catalyst. Both TDI- and PMDI-based flexible foams were prepared from the novel recycled polyols created by propoxylation of the initiator liquids.

The objective of the study on foam preparation was to demonstrate the feasibility of these recycled polyols in PU foams without targeting any specific application requirements. Thus, it is important to emphasize that replacement of commercial polyols with recycled polyols was carried out without any adjustment in the formulation. Some properties were greatly affected by the introduction of recycled polyols. The chemical structure of these new polyols is significantly different from that of the two reference polyols. In order to develop products with targeted properties, formulations must be specifically created, which is a common procedure.

The fate of brominated compounds has not been reported in this study. It should be assumed that flame retardant additives are present in the polyols, and are recycled into the new product.

7.3.4 Recycling of printed circuit boards containing BFR

Like PU foams, printed circuit boards have been subjected to supercritical alcoholysis or high-solvent treatment processes in order to depolymerize the thermoset backbone of printed circuit boards (Zhu et al. 2013; Xiu and Zhang 2010). As most printed circuit boards contain reactively bonded brominated flame retardants, the products of glycolysis do contain brominated moieties. This method is highly desirable for metal recovery, making the process economically compelling. Non-thermal approaches may open a hydrometallurgical recovery route for noble and critical metals. However, currently there are no reports on eliminating bromine from glycolysis products, which complicates reusing glycolysis products, and may require a thermal destruction process for their final safe disposal.

7.4 Discussion

Chemical and solvent based recycling of BFR containing plastics like PU and EPS foams or thermoplastics and thermosets from WEEE is well studied in laboratory and pilot scale. These studies demonstrate their technical feasibility, which many of them have reached a level of technical maturity that justifies commercialization. However, from an industrial perspective chemical recycling has only played a minor contribution to the end-of-life management of these waste streams.

The main reasons for their absence on commercial scales are twofold. First, chemical recycling requires a higher investment cost, because the processes require large facilities in order to be economically viable. Even if local waste streams are higher than these required amounts, such large investments are considered more risky than installations of small mechanical plants.

Second, industry knowledge and infrastructure is biased toward mechanical processes. Chemical processes applied in the production of virgin polymers are much more complicated than mechanical recycling processes. Additionally, experts in polymer production are typically not involved in operating recycling plants.

In this respect, the steps that the European EPS and flame retardant industry has taken are highly promising. Combining these stakeholders helped address important issues in this process, including investment, legal challenges and also the harmonization of sorting and transport. In contrast to WEEE plastics and PU foams, the composition of EPS and XPS foams is rather common throughout the world. After phase-out of HBCD, the industry seems to agree on a novel polymeric BFR, making the waste stream much more standardized than for mixed plastics. Stakeholders in the end-of-life treatment thus have the same issues all over the world, which should inspire more co-operation.

The situation is much more complex with respect to WEEE plastics and PU foams, as different collection systems and use patterns exist between Europe, Asia, and North America. However, once the PS Loop recycling action is in place, PU and WEEE recyclers may be encouraged to adapt.

Chemical processes like extraction, CreaSolv® Process, or the mechano-chemical ball mill can separate bromine from the matrix. However, the fate of BFR in chemical recycling needs to be controlled effectively

in two ways: 1) to guarantee a safe separation from the matrix, which is intended to be reused in industrial cycles; 2) to comply with strict requirements of POP disposal regulations.

Thermal processes are preferred as disposal options for BFR. However, from the perspective of a circular economy, bromine recovery such as the BRU process at ICL, are highly promising. They can help to allocate BFR rich fractions into industrial environments, which are able to treat halogen containing waste economically and safely.

7.5 Recommendations

As separation of BFR from PUR foams is not performed in industrial scale recycling operations BFR emissions may occur during reprocessing. Chemical processes may help to improve this situation, however, at least in the initial commercialization stages such processes will not be economically feasible as the market for resulting products have to be developed first.

Chemical recycling options like the CreaSolv® process have been suggested for recycling plastics from waste EPS foams and WEEE. These processes compete with combustion processes, where industrial installations have been financed largely by public entities. The market situation currently has not supported installation of chemical recycling plants. Therefore, it is recommended that more funding be diverted for large-scale chemical recycling projects for PU, EPS and WEEE plastics. Similar programs to the European CloseWEEE program might prove successful in the U.S.

Lack of chemical process knowledge in the recycling industry has been identified as another obstacle in commercializing chemical recycling. Thus, education programs with waste management experts are recommended, as well as initiating co-operation of producers of virgin plastics and recyclers.

End-of-life management of BR in chemical recycling should enable the recovery of secondary antimony. Antimony is a rare element and used in multiple industrial fields, with a dominant application as flame retardant synergist. China produces 90% of primary antimony, which has been listed as one of the most essential metals. Facing this monopolistic supply situation, the chance of antimony recovery may provide a funding opportunity for chemical recycling of WEEE plastics.

There is also a need for pilot scale studies on the separation of halogenated flame retardants from products using alcoholysis, glycolysis, and aminolysis methods.

8 Destruction and energy recovery technologies

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As described in [Chapter 1.2](#), many FR chemicals are toxic, persistent, and bioaccumulate. Removing these compounds from the environment is desirable, but many of the FRs have chemical properties that make them difficult to destroy. The following technologies share the goal of destroying (rather than containing or recycling) toxic species, and come with an added benefit of reducing the mass and volume of the waste. Many utilize the waste material to produce energy (usually electricity, steam, or hot water) or reduce the need for supplemental fuels.

The desired products of complete thermal destruction methods are CO₂, H₂O, N₂, HX or X₂, and the oxidized forms of other elements such as metals and sulfur. However, most thermal systems can also produce products of incomplete combustion, including CO, NO_x, various hydrocarbons (including aromatic and halogenated compounds), and particulate matter (PM). The impact of these products and byproducts span the range from essentially innocuous chemicals (such as N₂ and H₂O) to greenhouse gases to some of the most toxic chemicals in the environment (dioxins and furans)(Baukal Jr 2003).

8.1 Technologies and Methods

Technologies that use high temperatures to destroy toxic flame retardants by breaking chemical bonds, include incineration and other oxidative processes, pyrolysis, gasification, plasma treatment, metal processing, and super critical water oxidation (SCWO). These technologies are sometimes known as incineration, thermal treatment, and waste to energy. Some of these methods are established in commercial applications, while others need additional research and development (Stockholm Convention 2015c). Thermal treatment systems, including incineration and combustion, continue to be an area of basic and applied research and technology innovation. This has led to numerous demonstration and laboratory-scale units, but converting them into industrial systems has proven difficult (Altarawneh et al. 2009).

In general, foams and plastics have high calorific values, so energy recovery is a viable option for these materials. For example, the energy content for Waste from Electrical and Electronic Equipment (WEEE) polymers is slightly below 40 MJ/kg (Tange and Drohmann 2005), and for PUR foam it is 25.6 MJ/kg (Brunner, Mark, and Kamprath 2000).

However, there are significant issues that must be taken into consideration, because of the halogen content and potential to create undesired byproducts such as halogenated dioxins and furans in thermal processes. Shared issues with these techniques include: byproduct formation, products of incomplete combustion, greenhouse gas emissions, waste transportation, siting and environmental justice, process monitoring, and ash treatment. The amount and type of flame retardant in the waste can alter different aspects of the destruction processes. Foam and plastics with chemical flame retardants cannot simply be added to an existing thermal process without some consideration of how the system will be affected.

There are many reviews, journal articles, and government and non-governmental agency publications describing thermal treatment methods, including the advantages and disadvantages of different technologies (M. Zhang, Buekens, and Li 2016; Altarawneh et al. 2009; Weber 2007; Karstensen 2008; Addink and Olie 1995; Shibamoto, Yasuhara, and Katami 2007; Stanmore 2004; Tuppurainen et al. 1998; McKay 2002; Peng et al. 2016; Zhou et al. 2015; Bosmans et al. 2013).

The following is a summary of the most common systems designed for waste destruction.

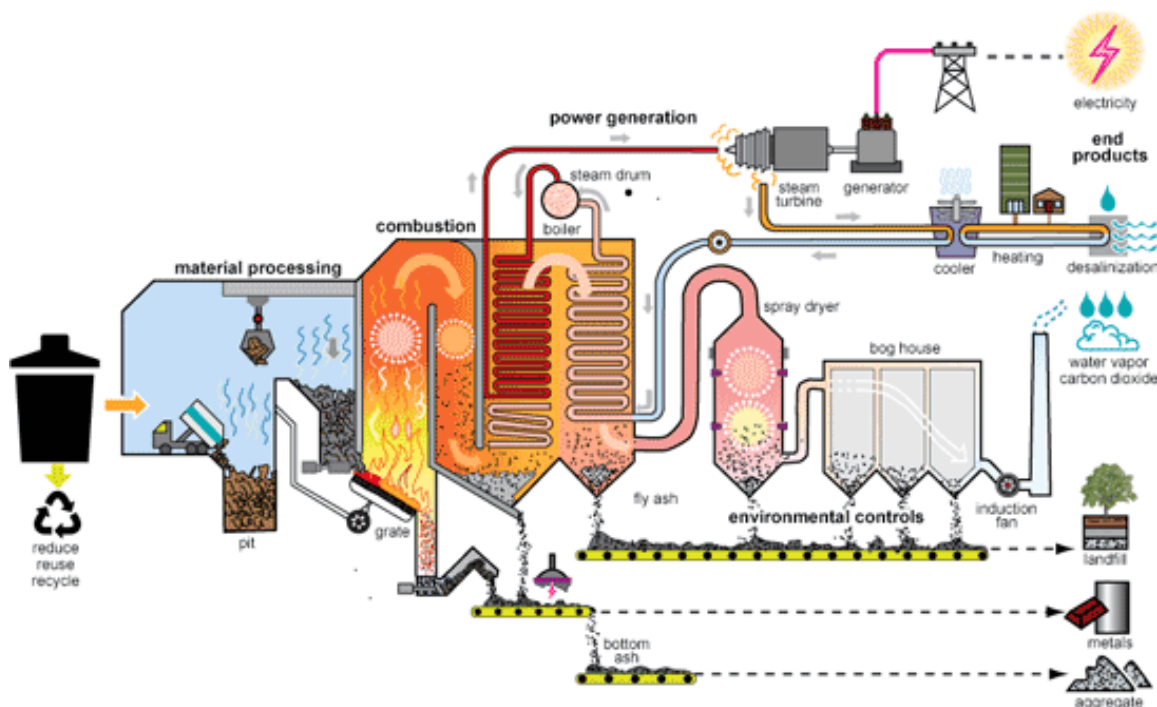
8.1.1 Incineration and Waste-to-Energy

Incinerators can be divided into three types: municipal waste, hazardous waste, and medical waste. The waste stream governs the type of operation used because of the specific regulations associated with handling and processing. Medical waste incinerators burn wastes produced by hospitals, veterinary facilities,

and medical research facilities,³⁵ and will not be discussed here. Hazardous waste incinerators handle wastes deemed hazardous according to regulatory definitions (see below), and have more stringent limits on their operation. They often share combustion and pollution control technologies with municipal waste incinerators.

Municipal and hazardous waste incinerators vary widely in their size, design type (e.g., moving or fixed grate, rotary kiln, fluidized bed), pollution control equipment, fixed location or moveable, and the type of waste and pretreatment needed (Niessen 2010; Klinghoffer, Castaldi, and Nzihou 2015).

Waste-to-energy plant



Source: Adapted from the National Energy Educational Development Program

Figure 8-1 Diagram of the waste-to-energy process. Source: United States Energy Information Administration (January 2016).³⁶

8.1.1.1 Process temperature considerations

While high combustion temperatures are favorable to the complete destruction of wastes, there are practical and material issues associated with real technologies. It should be noted that the carbon-bromine bond is less stable compared to the carbon-chlorine bond (270 vs. 330 kJ/mol), so a lower temperature than typically used might sufficiently destroy the brominated compound (Yang et al. 2012).

Higher temperatures are recommended for incineration when large amounts of halogenated FRs are present. The EU Waste Incineration Directive³⁷ mandates the following incineration temperature for various materials as described in Table 8-1.

³⁵ United States Environmental Protection Agency. (1995). Retrieved November 18, 2016, from <http://www.epa.gov/ttn/chief/ap42/ch02/final/c02s03.pdf>

³⁶ U.S. Energy Information Administration, Waste to Energy, http://www.eia.gov/energyexplained/index.cfm/data/index.cfm?page=biomass_waste_to_energy

³⁷ European Commission 2000, Directive 2000/76/EC of the European Parliament and of the Council

Table 8-1 Incineration temperature recommendations for various materials containing HFRs.

Material	Halogenated FR Content	Recommended Combustion Temperature
WEEE plastics	3-20% Bromine	1100 °C
WEEE plastic shredder	1.7-5.2% Bromine/0.1-4.4% Chlorine	1100 °C
PUR Foam –molded seating, arm, and head rests	0.5-1.0% BFR	850 °C
PUR Foam in carpet padding	2-5% BFR	1100 °C
EPS	0.5-0.7% HBCD	850 °C
XPS	0.8-2.5% HBCD	1100 °C

8.1.2 Conversion Technologies (pyrolysis, gasification, plasma gasification)

Gasification, plasma gasification, and pyrolysis are closely related and often referred to collectively as “conversion technologies” (the term typically encompasses other noncombustion technologies as well). They involve heating of waste in an oxygen-controlled environment to avoid combustion (Seltenrich 2016). The primary differences among them relate to heat source, oxygen level, and temperature, from as low as about 300°C for pyrolysis to as high as 11,000°C for plasma gasification (Stringfellow 2014). Conversion technologies are further distinguished from conventional combustion by the production of synthesis gas (or syngas) composed mainly of hydrogen and carbon monoxide, which can be burned or converted into other fuels (GSTC 2016). Similar to incineration and waste-to-energy, there is a wide range of system designs and operating conditions. These technologies are currently not listed as proven technologies for destruction of PBDE containing materials in the Stockholm Convention BAT/BEP guidance due to the lack of results from full scale studies.

8.1.2.1 Pyrolysis

Pyrolysis is the thermal breakdown of waste in the absence of air. Waste is heated to high temperatures (> 300°C) by an external energy source, without adding steam or oxygen (Lamers et al. 2013). There are two basic approaches of pyrolysis: standalone pyrolysis, and pyrolysis combined with an incineration/melting step.

8.1.2.2 Gasification

Gasification converts carbonaceous materials into carbon monoxide, hydrogen, and carbon dioxide by heating the material at high temperatures (>700 °C) with a controlled amount of oxygen and/or steam. The resulting gas mixture is called syngas or producer gas, and the mixture can be burned in a variety of combustion systems to produce energy or further reacted to produce a chemical product. Normally only the first treatment step is operated under oxygen deficiency conditions in staged combustion processes. The gases produced from the first step are then oxidized completely in a nearby downstream reactor area, or secondary combustion chamber (Quicker et al. 2015). Technically, these processes are classified as combustion processes with lower energetic efficiency than classic waste incineration (Lamers et al. 2013).

8.1.2.3 Plasmas

Plasma technologies employ an electric arc using an inert gas, such as argon in the absence of oxygen to heat materials to very high temperatures (up to 15,000 °C). Organic waste is converted into syngas, and metals and inorganics fuse into a slag. The syngas can be burned to produce energy.

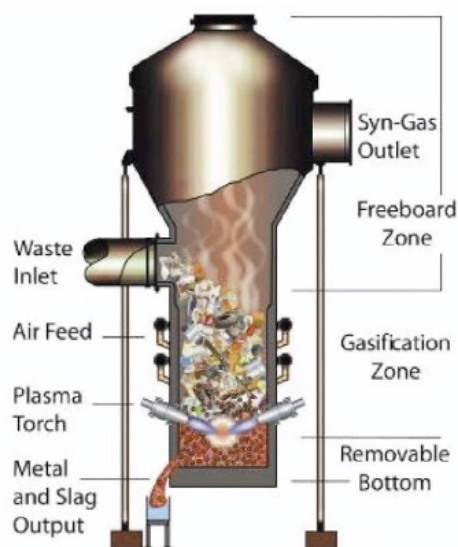


Figure 8-2 Schematic of Alter NRG system. Source: Alter NRG <http://www.alternrg.com>

8.1.2.4 Supercritical Water Oxidation

Supercritical water oxidation (SCWO) is a destruction technology for organic compounds and toxic wastes that makes use of the unique properties of water exhibited under supercritical conditions, that is, temperatures above 374°C and pressures above 3200 psia. Typical SCWO reactor operating temperatures and pressures are 600-650°C and 3400 psia, respectively. The oxidant is typically high-pressure air or oxygen. Organics and oxidant are miscible with SCW, creating good conditions for oxidation with minimal mass transport limitations, thus, organic materials are quickly destroyed to yield carbon dioxide and water. Heteroatoms such as chlorine, fluorine, phosphorus and sulphur, are converted to inorganic acids or to salts if sufficient cations such as sodium or potassium are present. If present, metals such as iron and nickel will produce the metal oxides.

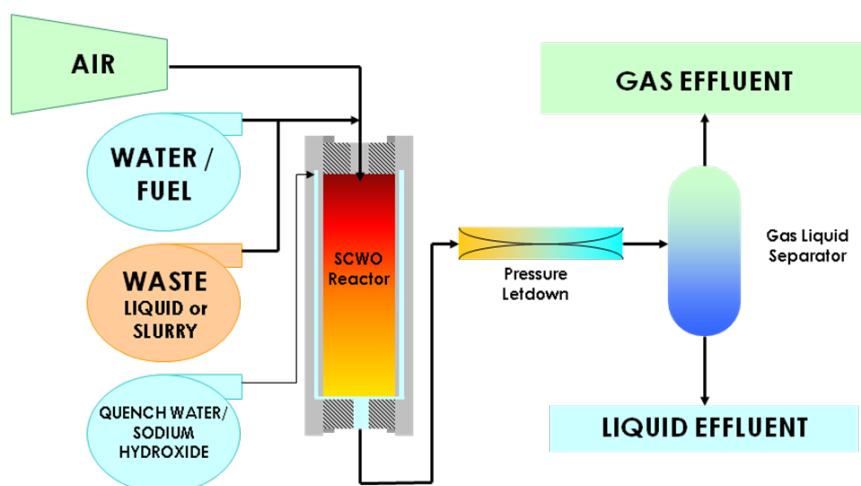


Figure 8-3 Simplified SCWO Flow Schematic. Source: General Atomics

8.1.2.5 Base Catalyzed Decomposition

The Base Catalyzed Decomposition (BCD) method destroys halogenated compounds, including high concentrations of POPs. The process treats liquid and solid wastes in a high boiling point hydrocarbon reagent mixture, such as oil-based fuel, sodium hydroxide, and proprietary catalysts. At 300° C, the process creates highly reactive hydrogen, which will in turn break down the chemical bonds of the toxic chemicals (Vijgen and McDowall 2009).

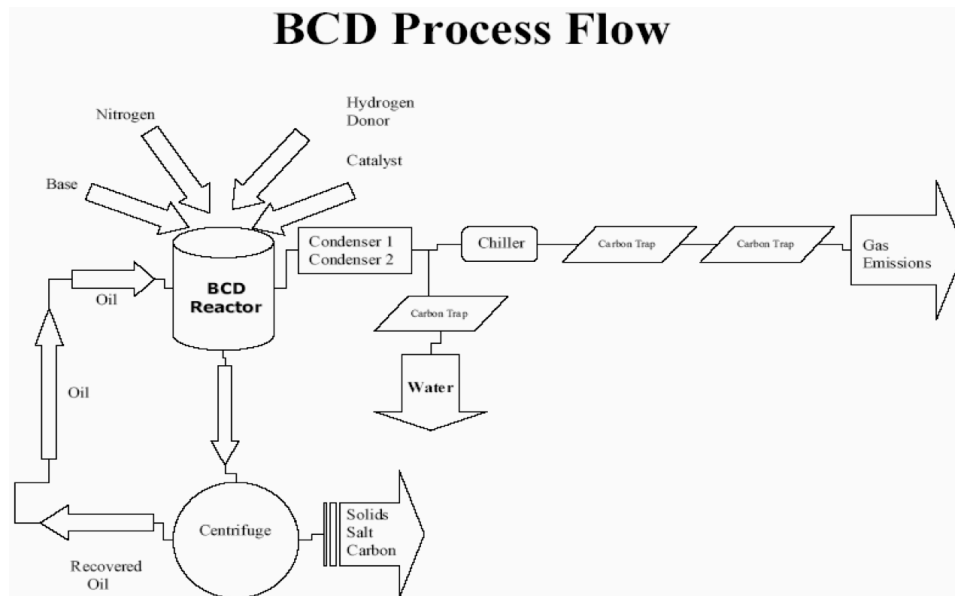


Figure 8-4 Illustration of the base catalyzed decomposition (BCD) process. Source: Basel Convention (Vijgen and McDowall 2009)

8.1.3 Cement Kilns

The process of cement manufacturing begins with extraction and crushing of raw materials such as limestone and shale, which are then blended with sand, mill scale and clay. Portland cement, the basic ingredient of concrete, is typically made in large rotary kilns, with temperatures in the range of 1,500 °C and residence times of seconds. Kilns can be as large as 6 m in diameter, and over 200 m long. The kilns are very energy intensive, and a variety of fuels can be used, including municipal and hazardous waste, tires, and biomass. The raw material, called a slurry, is fed at the high end of the kiln. The alternative materials for fuel are fed in a precisely controlled burning process at the bottom. This bottom section is where any foams or plastics with flame retardants should be fed into the process (LeHigh Hanson 2016).

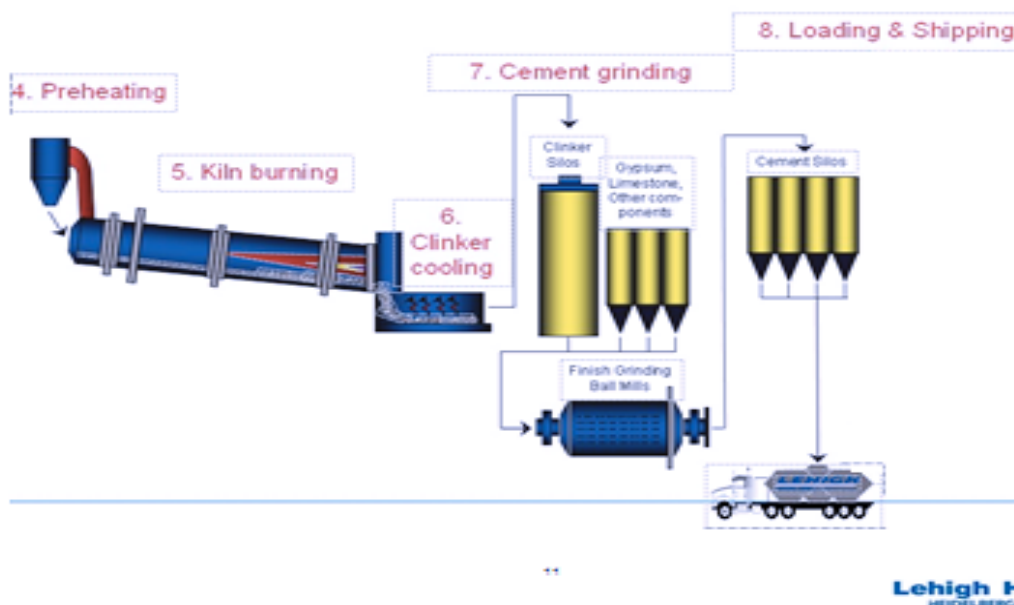


Figure 8-5 Cement manufacturing process in a simplified schematic. Source: LeHigh Hanson.

8.1.4 Other Thermal: Metal Processing

Some metal processing technologies, such as copper smelters, primary steel production, and electric arc furnaces, can involve halogen-containing materials. In most cases such material is mixed with other primary

(ore concentrates, anode slimes, etc.) or secondary materials, e.g., catalysts, industrial residues (Stockholm Convention 2015c).

8.2 Review of Potential Health and Environmental Impacts

In addition to the toxic flame retardants themselves, the primary health and environmental concern for destruction technologies is in the combustion of the halogenated compounds. There is a high likelihood of formation of PXDD/PXDFs with incomplete combustion if the appropriately high temperatures are not reached. The method of how the waste is fed into the chambers, and cooling can affect this process. Chlorinated dioxin and furan health risks have been extensively studied and are well known. The EPA regulations on dioxins are broad and include TSCA, CERCLA, SDWA, and the CAA. The World Health Organization has established total equivalency factors (Van Den Berg et al. 1998).

This Chapter reviews the regulations, and possible environmental and health concerns associated with destruction technologies, including the specific toxic byproducts due to halogenated flame retardants.

8.2.1 Health and Environmental Regulations

The U.S. EPA regulates thermal treatment methods based on the health and human risks associated with combustion practices. EPA Regulations require that an incinerator destroy and remove at least 99.99 percent of each harmful chemical in the waste it processes. When extremely harmful chemicals are present (e.g., hazardous waste), incinerator facilities must show that at least 99.999 percent of the contaminants are destroyed and removed. During thermal treatment of wastes, two ash streams can be produced. The bottom ash is typically composed of heavier material that remains on the combustor grate. Fly ash is large particulate matter that is light enough to be carried with the flue gases of the combustors or gasifiers. Importantly, all ash from hazardous waste systems is considered hazardous whereas ash from the thermal treatment of municipal waste contains non-hazardous bottom ash and hazardous fly ash. (EPA 2015) Modern cement kilns do not waste cement kiln dust; therefore, there is no “ash”. Everything including ash or cement kiln dust stays in the kiln and is incorporated into the product.

The national emission standards (NESHAP) for hazardous air pollutants for hazardous waste combustors (including hazardous waste burning incinerators, cement kilns, lightweight aggregate kilns, industrial/commercial/institutional boilers) implement section 112(d) of the Clean Air Act (CAA) by requiring hazardous waste combustors to meet HAP emission standards reflecting the performance of the maximum achievable control technology (MACT). The standards include a wide range of hazardous pollutants, including dioxins and furans, HCl and Cl₂, particulates (including fly ash, fine particles that escape the combustion zone with gaseous emissions), and certain heavy metals. Existing sources are limited to 0.20 or 0.40 ng TEQ/dscm for dioxins and furans. New or reconstructed sources are limited to 0.11, 0.20, or 0.40 ng TEQ/dscm.

However, the vast majority of cement kilns are not permitted to burn hazardous waste. There are 14 hazardous waste certified kilns in the U.S., and 94 kilns that are not certified. Those 94 kilns that are not permitted to burn hazardous waste are subject to the Portland cement MACT/NESHAP rule³⁸, and not the combustor MACT rule. Current NESHAP rule limits are provided in Table 8.2.

Table 8-2 EPA MACT and NESHAP rule limits for Portland cement existing and new source standards.

Pollutant Source Standard	Existing Source Standard	New
Mercury	55 lb/MM tons clinker	21 lb/MM tons clinker
THC	24 ppmvd	24 ppmvd
PM	0.07 lb/ton a clinker (3-run test average)	0.02 lb/ ton b clinker (3-run test average)
HCL	3 ppmvd	3 ppmvd

³⁸ See the EPA Air Quality fact sheet for Portland cement:

https://www3.epa.gov/airquality/cement/pdfs/20121220_port_cement_fin_fs.pdf

Organic HAP (alternative to Total Hydrocarbons)	12 ppmvd	12 ppmvd
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In the EU, technology requirements for incinerators are described and defined in the EU BAT Reference (BREF) document on waste incineration (Integrated Pollution Prevention and Control 2006). The Protocol on persistent organic pollutants sets legally binding limit values for the emission of dioxins and furans of 0.1 ng/m; TE (Toxicity Equivalents) for installations burning more than 3 tonnes per hour of municipal solid waste, 0.5 ng/m; TE for installations burning more than 1 tonne per hour of medical waste, and 0.2 ng/m; TE for installations burning more than 1 tonne per hour of hazardous (European Commission -Environment 2014) waste. As in the U.S., other pollutant emissions are also regulated.

8.2.2 Formation of Halogenated Dioxins and Furans

While there are many hazardous species that can be formed in combustion systems (including PCBs), dibenzo-*p*-dioxin and dibenzofurans (PXDD/PXDF) (typically called dioxins/furans or simply dioxins) from combustion systems that contain carbon, halogens, and oxygen are a major concern of many scientists, engineers, government agencies, and environmental groups. Their formation is discussed below and can be viewed as being representative of unintentionally formed POPs (including PCBs).

Dioxins are produced through two main mechanisms: formation from precursors and formation by de novo synthesis (H. Liu et al. 2012; Addink and Olie 1995). Dioxins can be created through the synthesis of various precursors, such as chlorobenzene and chlorophenol. These precursors are produced through incomplete combustion, or heterogeneous catalytic reaction on the surface of fly ash. De novo synthesis forms dioxins via macromolecule carbon and chlorine in fly ash at temperatures between 200 and 600 C. The mechanism of formation chlorinated dioxin/furans, biphenyls and naphthalenes and benzenes has been documented (Weber et al. 2001). Although the exact detailed reactions and mechanisms are complicated, there is a good understanding due to extensive research over the past 30 years. Yet, complicating factors still persist due to the heterogeneous nature of the waste streams and the usually unknown input conditions. Zhang et al. (2016) recently published a comprehensive review of this subject (M. Zhang, Buekens, and Li 2016).

For BAT incinerators it is not the chlorine content but the combustion quality that is the determining factor for dioxin formation. The hypothesis that fuel chlorine content and combustor flue gas PCDD/F concentrations are related was not confirmed by the data analyzed in the study by Rigo et al. (1995). However for non-BAT incineration or pyrolysis processes the chlorine content is the triggering factor for dioxin formation with extremely high dioxin release at high chlorine concentrations (Ikeguchi and Tanaka 2001; Ikeguchi and Tanaka 2000; Weber and Sakurai 2001).

It should be noted that air emissions of dioxins from 53 waste to energy plants in the U.S. have been reduced significantly over the past 25 years (shown in Table 8-3), and most of the air emissions are now from fires and open burning processes (Dwyer and Themelis 2015). However, the major dioxin release from BAT incineration and other thermal facilities is from ashes, which are often not accounted in dioxin release inventories. These ashes with their high dioxin and heavy metal content need strict management and control.

By their design BFR/CFR-containing materials have reduced flammability, which can result in increased incomplete combustion in facilities not equipped with BAT combustion equipment (Weber and Kuch 2003). Materials containing brominated aromatic compounds (e.g., PBDE; brominated phenols; Firemaster 550) are excellent precursors of PBDD/PBDF, therefore, the formation of more toxic compounds is a crucial parameter to evaluate during thermal recovery and destruction operations (Melber et al. 1998; Sakai et al. 2001; Vehlow et al. 2002; Weber and Kuch 2003; UNEP 2010). Because chlorine is normally present at relevant levels in PBDE-containing materials (e.g., WEEE plastic, ASR, PUR foam), the formation of brominated-chlorinated dibenzo-*p*-dioxin and dibenzofurans (PXDD/PXDF) can also comprise the highest

share of dioxin-like compounds (Hunsinger, Jay, and Vehlow 2002; Zennegg et al. 2009). Therefore the measurement of only PCDD/PCDF in such operations is not sufficient and rather misleading.³⁹

Table 8-3 WTE as a % of total dioxin emissions (g TEQ/year)

Source: Dwyer and Themelis (2015).

Year	1987	1995	2000	2012
Total controlled Sources	14,024	2,789	1,173	634
WTE as % of controlled emissions	67.7	43.0	6.6	0.54
Total of all sources	16,349	5,123	4,174	2,901
WTE emissions as % of all sources	58.1	23.4	1.8	0.09 ⁴⁰

Combustion engineers follow the “3-T Rule” when considering if complete combustion will occur: the **temperature** must be high enough to break chemical bonds present in the waste, the residence **time** in the reaction zone must be long enough for equilibrium to be reached, and **turbulence** should ensure that all parts of the combustor are well-mixed.

Well-designed and controlled combustion systems can effectively destroy dioxins and precursors, but there are some conditions that could lead to dioxin emissions. These include:

- Startup and cool down
- Off-optimal conditions
- Overload conditions, such as when a waste container ruptures or too much waste is loaded
- Incomplete mixing
- Non-functioning or faulty measurement devices
- Non-functioning or faulty pollution control equipment
- Leaking combustion chambers
- Catastrophic failure (e.g., rupture or explosion)

While these conditions may last only for short periods of time, there is concern that significant dioxin emissions could happen during these periods.

Even when combustion conditions are optimized, de novo synthesis of dioxins can occur. This happens post-combustion, and can be minimized by cooling gases quickly from higher temperatures through the temperature range of approximately 400 °C to 250 °C, and minimizing the amount of certain metals, such as copper on or in particulate matter known to facilitate dioxin and furan formation.

³⁹ The addition of bromine can result in reduced levels of PCDD/PCDF, partly by bromination of the chlorinated aromatics and formation of PXDD/PXDF.

⁴⁰ The most extensive study was performed in the United States, where the impact of the waste feed chlorine content on PCDDs and PCDFs emissions was analyzed on 155 facilities. The conclusion was: “The hypothesis that the amount or type of chlorine in the waste feed to combustion units is directly related to PCDDs/PCDFs concentrations measured at the combustion outlet is not supported by the preponderance of the data examined during this study.” A study included chlorine feed concentrations from less than 0.1% to 80%²⁰ (1900 test results, 169 facilities, MSWI, HWI, Hazardous Waste Incinerators, Hazardous Waste Fired Boilers, Cement Kilns, Biomass Combustors, Laboratory, Bench-, Pilot-Scale Combustors). The study showed no statistically significant relationship between chlorine input and PCDD/F stack concentration. A study later performed at the University of Umeå showed that the chlorine source and level are unimportant for formation of chlorinated organic pollutants at controlled combustion conditions.

8.2.3 Measurement of dioxin/furan congeners and TEQ

When both bromine and chlorine are present in a combustion system, there are >5000 congeners of PXDD/PXDFs, with several hundred 2, 3, 7, 8-substituted congeners. A complete chemical analysis is extremely complex and costly. At present, no brominated (PBDD/Fs) or mixed (PXDD/Fs) congeners have been assigned a TEF or TEQ value. For many compounds, particularly the mixed congeners, this stems from insufficient environmental and toxicological data.

To overcome this dilemma of instrumental analysis of the mixed halogenated PXDD/PXDF, monitoring by using accredited bio-assays measuring total dioxin-like toxicity like CALUX, DRCALUX or EROD is recommended (Stockholm Convention 2007). Their ability to assess such complex dioxin-like mixtures has been demonstrated at open e-waste recycling sites (Xiezhi Yu et al. 2008).

Corrosion caused by halogens

Both Cl and Br in combustion systems can cause corrosion in metal parts, with Br being especially corrosive (Ozturk and Grubb 2012). If bromine is considerably lower compared to the chlorine input, the corrosion is mainly caused by chlorine (Rademakers, Hesselings, and van de Wetering 2002). The process needs to be closely monitored and the economic benefits and drawbacks assessed for the respective facilities, including the cost of maintenance and repairs (Stockholm Convention 2015c). Operators of facilities with boilers are often reluctant to burn large amounts of bromine-containing waste (Rademakers, Hesselings, and van de Wetering 2002).

Removal of HBr and bromine in flue gas treatments

For all thermal treatment technologies, the behavior of halogens within the facility and the flue gas line need to be considered. Bromine is present in the flue gas both as HBr and Br₂. The ratio is influenced by, for example, the level of sulfur present. HBr, HCl, and other acid gases can be removed by the conventional removal technologies (dry/semi dry scrubbing with basic adsorbents, NaOH solution scrubbing, etc.). However elementary bromine in the flue gas need a reductive wet scrubber stage with the addition of sulphite or bisulphite (Stockholm Convention 2015c).

8.3 Examples and Case Studies

Some of the technologies described are well-developed, and results are available regarding destruction and emissions. While the developing alternative technologies show promise, pilot tests or full scale tests for destruction of BFR containing wastes from any of the technologies described here have not yet been published. Below are examples of technologies from UNEP technical fact sheets created from 2012-2014. While they are not officially published, they serve as a reference to describe the ability of these technologies to handle foams and plastics mixed with flame retardants.

This summary does not address non-POPs BFRs. Based on the available information, most of these technologies currently cannot be recommended for destruction of CFR and BFR containing wastes but would need additional basic research, as well as pilot and full scale tests.

8.3.1 Hazardous and Municipal Solid Waste Incinerators

Hazardous waste incinerators built with best available technology (BAT) can destroy BFR containing waste while meeting stringent release limits (Weber and Kuch 2003). Municipal solid waste incinerators (MSWI) built according to BAT standards can also be used for the treatment of BFR containing waste material (Mark, Fisher, and Smith 1998; Mark et al. 2015; Nordic Council of Ministers 2005; Hunsinger, Jay, and Vehlow 2002; Sakai et al. 2001). BAT waste incinerators operating according to best environmental practices (BEP) can co-incinerate BFR-containing waste material without significant releases of BFRs or unintentionally formed brominated or chlorinated dioxins (Sakai et al. 2001; Vehlow et al. 2002; Weber and Kuch 2003). Dioxin and furan flue gas emissions from different MSWI were reviewed by Zhang et al. (2016); Table 8-4 lists results from different incinerator sizes as well as a number of industrial waste incinerators (IWIs) as adapted from Table 1 in the Zhang et al. Note that very high levels of PCDD/PCDF can be formed during the solid fuel burnout of WEEE with a mixture of municipal waste (Hunsinger, Jay, and Vehlow 2002).

Table 8-4 PBDD/Fs and PCDD/Fs flue gas emissions from different incinerators

	PBDD/Fs Total TEQ (pg TEQ/Nm ³)	PCDD/Fs Total TEQ (pg TEQ/Nm ³)
Large-scale MSWIs (mean)	0.557	274
Small-scale MSWI-1	0.786	239
Small-scale MSWI-2	2.91	10,200
IWIs (mean)	4.17	242

Table 8-2 MSWI data from Zhang et al. (2016). The results above are from nine continuous large scale municipal waste incinerators (MSWIs), two different small-scale batch municipal waste incinerators (MSWI-1 and -2, and nine industrial waste incinerators (IWIs)

In general, polymer shredder waste from the electronic or transportation sectors is not suited for mono-incineration (Moakley 2010). Co-incineration of such high calorific shredder waste can be conducted in various types of incinerators.⁴¹ Wastes with a halogen concentration exceeding 1% can be disposed of in hazardous waste incinerators, or mixed with other fuels streams to reduce the total halogen concentration.

Non-BAT incinerators, small-scale incinerators and mobile incinerators normally cannot be used for the destruction of plastics and foams containing FRs due to their limitations in operation stability, secondary combustion quality, and flue gas cleaning technology (Stockholm Convention 2015c).

8.3.2 Co-incineration of Automotive Shredder Residue (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% ASR was co-incinerated (Jody et al. 2010), and up to 20% in a test in Sweden (Redin, Hjelt, and Marklund 2001). The co-incineration met the regulatory environmental limits. Flue gas emissions did not change significantly compared to the incineration of MSW. Due to the presence of heavy metals in ASR the concentrations of Zn, Pb, Sn, Sb, Cu and Co in the fly and boiler ashes increased significantly. For a test with co-incineration of 31% ASR in a MWI the respective concentrations of Pb and Zn were up to 18 and 16 times higher than the average baseline level (Mark, Fisher, and Smith 1998).

In some countries, bottom ashes from MSW incinerators are used as a secondary raw material in construction (Arickx et al. 2007; Vandecasteele et al. 2007). In the U.S. it is also common for the cement industry to use flyash and bottom ash from coal fired power plants for raw material substitute for alumina. Therefore, it is important to monitor toxic components (heavy metals, POPs) in the bottom ashes when ASR is co-incinerated (Vermeulen et al. 2011) to avoid environmental contamination 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 (Moakley 2010). In Switzerland some incinerators leach the ashes by acidic washing to remove the heavy metals.

8.3.3 Cement kilns

Cement kilns are increasingly used in waste management schemes in both industrial and developing countries (Holcim 2006; Reijnders 2007). Stable molecules (and dioxin precursors), including PCBs and HCB, need to be fed at the “hot end” of the kiln into the burner flame where temperature up to 2000° C and residence time of more than 2 seconds can produce a high destruction efficiency. This also assures the destruction of halogenated FRs in secondary fuels and the suppression of PBDD/PBDF formation at this

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. 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).

feeding point. BFR-containing waste, 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 (Stockholm Convention 2015c). Similar to PCB and other POPs, the treatment of 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, products and the bypass stack, should be carried out before any POPs waste is considered for routine disposal. Ideally POPs destruction projects are monitored continuously by long-term sampling of unintentional POPs and POPs in the feeding material (Weber 2007).

8.3.3.1 PBDE in soils

In one study, PBDE contaminated soil was fed at the kiln inlet at 975 to 1035° C (Yang et al. 2012). The PBDE destruction and removal efficiencies were 99.9997% and 99.9998%, respectively. PBDD/PBDF were detected in the flue gas at levels of around 0.01 ng TEQ/m³. This indicates that at high kiln inlet temperatures of 1000 °C BFR containing waste can be destroyed in a BAT cement kiln.

8.3.3.2 Auto-shredder Residue (ASR)

ASR as alternative fuel and mineral feedstock for cement production contains about 50 wt % of combustible matter such as plastics, foams and rubber, 40 wt % silicates, calcium, aluminum and iron (Boughton 2007; Vermeulen et al. 2011), and other heavy metals such as Pb, Cd and Cu. 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 were noted (Gendebien, Leavens, and Godley 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, Leavens, and Godley 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 et al. 2011).

8.3.4 Gasification

When evaluating gasification processes, it is necessary to distinguish whether gasification is only one step within a staged combustion process or if it is “sole” gasification, meaning that the target product allows variable use as (fuel) gas. The following focuses on gasification processes aiming to produce syngas or fuel gas. Major advances are postulated for these processes in comparison to incineration (Lamers et al. 2013). These include: higher electric efficiency by using the gases in combustion engines, lower emissions, and better slag produced by the high temperatures ($T > 1500$ °C).

8.3.5 Pyrolysis

One study compares, several advantages of pyrolytic treatment to treat MSW in comparison to waste incineration, including reduced emissions, more efficient use of pyrolysis oil and gas in engines and turbines, and better metal and carbon black recovery (Lamers et al. 2013; Quicker et al. 2015).

Information on long-term operation and economy on waste pyrolysis is lacking in the literature. Many attempts at implementing the pyrolysis technologies suffered from major problems. In general, the following aspects of pyrolysis processes are considered to be problematic (California Integrated Waste Management Board 2007; Lamers et al. 2013; Quicker et al. 2015):

- Reactors and process management commonly require high intensity material processing with according pre-treatment costs.
- Generated pyrolysis gases contain high concentrations of tars, impeding energetic utilization.

- Marketing of generated coke is hindered by low coke quality.
- Complex systems engineering requires high maintenance efforts.
- In some processes, fossil fuels are used for heating purposes.

8.3.6 Plasma

Plasma technologies have been successfully introduced internationally (e.g., in China and the UK) in recent years in the field of MSW and energy, and there has also been some progress in treating MSW from old landfills to produce valuable by-products.

The use of plasma technology in a treatment system was proposed for the cleanup of the Love Canal Superfund site (Niagara Falls, NY, USA) in the 1980s. The challenge was to develop a mobile technology that could achieve the high destruction and removal efficiencies (DRE) established by the U.S. EPA for PCBs, PCDD/PCDF, and other chemicals. The final design of the system directly introduced the liquid waste into a modified non-transferred plasma torch. Tests using actual PCBs achieved a DRE of 99.9999% to satisfy regulatory requirements. Despite the positive test results, operating permits were extremely difficult to obtain. Two years after the data was submitted, permits to allow additional testing were still not issued, and the unit never processed any targeted waste at Love Canal (Counts et al. 1999)

Two of the world's largest hazardous waste to energy conversion facilities operate in India, using Plasma Gasification Vitrification Reactors (PGVR), a combination of an atmospheric pressure, moving bed gasifier with plasma torches. Both plants together receive hazardous waste from more than 1800 industries (SMS, 12 January 2012). (Alt NRG-3, 2015) HCB was the only POP treated at full-scale.

A hazardous waste facility in Shanghai, China, successfully completed a >120 day operation in August, 2015. The facility processes 30 tonnes per day of medical waste and incinerator fly-ash, creating syngas and vitrified slag (Alter NRG, 2015). This plant includes the Westinghouse Plasma Technology as the core technology. Treatment data are not yet available.

The first plasma-based gasification process, Plasma Enhanced Melter® (PEM®), for recycling hazardous waste was installed at a silicon-based materials manufacturing facility of Dow Corning in Midland, Michigan, USA. The plant began operation in 2009, and recycles hazardous chemical residuals into reusable process chemicals and clean syngas used as fuel for steam. More than 6,600 tons per year of hazardous chlorinated organic liquid waste are converted into 5500 tons per year of aqueous hydrochloric acid and 875 tons of clean synthesis gas. No treatment data are available.

The Tetronics DC plasma arc system can be used to treat a range of waste streams to destroy and transform hazardous components and to recover valuable materials. One of the applications of the technology is the destruction of organic wastes, including polychlorinated biphenyls (PCBs) and other types of PBT pollutants. Tetronics has supplied over 80 commercial plasma treatment facilities for a range of applications, of which 28 were for hazardous waste applications. These include organic wastes containing PBTs and air pollution control (APC) residues containing PCDD/PCDF. Tetronics is now involved in the construction of an e-waste plasma R&D facility in the UK. Valuable information pertaining to tests and trials might be available within the year as the plant is scheduled to start-up mid-2016, as within this coming year start-up of the plant is scheduled. They are also building a plant in Osceola, AR, USA to process up to 7,000 tonnes per year of printed circuit board scrap.

“In-flight” plasma arc technology has been operating commercially since 1992. Through 2014 13 commercial plants using this technology have operated around the world in Australia, UK, USA, Mexico, and Japan. Through January of 2013, these plants have destroyed more than seven thousand tons of agriculture waste including POPs pesticides, and three thousand tons of concentrated PCBs, halons, and freons. All plants are standardized and can be used as fixed or portable plants. This technology has proven wide scale treatment of POPs and BFRs. As these plants are quite small (1 – 20 tonnes/day) they could only be considered if they were part of a network of treatment centers. Treatment data are available for solid but not for BFRs or liquid wastes.

8.3.7 Supercritical Water Oxidation

The targeted niche for most commercial SCWO applications are aqueous organic wastes in the range of 1–20 wt% organic; too concentrated for activated carbon to remove economically, but too dilute for incineration to handle efficiently. The easiest wastes to process are those that contain only the elements C, H, O, and N. Heteroatom-containing wastes are more difficult to process, since the associated acids and/or salts that form led to the two biggest challenges for SCWO processes: corrosion and salt precipitation/accumulation (Marrone 2013). As of 2012, there were 2 SCWO plants operating, with 5 being built and 9 planned. GA SCWO systems have logged greater than 25,000 hours of operation processing numerous aqueous based and organic based waste materials. There are 10 full-scale SCWO plants that are now inactive. A review by Vadillo et al. (2013) discusses some of the issues associated with this technology (including economic feasibility) and possible solutions (Vadillo et al. 2013).

8.3.7.1 Mitsubishi Heavy Industries

Operating since 2005, this plant was designed to destroy Japan's stockpile of PCBs using Advanced Hydrothermal Oxidation (AHO), which uses sodium carbonate to assist oxidation and react with the chloride produced. It has a capacity of 2,000 kg/day of PCBs and processes 100,000 kg/day of water.

8.3.7.2 Innovex/CNRS

This plant in southwestern France was built to treat hazardous industrial waste. It has a capacity of 100 kg/hr, and the feed composition is limited to <1g/L chloride and <10g/L salt (Vadillo et al. 2013). It began operation in 2011.

It should be noted that SCWO remains an area of active research and development, and there are many companies continuing to work in this area. Three universities (Valladolid (Cocero et al. 2000), Cadiz (Vadillo et al. 2013), and British Columbia (Asselin, Alfantazi, and Rogak 2008) and the Boreskov Institute of Catalysis (Anikeev and Yermakova 2011) operate SCWO systems with 20kg/hr capacity or higher.

8.3.7.3 General Atomics

General Atomics has developed a small scale plant that can destroy chlorinated species, including PCBs and pesticides. The process usually requires no pollution abatement equipment, and they have data that shows 99.9999% destruction the TOC, with emissions of dioxins/furans of <0.0006 ng/DSCM (TEQ), <4 mg/DSCM particulates, <0.4 ppmv HCL, <1 ppm NO_x, and <10 ppm CO and HC.

8.3.7.4 Innoveox

Innoveox uses multiple injection points to control efficiency, with corrosion and salt precipitation controlled by limiting certain waste concentrations. They have a system at Arthez-de-Béarn, France, and are building systems with a 1000 kg/hr capacity (Marrone 2013).

8.3.7.5 SuperWater Solutions LLC

This company focuses on processing non-corrosive wastewater sludge. They have built a 5 ton/day SCWO plant for city of Orlando, FL. In 2015 the plant suffered a violent blowout.

There are a number of facilities in operation that handle POPs waste, such as pesticides, and could destroy halogenated flame retardants in foams and plastics. These facilities generally cannot handle the scale of FR wastes. We include more of these examples in [Appendix 1](#).

8.4 Discussion

In the U.S., there are 84 facilities that recover energy from the combustion of municipal solid waste in 23 states, but few facilities have opened in the U.S. since 1995 (the newest facility was opened in Florida in 2015). In 2013, they handled about 12% of MSW. It is difficult to site and construct new WTE facilities due

to expense, rigorous environmental considerations and public resistance. Currently there are 34 states that consider WTE renewable.⁴²

Historically, incinerator, or hazardous waste burning facilities have been placed in low-income communities, communities of color, and tribal land, which poses significant environmental justice concerns.⁴³ The lack of transparency and inconsistency in the reporting of some facilities has led to distrust between the public and developers. Despite efficient technologies in modern facilities, there are those that continue to fail tests, and as a result are cited and fined, and even brought to court.⁴⁴

Thermal treatment covers a wide range of technologies from novel experimental systems to mature methods with a long history of operation. When treating foam and plastic with XFRs they all share a set of common advantages and problems. A major advantage is that the toxic species concentration can be greatly reduced, and that the overall toxicity of the waste and byproducts produced can be lowered. Problems include collection, storage, pre-treatment, transportation, cost, energy consumption or generation, atmospheric and water emissions, solid waste produced, and environmental justice issues. Each technique has a different set of parameters to consider, and any ranking methodology would include many subjective determinations. Table 8-5 below includes some of the major attributes of the different technologies.

8.4.1 Municipal Solid Wastes Combustors

The formation of mixed brominated-chlorinated PXDD/PXDF in relation to PCDD/PCDF strongly depends on the Cl/Br ratio of the waste mixture⁴⁵ (Stockholm Convention 2015c). 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 formed in the first combustion stage can be destroyed in the secondary combustion zone operated with sufficient residence time (2 seconds), temperature control (>850°C) and turbulence with appropriate design. To meet an emission limit of 0.1 ng TEQ/Nm³ further air pollution control devices are necessary (Stockholm Convention, 2007; European Commission, 2006).

8.4.2 Cement Kilns

An important consideration in treating FR/POP/PBDE-containing waste in cement kilns is the sensitivity to halogen input, particularly with BAT cement kiln types with pre-heaters. Pre-heater kilns (with or without a pre-calciner) was the main kiln type considered in the Stockholm Convention BAT/BEP guidelines (Stockholm Convention 2007). It is a viable option for waste treatment, but 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 for kilns without a chlorine bypass (Stockholm Convention 2015c). As bromine has similar physico-chemical properties as chlorine it will probably react in a similar way. However, the detailed behavior of bromine in cement kilns and associated releases of unintentionally produced POPs/by-products or elemental bromine have not been investigated or described.

⁴² Energy Recovery Council. 2014. Directory of Waste-to-Energy Facilities. Available here: http://energyrecoverycouncil.org/wp-content/uploads/2016/01/ERC_2014_Directory.pdf

⁴³ Recently, strong opposition in the Curtis Bay, Baltimore area, halted incineration facility construction. The Baltimore Brew's special series "Curtis Bay Incinerator" is available here: <https://www.baltimorebrew.com/special-series/curtis-bay-trash-incinerator>.

⁴⁴ Detroit Renewable Power in Detroit, Michigan is being sued by Great Lakes Environmental Law Center. This facility incinerates thousands of tons of Detroit's trash daily. Lynch, J. 2016. "Detroit incinerator faces lawsuit over emissions." Detroit News. October 18, 2016. Available here: <http://www.detroitnews.com/story/news/local/detroit-city/2016/10/18/detroit-incinerator-faces-suit-safety-violations/92351000/>

⁴⁵ 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).

Cement kilns with pre-heaters normally have PCDD/PCDF emission levels well below 0.1 ng TEQ/Nm³ (Karstensen et al. 2006), but levels as high as 136 ng TEQ/Nm³ have been reported (Karstensen 2008; Stockholm Convention 2007). Wet and long dry kilns can reach emission levels well above 1 ng TEQ/Nm³ high chlorine levels. With increased input of bromine via BFR-containing waste fractions, the risk of possible formation of brominated and brominated-chlorinated PXDD/PXDF and other brominated organics needs to be considered and assessed for all kiln types (but in particular for wet and long dry kilns).

8.4.3 Gasification

Only limited data on operation experiences, energy efficiency, emissions, costs and long term operation are published (Lamers et al. 2013). Gasification technology faces several challenges, most of which refer to the quality of the generated product gas. These include the need to characterize and pre-treat waste, high tar and dust levels that require extensive gas purification, and high maintenance efforts.

8.4.4 Pyrolysis

While pyrolysis has been suggested as an alternative for incineration of WEEE plastic (R. Wang and Xu 2014; Alston and Arnold 2011), their conclusions are based on laboratory scale studies (Alston and Arnold 2011), which do not include the above listed issues. Therefore at this stage pyrolysis cannot be considered BAT/BEP for treatment of BFR-containing materials until long-term full-scale applications have shown to result in product flows that can be considered environmentally and economically sound. In addition, for BFR containing waste elevated concentrations of PBDD/PBDF can be expected from pyrolysis processes when aromatic BFRs (e.g., PBDEs, brominated phenols) are present in the waste (Ebert and Bahadir 2003; Weber and Kuch 2003). Thus, for the feedstock recycling of BFR and PVC containing waste via pyrolysis such as WEEE plastic, ASR and other materials, the formation of PBDD/PBDF, PCDD/PCDF and PXDD/PXDF can be problematic (Weber and Kuch 2003; Weber and Sakurai 2001).

During pyrolysis/gasification significant debromination of DecaBDE to lower-brominated PBDEs (including POP-PBDEs) can occur (W. J. Hall and Williams 2008). Another issue to consider is the halogen content of the resulting oil. Pyrolysis oil used as a fuel should have a halogen content below 50 ppm (Stockholm Convention 2015c), while another study suggests that oil with a halogen content below 2000 ppm can be used (Wajima et al. 2015). Nevertheless the status of the product “pyrolysis oil” is questionable and depends on the legal situation and requirements for fuel products in different countries (Stockholm Convention 2015c). The resulting pyrolysis coke should be analyzed for its content of PBDD or mixed PBCD/ PBDD-PBDF. In some EU Member States, pyrolysis coke would be considered a hazardous waste.

8.4.5 Metal Industry

Only limited conclusions can currently be drawn about the effectiveness and environmental impact of these processes for recovering energy and materials from articles containing FRs. These processes need further assessment for treatment of CFR- and BFR-containing materials in such facilities.

In addition to technological considerations, regulations and acceptance by the government, environmental groups, and the general public need consideration. Thermal treatment has not been widely accepted in the U.S., especially compared to Europe, where space constraints limit landfilling. The U.S. burned about 29 million tons of MSW (about 12 percent) for energy recovery in 2013 (USEPA 2015). Concerns about incineration, raised by many environmental organizations, generally focus on byproduct emissions such as dioxin and furans, and the perception that thermal treatment reduces the need for reuse and recycling. Older MSW plants did not always have advanced air pollution control equipment, and gained a reputation as high polluting.⁴⁶ These concerns need to be addressed so that meaningful changes in regulations and disposal programs can be explored and implemented.

A major concern is the lack of effective monitoring of the mixed halogenated PXDD/PXDFs. Until real-time analytical monitoring is improved, using accredited bio-assays measuring total dioxin-like toxicity like

⁴⁶ EPA FAQ “Energy Recovery from the Combustion of Municipal Solid Waste”. Available: <https://www.epa.gov/smm/energy-recovery-combustion-municipal-solid-waste-msw#pane-5>

CALUX, DRCALUX or EROD is recommended (Stockholm Convention 2007). Their ability to assess such complex dioxin-like mixtures has been demonstrated with the assessment of open e-waste recycling sites (X Yu et al. 2008). In state-of-the-art waste incineration facilities equipped with dioxin abatement technologies which continually comply with an emission limit for PCDD/F of less than 0.1 nanogram/Nm³, it can be assumed that brominated and mixed halogenated dibenzodioxins and furans are also adequately captured.

8.4.6 Classification of wastes

In the U.S., the EPA excludes certain solid wastes from the definition of hazardous waste. If a material meets an exclusion from the definition of hazardous waste, it is not regulated as a hazardous waste, even if the material technically meets a listing or exhibits a characteristic that would normally meet this definition. It is important to note that household hazardous waste is not considered a hazardous waste by the EPA⁴⁷ (including foams and plastics, even when they contain chemical flame retardants that have been regulated or removed from the market due to their toxicity).

Table 8-5 Summary of thermal treatment technologies.

Technology	Major Advantages	Major Disadvantages	Other Advantages	Other Disadvantages	Comments
Hazardous Waste Incinerators	Well-regulated High DRE Mature technology Less pre-treatment needed	High cost Few facilities Permitting, siting difficulties No CEM for all toxic byproducts Byproducts: Hazardous Ash, PXDD/PXDF congeners	Can handle a variety of waste	No energy recovery No resource recovery Halogen levels must be monitored Corrosion issues	Could be used for foams and plastics
Municipal Waste Combustors	High DRE Reasonable cost Available facilities Energy recovery Mature technology Large capacity	Not all employ BAT Permitting, siting difficulties No CEM for all toxic byproducts Byproducts: Hazardous Ash, PXDD/PXDF congeners	Can handle a variety of wastes	Halogen levels must be monitored Upset conditions caused by other waste Corrosion issues	Could be used for foams and plastics
Cement Kilns	High DRE Waste energy offsets other energy sources Mature technology Large capacity	No CEM for all toxic byproducts Halogens levels must be monitored to keep cement quality Byproducts: Ash (old kilns), PXDD/PXDF congeners	Long residence time, high temperatures	Not all operators want to handle toxic materials No resource recovery other than cement	Could be used for foams and plastics
Gasification	High DRE possible Energy recovery	Gas produced must be cleaned/processed Need data on brominated/mixed halogen wastes		Cost data needed if XFR waste processed Corrosion issues	

⁴⁷ EPA excludes household hazardous wastes from hazardous waste in CFR §261.4(b)(1). See <https://www.epa.gov/hw/criteria-definition-solid-waste-and-solid-and-hazardous-waste-exclusions>

Pyrolysis	High DRE possible Energy recovery	Gas produced must be cleaned/processed Need data on brominated/mixed halogenated wastes Byproducts: VOCs/SVOCs, oil and coal		Complex system engineering Corrosion issues	
Plasma	High DRE Small plants in operation	Large capacity systems needed Treatment data for XFRs needed		Energy intensive Needs significant pre-treatment	Could be viable for plastic wastes
SCWO	High DRE Low gas emissions Low solid byproducts	Small capacity Pre-treatment required if treating solids-waste must be a slurry	Does not form dioxins or furans. SCWO systems have small footprints and can treat wastes at the source rather than transporting wastes to a treatment facility		Not an ideal treatment technology for brominated /mixed halogenated wastes without first dissolving foams and plastics in a waste solvent
Metal Processing	Mature technologies High temperatures High residence times	Halogen issues not well understood Emissions controls may be needed Byproducts:??	Potential for destruction of XFRs	Fundamental research needed for XFRs Capacity/operator acceptance of wastes not known Costs not known	

8.5 Recommendations

Fundamental research needs:

- Formation, relevance and control of mixed halogenated dioxins and PAHs. There is limited data on mixed halogen PAH and dioxin emissions from lab studies - almost all lab studies use chlorinated or brominated compounds alone, but real-world waste is a mixture (Xiezhi Yu et al. 2008). More complex waste streams need to be investigated in addition to model compound studies.
- Faster and more comprehensive diagnostic methods for toxic species are needed. Better real-time methods and continuous monitoring that do not use limited batch sampling and processing that take days or weeks. This would allow detection/reporting of upset conditions as they occur.
- Chemical modeling aimed at developing markers to provide quantitative real-time data and feedback for emissions control.
- Standardized toxicity measures for brominated and mixed halogen dioxins and furans are needed (TEF/TEQ values).
- Alternative technologies such as plasma processing, pyrolysis, and gasification need fundamental studies to learn how XFRs react (chemistry) and how materials react to different halogen levels (material science).

- Additional research is needed on the basic chemical mechanisms involved with dioxin/furan formation. This includes de novo synthesis and the formation of toxic byproducts in the post-flame region. There is also a need to better understand the role of metals in chemical mechanism.
- Other toxic species formed in thermal processes need fundamental research on both their formation and health effects. One example is environmentally persistent free radicals that form reactive oxygen species in a catalytic cycle.
- Rigorous schemes for quantifying toxicity reduction when processing toxic wastes
- Better chemistry/fluid mechanics interactions are needed to properly scale treatment methods.
- Research on how halogens affect corrosion and fouling of the materials currently used in thermal treatment systems could reduce failures and lead to new materials, coatings, or protective measures.

In addition to fundamental research needed, there continues to be a need for pilot- and full-scale tests of the different technologies with different types of FR containing waste, both in terms of chemical composition and concentration.

9 Summary and Recommendations

Until more responsible methods are developed for managing waste products containing flame-retarded foams and plastics, these products will continue to pose hazards to humans and ecosystems after reaching the end of their useful life. Chemicals of concern that are no longer used in manufacturing in the U.S. (like PBDEs) will remain an issue for human and ecological health as “legacy” products enter the waste stream. Long-term solutions will require the destruction of the hazardous chemicals and their byproducts. As outlined in this paper, scientific, engineering, regulatory, and political challenges must be addressed to improve current waste management practices. Research should be prioritized both at the laboratory scale and larger pilot-scale to identify best practices to minimize harm to human health and the environment. This report has identified a variety of opportunities where basic science and engineering research can contribute to improved waste management for these products. These problems must be addressed soon to limit continued harm from hazardous flame retardants.

Unfortunately, existing market-scale waste management facilities (e.g., landfills and incinerators) are sometimes located in or near marginalized communities, placing an undue and disproportionate burden on families that already face higher exposures to harmful chemicals (National Research Council 2000; Martuzzi, Mitis, and Forastiere 2010). Addressing this environmental injustice should be a policy priority.

9.1 A need for improved policies and regulations

Regulators play a key role in establishing policies and financing for waste management. It can be challenging to implement changes in waste management due to costs and the political environment. However, there may be opportunities to improve policies and regulations in both the short- and long-term to reduce human and ecological hazards from wastes that contain flame retardants. These range from reducing potential emissions from waste treatment facilities to improving siting and reporting requirements and establishing funding mechanisms for improved waste management.

Currently, circular economy and zero-waste movements are gaining traction in developed countries, especially in Europe (European Commission 2015). Mixing household products with hazardous additives such as halogenated flame retardants poses a significant problem for reuse or recycling. In order for such materials to be a part of a circular economy, it will be critical to properly process waste materials so that hazardous chemicals, such as PBDEs, are removed before recycling (Stockholm Convention 2015c; Kral, Kellner, and Brunner 2013). The use of hazardous additives should be reduced or eliminated wherever possible – this not only reduces hazards during product use, but would also significantly lower barriers to safe recycling or product re-use. The U.S. lags behind other countries in considering a Circular Economy approach (although the circular economy is being promoted in the U.S. (U.S. Chamber of Commerce Foundation 2015)). The U.S. would benefit from adopting such principles in waste management and product manufacturing.

Below is a list of opportunities for policy changes that could support improved management of flame retarded wastes:

- Funding mechanisms that could enable separate handling and treatment of wastes containing flame retardants should be explored. Funding could initially support smaller pilot-scale programs and research and potentially be scaled-up for broader adoption. Current funding mechanisms in states and other countries should be considered.
- If new waste facilities are to be constructed, they should not be located in already-disadvantaged or marginalized communities.
- Improved monitoring and disclosure could be implemented for facilities that process or treat waste products. This is an important way to both improve operation of new and existing facilities and create more trust between communities and waste management facilities. Increased transparency could also improve acceptance of existing and new technologies.
- Encourage development of manufacturer sponsored product stewardship policies and programs for FR materials.
- Use of hazardous additives should be limited in new products. These additives are often used in applications where they may not be needed, and represent health hazards throughout every stage of

the product lifecycle (not just during the waste management stage). In some cases, product re-design, or substitution with better alternatives based on green chemistry, can eliminate unnecessary uses of harmful chemicals. In other cases, regulations and standards may need to be improved.

- Labeling or other waste designation methods could improve separation and recycling, allowing for better diversion of hazardous materials from the waste stream. This would also provide important information to consumers.
- Products that contain flame retardants could be designated as a separate waste category (such as “universal waste”⁴⁸). This would require such waste to be handled separately from standard MSW and to be diverted from MSW landfills, and research would be needed to support the economic and health/ environmental case for such a designation.
- Increasing public awareness of product contents and how waste is processed may support improved siting and other policies.

9.2 Recommended areas of research

Responsibly disposing of household products mixed with flame retardants presents numerous challenges, and will require engagement and interaction between diverse sectors.

We identified four major areas where research is needed that are non-specific to a particular technology. These, along with specific research needs identified in Chapters 3 – 8, are listed below. Note that each chapter has a more exhaustive list.

We identified the following major areas where research is needed:

1. Practical and cost-effective methods to identify, categorize, and quantify flame retardants in products.
2. Assessment of occupational exposures at all stages of handling or processing products mixed with toxic flame retardants.
3. Evaluation of exposures and hazards to human health and the environment near existing waste processing, treatment, and storage facilities.
4. Pilot scale research, to be conducted concurrently with bench-scale and basic science research, to accelerate scale-up of improved technologies and to help identify best practices.
5. Assessment of how technologies can be combined for the most effective management of high volume mixed waste with low concentrations of toxic flame retardants.

The following are suggested fundamental or priority research topics excerpted from each chapter:

9.2.1 Collection and Pretreatment

- Efficient ways to identify and quantify FR substances in wastes to determine the best pretreatment needs.
- Monitor the air and dust at dismantling and shredding facilities, and at transfer stations for release of toxic flame retardants.

9.2.2 Municipal Disposal: Landfill

- Evaluate the potential for halogenated flame retardants to volatilize with landfill gas and the extent to which they are attenuated by gas combustion. Determine if toxic byproducts, such as dioxins, form during combustion, landfill fires, and evaporation of landfill leachate using landfill flare.
- Evaluate the presence of flame retardants in MSW leachate. Some parameters that may affect leaching are the age of leachate and use of leachate recirculation. Transformation products, such as debrominated or hydroxylated flame retardants, should also be evaluated as part of this effort.

9.2.3 Mechanical Recycling: Flexible Polyurethane Foam

- A need for practical and cost-effective ways to identify and quantify FR substances in potentially contaminated foam waste and bonded cushion products.

⁴⁸ 40 CFR 273.9 defines “Universal Waste”; also see EPA descriptions here: <https://www.epa.gov/hw/universal-waste>

- Testing is needed to develop a better understanding of existing PentaBDE substitute concentrations in the potential waste stream of existing carpet cushion.

9.2.4 Mechanical Recycling: Waste Electronics and Electrical Equipment

- More research into developing a universal method for identifying commonly used flame retardants in mixed plastics waste.
- Testing is needed to develop a better understanding of existing halogenated DecaBDE substitute concentrations in the waste stream of existing products.

9.2.5 Chemical Recycling

- Assessment and possible development of large-scale chemical recycling projects for PU, EPS and WEEE plastics. Similar programs to the European CloseWEEE program might prove successful in the U.S.
- There is a need for pilot scale studies on the separation of halogenated flame retardants from products using alcoholysis, glycolysis, and aminolysis methods.

9.2.6 Destruction and Energy Recovery Technologies

- Formation, relevance and control of mixed halogenated dioxins and PAHs. There is virtually no data on mixed halogen emissions from lab studies - almost all lab studies use chlorinated or brominated compounds alone, but real-world waste is a mixture. More complex waste streams need to be investigated in addition to model compound studies.
- Faster and more comprehensive diagnostic methods for toxic species are needed. Also better real-time methods and continuous monitoring that don't use batch sampling for a very limited time and processing that take days or weeks. This would allow detection/reporting of upset conditions as they occur, rather than weeks later.

Acknowledgements

This material is based upon work supported by the National Science Foundation (www.nsf.gov) under NSF award number 1500091. Research reported in this report was supported by *National Institute of Environmental Health Sciences* of the National Institutes of Health under award number R13ES025490.

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11 Appendix

This appendix lists some other destruction technologies that can or have the potential to deal with hazardous flame retardants. These technologies may have too little capacity, are too expensive, or need significant additional research and development before they can be applied widely. However, these technologies could be used in combination with high capacity incinerators or cement kilns to completely destroy byproducts. Thus, a total destruction treatment is possible.

11.1 Alternative plasma methods

11.1.1 Advanced Plasma Power Limited

Advanced Plasma Power Limited uses a combination of gasification and plasma conversion to generate Plasmarok®, a fully recovered vitrified aggregate. This product is inert, and has been endorsed by the UK Environment Agency for use in a wide variety of applications in the construction and ceramics industries. The Plasmarok® product accounts for 70-80% of the input waste mass of an incinerator plant or other thermal waste treatment facilities listed below. As it qualifies as a product rather than a waste, it offers the potential to increase the revenue generated from the plasma process.

During the plasma process, chlorine in the gases can be collected as hydrochloric acid. Not only does this generate a product for sale, but it also avoids the generation of large amounts of secondary waste and the associated waste management costs.

11.1.1.1 Tetronics

Tetronics has two plants already in production or planned to go into production in 2016. Test results at their plants on the treatment of BFRs in matrices like would be useful. Tetronics has proven experience with plasma trials in its pilot facilities in Swindon, UK. Bromine compounds were deliberately added to e-waste in order to test the ability of the plasma system to handle elevated levels (up to 4 wt% bromine) of bromine. Essentially all the bromine to the off gas and nearly all of the bromine was captured as bromine salts in the off gas system filtration unit.

Independent data from MCerts contractor (EnviroDat) showed that the generic off-gas abatement system, not designed specifically for the task, achieved maximum emission levels for bromine gas of 121 ng/m³ and hydrogen bromide of 13 ng/m³. The off-gas abatement system consisted of a thermal oxidizer, combined air and water injection for gas cooling and simple bag filtration without dry scrubbing and before the acid gas neutralization stage in a wet scrubber.

11.1.2 Plasma Enhanced Melter® (PEM®)

In 2003, Kawasaki Heavy Industries (KHI) contracted with Future Integrated Technologies (FIT) to purchase a Plasma Enhanced Melter™ (PEM™) from Integrated Environmental Technologies, LLC (IET) for use as a medical waste treatment facility. However, prior to the medical waste application, the facility was installed to demonstrate PCB destruction in a commercial scale facility. The system was a full scale designed to process up to 4 tons per day of a mixed organic and inorganic waste (medical waste). No changes to the original system design (except the feed system) were required to adapt the system for the PCB destruction demonstration mission.

The results of a very detailed set of dioxin and PCB measurements taken from a series of eight tests where PCB oils were batch fed in different feed matrices were reported at the May 2004 IT3 Conference (Okita et al. 2004). These tests established that the PEM® system is an effective process for the destruction of diverse waste materials. The syngas from the PEM® system can be used for the production of energy, or for subsequent production of hydrogen. All data established that the emissions from the offgas, bag filter dust, and scrubber liquid were well below the appropriate regulatory standards.

Inentec of Dow Corning in Midland, MI installed the PEM[®] system beginning in 2007 to recycle hazardous waste at a silicon-based materials manufacturing facility. More than 6,000 tonnes per year of hazardous chlorinated organic liquid waste are converted into 5,000 tonnes per year of aqueous hydrochloric acid and 875 tons (10.5 million BTU per hour) of clean synthesis gas. The recycled materials replace raw materials that the company would otherwise purchase to make its silicon and solar cell products. This is the first commercial site for the operation of this technology.

1.1.3 Argon Plasma arc (“in-flight” plasma arc technology), Saliency Solutions, Australia

The argon plasma arc (“in-flight” plasma arc technology) has been operating commercially since 1992. To date, February 2014, from this technology 13 commercial plants have been operating around the world in Australia, UK, USA, Mexico and Japan. Through January 2013, these plants have been destroying more than seven thousand tons of agriculture waste including POPs pesticides, three thousand tons of concentrated PCBs and halons and freons. However, according to Saliency Solutions, the economics do not justify up-sizing a plasma plant of their design very much beyond 500 tons per annum (e-mail Neville Taylor to John Vijgen 20 August 2016).

11.2 Other Alternatives

These technologies normally treat small volumes (tonnes/year) of WEEE plastic. A program would need to be implemented to scale the technology for a particular regional need.

11.2.1 Gas Phase Chemical Reduction (GPCR, or GPR, or Hydrogenation)

GPCR technology involves the gas-phase chemical reduction of organic compounds by hydrogen at a temperature of 850°C or higher. Chlorinated hydrocarbons, such as HCB, polychlorinated dibenzo-p-dioxins (dioxins) and other POPs, are chemically reduced to methane and hydrogen chloride (HCl). Unlike oxidation reactions, the efficiency of these reduction reactions is enhanced by the presence of water, which acts as a heat transfer agent as well as a source of hydrogen. Solid and bulk waste materials are processed in a Thermal Reduction Batch Processor (TRBP). Waste is placed in the TRBP, which is sealed and heated in an oxygen-free atmosphere to about 600 °C. Organic components are volatilized and swept into the GPCR reactor, where complete reduction takes place at 850-900 °C (Vijgen 2002).

Gas phase reduction (GPR) has not been used to treat foam and plastics mixed with halogenated flame retardants. However, it is rated very efficient by UNEP for destruction of PCBs (McDowall and Vijgen 2002). For facilities that were built specifically for hazardous waste treatment, the capacities averaged 45 dry tonnes per day. While this is a smaller capacity compared to a municipal waste incinerator, GPCR would be able to completely destroy the halogenated flame retardants and at least work on a local or small-scale level to reduce the amount of toxics heading to landfills, or incinerators.

A test of the GPR process by Eco Logic yielded the following results:

- At least 99.99 percent destruction and removal efficiency for PCBs during all runs
- A 99.99 percent destruction efficiency for perchloroethylene, a tracer compound, during all runs
- Net destruction of trace feedstock dioxin and furan compounds during all runs

(Information forwarded by Douglas Hallett to John Vijgen 23 May 2016)

At the Ontario facility, further tests on the destruction of CFC R12 (dichlorodifluoromethane), demonstrated a 99.999% destruction of R12, while the chlorine and fluorine ended up in the scrubber water.