

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

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Abstract

This is Part II of a review covering the wide range of issues associated with all aspects of the use and responsible disposal of foam and plastic wastes containing toxic or potentially toxic flame retardants. We identify basic and applied research needs in the areas of responsible collection, pretreatment, processing, and management of these wastes. In Part II, we explore alternative technologies for the management of halogenated flame retardant (HFR) containing wastes, including chemical, mechanical, and thermal processes for recycling, treatment, and disposal.

Keywords: flame retardants; hazardous materials; solid disposal

Introduction

THIS IS THE SECOND part of a review that resulted from a series of workshops hosted by UC Berkeley and the Green Science Policy Institute in 2016–2017 with an international group of experts in varied fields. It discusses a wide range of issues associated with the responsible disposal of wastes containing flame retardants (FRs), and identifies basic and applied research needs in the areas of responsible collection, pretreatment, processing, and management of these wastes. Our intent is to focus on regions that do not have comprehensive and accepted protocols (e.g., the United States), using substantial input from other countries and regions with more concrete protocols (e.g., the EU).

Mechanical Recycling of Waste Electrical and Electronics Equipment and End-of-Life Vehicles

Electronics and vehicle components, including seats, consoles, wires, and circuit boards, often contain FRs. Recycling these materials includes a multistep presorting and pretreatment process.

Waste electrical and electronics equipment recycling

In 2014, 41.8 million tons of electrical and electronics equipment reached the end of life globally (Baldé *et al.*, 2015); waste electrical and electronics equipment (WEEE) often contains a significant amount of plastics—potentially providing hundreds of thousands of tons for recovery (Haig *et al.*, 2012).

Plastic casings for televisions and monitors are often dismantled by hand. Ideally, this provides a more pure ABS and HIPS polymer fraction for recycling, but there can be considerable operator error and mislabeling. The polymers are

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often sorted by color and type before compaction into bales. Another method involves shredding mixed materials after removing cords and batteries. Metal is recovered from the shredded mixture, and the remaining material rich in plastics is called electronics shredder residue (ESR).

ESR 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. 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 is less expensive and more environmentally favorable than incineration, although limits on halogens and heavy metals must be met (Stockholm Convention, 2015a). Small amounts of metals can also be enriched and sold.

End-of-life vehicles

In the United States, nearly 13 million cars are recycled per year.¹ A car contains nearly 150 kg of plastic (~2 million tons/year). Damuth (2010) suggests that 1.6 million tons/year could be recovered from ASR in the United States, leading to a number of environmental and economic benefits.

Quantifying FRs in ASR is difficult. Foam and plastics generally comprise 20–49% of ASR (Vermeulen *et al.*, 2011). This number is highly dependent on the shredding processes, and 27 types of plastics are in ASR. Besides FRs that are mixed into the FPF foam, ASR contains halogens from PVC and plastics, and heavy metals.

Recycling for End-of-life Vehicles (ELVs) is significantly more complicated than for WEEEs, because of the multiple components and materials. Much of the plastic, composites, and polyurethane foam remain 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).

Different postshredder techniques are used to separate materials from ASR. Most plastics are recovered in the secondary recovery processes. Recovery techniques include air classification, magnetic separation, optical sorting, manual sorting, drying, and float/sink separation (e.g., Table 8 in Vermeulen *et al.*, 2011). ASR plastic is generally not 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 FRs could remain in the final product. The shredder residue is a fine fluff that does not have value for foam production.

A small number of European companies do separate and recover plastics from ASR, including MBA Polymers UK Ltd. (United Kingdom) and Galloo Plastics (France). Other metal recyclers are making progress into recycling these plastics, especially in Europe, where the ELV Directive requires 95% reuse and recovery from ELV (European

Parliament and Council Directive 2000/53/EC), and high landfill costs or restriction of disposal of waste with high carbon content (5%) discourage or restrict disposal of the ASR. In the United States, restrictions on levels of polychlorinated biphenyls (PCBs) 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 (Toto 2016).

Health and environmental impacts

WEEE and ASR wastes include many plastics, including some containing FRs (Samsonok and Puype, 2013; Shaw *et al.*, 2014; Abbasi *et al.*, 2016). Analyzing plastics for the amounts and types of FRs is costly and inefficient for manufacturers of new products. This increases the likelihood of some products having toxic FRs where it is unsafe for them to be. A study on black plastic food contact items found that thermal cup lids contained TBBPA and decaBDE with levels as high as 1,294 mg kg⁻¹ (Samsonok and Puype, 2013); these FRs are associated with WEEE recovered plastics. DiGangi and Stravoka (2015) studied 21 toy products, and 17 contained octaBDE and decaBDE. Three of the products contained octaBDE and six contained decaBDE at levels >50 ppm.

While FRs 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 other environmental impacts (Shonfield, 2008; Huysman *et al.*, 2015; Wäger and Hirschler, 2015).

Discussion

The United Nations Environment Program (UNEP) BAT/BEP Guidance document (Stockholm Convention, 2015b) lists four main difficulties for recycling WEEE plastics: tight specifications for types of plastic (purity); 15 or more types of plastics mixed in WEEE; waste with POP-BDEs that remain in recycled products; and manufacturers require larger quantities of plastic, which encourages more recycling.

The largest costs associated with WEEE recycling are their separation and compounding; however, the full-scale recycling in Europe and China demonstrate that recycling with appropriate separation can be economical. Many techniques have been developed, but a significant portion of plastics is not recycled because the technology to separate and create a product from the plastic is not yet available, the plastic contains substances (e.g., BFRs) that prevent its use in new products, or the amount of the plastic is too small to recover economically. Currently, the plastic fraction containing BFR and PVC plastics in WEEE/ELV plastic recycling facilities are incinerated for energy recovery.

Recommendations

- More research in developing methods to identify commonly used FRs in mixed plastic waste.
- Testing to understand existing halogenated decaBDE substitute concentrations in the existing waste streams.

¹World Auto Steel www.worldautosteel.org/life-cycle-thinking/recycling.

- Research into compositions of e-waste in the United States, and recommendations for how to segregate FR streams from non-FR plastics.²
- Incentives for using recycled plastics in new products, such as the Electronics Products Environmental Assessment Tool (EPEAT).
- Stabilize regulations, as changes lead to economic uncertainties that discourage investment in increasing capacity for legitimate recycling.
- Harmonization of regulations on a global basis should be investigated.
- Separation of BFR-containing plastic and assurance that BFRs (and also PFRs and other toxic chemicals) are not recycled into sensitive products such as toys and food contact materials (Stockholm Convention, 2015a).
- Regulations that encourage complete recycling locally to minimize transport costs, better control hazardous emissions, create green jobs, and reduce incentives to export WEEE plastics.
- Investigate occupational exposure to FRs and other hazardous substances during dismantling and recycling handling (Julander *et al.*, 2014).

Chemical Recycling

Chemical recycling processes, including depolymerization for PUR that produces oligomers and monomers, which can be used in the synthesis of recycled PUR. Solvent-based approaches, such as the CreaSolv process selectively dissolve polymers and BFR additives without any chemical reactions, but instead apply a sequence of dissolution and mechanical separation steps. In this study, we treat them as chemical processes with solvents and need of significantly different equipment. Dehalogenation and extractive technologies are also discussed, which eliminate halogens from BFRs or separates BFRs from the polymer.

Methods

Chemical recycling of PUR. 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.

Alcoholysis. Alcoholysis is where foam reacts with an alcohol (e.g., methanol) at elevated temperatures. If the boiling points of the alcohols are lower than the required reaction temperature, the processes occur under pressure. Given correct reagent and degradation conditions, alcoholysis delivers high-quality polyol, not only with low reaction temperature and short reaction time, but also with higher degradation efficiency. If diols or glycols are used, the term glycolysis is applied.

²MBA 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 WEEE products go into the mixtures. In the United States, 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).

Asahi *et al.* (2004) reported degradation of a PUR foam by methanol at temperatures of 160–300°C and pressures up to 15 MPa, partly in the supercritical state of methanol. Decomposition was >90% at temperatures >200°C. Reactions with 1,2-propanediol produced polyols and amines (Feng *et al.*, 2004). Other results using ground rigid PUR foams reacting with diols >200°C showed efficient production of recycled polyols comparable to virgin polyols (Molero *et al.*, 2010; Aguado *et al.*, 2011).

Most alcoholysis processes apply catalysts, such as diethanolamine or bases (NaOH or KOH), to reduce reaction temperatures and achieve high degradation rates. 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).

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

Hydrolysis. Hydrolysis is a steam process of heating PUR in an oxygen-free environment, producing polyols and intermediate products that can be recovered for reuse. Hydrolysis applies alkali metal hydroxides as catalysts (Wang and Chen, 2003) or amines such as diaminotoluene (Dai *et al.*, 2002).

Hydroglycolysis. A hydroglycolysis process applies superheated water, catalysts, and glycols. Nikje and Tavassoli (2012) reported good results by the addition of PUR to water, diethylene glycol, water/sorbitol with 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 ~200°C (Chuayjuljit *et al.*, 2002).

Extraction. Solid–liquid or supercritical fluid extractions of PUR foams remove additives, such as foaming agents or FRs from the solid matrix. Filardo *et al.* (1996) applied liquid and supercritical CO₂ and CO₂/propane mixtures to extract chlorofluoroalkanes from rigid PUR foams.

PUR foams are used to trap BFRs in air samples, with subsequent solvent extraction of the BFRs. Extraction protocols vary extensively and use solvents such as hexane, toluene, or dichloromethane (Hazrati and Harrad, 2007; Chaemfa *et al.*, 2008; Fromme *et al.*, 2009). However, extraction processes are not available for industrial scale removal of BFR from waste PUR foam.

Recycling polymers from WEEE. Studies revealed the presence of BFRs in WEEE casings (Morf *et al.*, 2005; Schlummer *et al.*, 2007; Herat, 2008; Wäger *et al.*, 2012). DecaBDE, octaBDE, TBBP A, and 1,2-bis-tribromophenoxyethane (TBPE) are the most common FRs in thermoplastics from recent WEEE, whereas no significant amounts of polybrominated biphenyls (PBB) were observed in 2000 (Riess *et al.*, 2000). Processing of plastics has the potential of producing polybrominated dioxins and furans (PBDD/F). This includes compounding of BFR into plastics, injection molding of BFR-containing granules, and recompounding of shred BFR-containing casings. The highest precursor potential is reported for PBBs and

PBDEs (Weber and Kuch, 2003) with PBDEs responsible for an estimated total PBDF amount of 1,000 tons for historic produced/used PBDEs (Sindik *et al.*, 2015). TBPE and TBBP A may produce PBDD/F, but at considerable lower quantities, including lower quantities of the highly toxic 2,3,7,8 substituted congeners (Sindik *et al.*, 2015). PBB and PBDE in electronics are regulated by the European RoHS directive and comparable acts throughout the world.³ California and a few other U.S. states limit PBDE.

The mentioned BFRs are mainly used in ABS and HIPS, whereas phosphorous-based FRs are applied in blends of ABS and HIPS, namely PC/ABS and PPO/HIPS (Roth *et al.*, 2012).

Solvent-based plastic recycling processes make use of selective organic solvents that can dissolve a target polymer while not interacting with any nontarget polymers. It enables efficient separation of dissolved target polymers from undissolved polymers, foreign materials, and even codissolved contaminants. After polymer purification, the solvent is evaporated and reused. 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).

The CreaSolv[®] process was developed and optimized at the Fraunhofer Institute IVV (Germany). CreaSolv solvents target and extract polymers, such as EPS, ABS, PP, PE, PET, PC, PBT, or PA. After mechanical and extractive cleaning, 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). The purification step is effective in removing BFRs, 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. The separated BFR fractions destroyed by incineration.

Mechanochemical processes. Mechanochemical (MC) reactions can dispose solid waste containing chlorinated persistent organic pollutants (POPs) (Rowlands *et al.*, 2004; Tanaka *et al.*, 2004). 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 (Rowlands *et al.*, 2004). This process was successfully applied to halogenated organic pollutants, such as DDT (Hall *et al.*, 1996), hexabromobenzene (Zhang *et al.*, 2002), and PCBs (Aresta *et al.*, 2005). Zhang *et al.* (2012) tested tetrabromobisphenol A (TBBPA) in a ball mill using CaO or a mixture of SiO₂ and Fe as reactants. Complete degradation of TBBPA occurred within a 5-h treatment, and suggests a better reaction yield of the Fe/SiO₂ approach compared with the reaction with CaO. Hexabromocyclododecane (HBCDD) was eliminated from contaminated soil using a planetary ball mill with Fe-SiO₂ as a reactant (Zhang *et al.*, 2014). Using HBCDD as a model for organobromides, they showed efficient destruction, with HBCDD completely destroyed and transformed into inorganic bromide.

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

One chemical recycling approach dissolves EPS in a limonene solution (Noguchi *et al.*, 1998), but this approach does not remove HBCDD.

The CreaSolv Process successfully separated HBCDD in a laboratory- and small-scale trial (Schlummer *et al.*, 2016). A polystyrene-specific solvent formulation selectively dissolves the polymers from the EPS. Any undissolved matter can then be mechanically separated leaving a polymer solution. For the case of HBCDD, it is codissolved in the first step, meaning that the undissolved matter is HBCDD free. In a separate extractive, purification step, a polystyrene gel is extracted from the codissolved solution, isolating the HBCDD in a single phase. Once the polystyrene gel is dried, the polystyrene is ready for reuse. A demonstration plant is currently being constructed in The Netherlands (Tange *et al.*, 2016).

Health and environmental impacts

BFRs in PUR recycling. Alcoholysis and glycolysis can recover a polyol from rigid PUR. However, these processes do not separate the FRs from the polyol. The extracted polyol use may be restricted or would require specific certification before reuse. Purification is technically feasible, but it is expensive and not state of the art.

A MC approach may be used for rigid PUR foam mixed with BFRs. Steps include: size reduction into small particles; eliminate the bromine by adding CaO or Fe/SiO₂; and produce a bromine-free PU feedstock. However, there are no reports on the purity of recycled rigid PUR, the downstream fate of eliminated bromine, or processing costs.

During chemical recycling (alcoholysis/glycolysis) gaseous emissions are minimized by proper condensation and trapping of glycolysis products, including BFRs and related degradation products. Byproducts of chemical recycling include dissolved polyols in solution, and other undissolved materials that are filtered. If the FRs are not further separated from the polyol, the solution will contain a comixture of the polyols and FRs. Extractions of FRs, because they are separated, enable a separate and safer disposal. Chemical treatment options would debrominate PUR with BFRs, but not at a scale to be economical.

If particle-bound or gaseous emissions of FRs are not well controlled at recycling sites, workers may be exposed, necessitating strict monitoring. Worker exposure to these emissions has not been studied.

BFRs in chemical recycling of WEEE. MC ball milling can destroy BFRs successfully, but may create byproducts or degradation products containing FRs or brominated dioxins if not operated under appropriate conditions (Cagnetta *et al.*, 2016; Lu *et al.*, 2017). For highly brominated species, such as decaBDE, the ball mill will dehalogenate BFRs

³European Commission Directive, 2002/95/EG, Directive 2011/65/EU, Health and Safety Code sections 25214.9–25214.10.2.

successively and may lead to the production of more toxic lower brominated PBDE such as 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.

Recycling of WEEE plastics by the CreaSolv Process separates more than 98% of BFR from the polymer phase. However, the small amount of BFR that remains in the recycled polymers must be monitored to comply with RoHS or POP legislation on recycled plastics.

Human exposure to BFR from recycled plastics in this process may occur (Kuang *et al.*, 2018). Even if BFR migration from rigid plastics is very slow, these recycled polymers should not be used in sensitive applications such as 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 with incineration or simple mechanical recycling.

BFRs in EPS recycling. Due to its low density, these 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. However, HBCDD was found in some packaging products in Asia (Rani *et al.*, 2013).

Treatment of BFR-containing EPS with the CreaSolv process will result in: <100 ppm levels of residual HBCDD in recycled product, which may exclude recycled plastics from repurposing into certain products, but with safer disposal of HBCDD through thermal destruction with or without bromine recovery, and low exposure through product levels.

Other available techniques and practices for EPS treatment include regranulation of EPS into resin compounders without elimination of HBCDD. This is not allowed in countries where the Stockholm Convention prevents recycling of HBCDD. Selecting and sorting FR-containing EPS using automated spectroscopic sorting is currently not available for EPS foams.

Discussion

Chemical and solvent-based recycling of BFR-containing plastics, such as PUR and EPS foams or thermoplastics and thermosets from WEEE are well studied in the laboratory and pilot scale. These studies demonstrate their technical feasibility, and many of them have reached a level of technical maturity that justifies commercialization.

However, chemical recycling is only a minor contributor to the end-of-life management of these wastes. There are two main reasons for their absence on commercial scales. Chemical recycling requires a higher investment cost, with large facilities required to be economically viable. Even if needed, local waste streams are present, and these investments are considered more risky than small mechanical plants. Second, industry knowledge and infrastructure is biased toward mechanical processes, as chemical processes for production of

virgin polymers are much more complicated. Additionally, experts in polymer production are typically not involved in operating recycling plants.

Steps taken by European EPS and FR industries are highly promising. Combining these stakeholders helped address important issues in this process, including investment, legal challenges, and the harmonization of sorting and transport. In contrast to WEEE plastics and PUR foams, the composition of EPS and XPS foams is rather uniform 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 cooperation.

The situation is much more complex with respect to WEEE plastics and PUR foams, as different collection systems and use patterns exist in North America compared with Europe and Asia.

Chemical processes, such as extraction, CreaSolv Process, or mechanochemical ball mills, can separate bromine from the matrix. However, the fate of BFRs needs to be controlled to guarantee a safe separation from the matrix. Although, in some parts of the world thermal processes are preferred for disposal of BFRs, it is not widely available in the United States. From the perspective of a circular economy, bromine recovery, such as the BRU process (ICL), is highly promising in combination with separation processes such as CreaSolv (Tange *et al.*, 2016). They can help allocate BFR-rich fractions into industrial environments, which can treat halogen-containing waste economically and safely.

Recommendations

- While chemical processes may be technically available, initial commercialization stages will not be economically feasible, as the market for resulting products needs development.
- Chemical recycling competes with combustion, with industrial installations financed largely by public entities. The market situation currently has not supported installation of chemical recycling plants. More funding should be diverted to research the feasibility of large-scale chemical recycling projects for PUR, EPS, and WEEE plastics.
- Lack of chemical process knowledge and permitting issues in the recycling industry was identified as another obstacle in commercializing chemical recycling. Education programs with waste management experts are recommended, as well as initiating cooperation of producers of virgin plastics and recyclers.
- End-of-life management of Br in chemical recycling should enable the recovery of antimony, a rare element used in multiple industrial fields. China produces 90% of antimony, which is listed as one of the most essential metals. Facing this monopolistic supply situation, antimony recovery may provide a funding opportunity for chemical recycling of WEEE plastics.
- There is a need for pilot-scale studies on the separation of halogenated FRs from products using alcoholysis, glycolysis, and aminolysis methods.

Destruction and Energy Recovery Technologies

Many FRs have chemical properties making them difficult to destroy. The following technologies share the goal of destroying (rather than containing or recycling) toxic species, with the added benefit of reducing waste mass and volume, and can produce energy or reduce the need for supplemental fuels.

The desired products of thermal destruction are CO₂, H₂O, N₂, HX, or X₂, and the oxidized forms of elements such as metals and sulfur. Thermal systems can also produce products of incomplete combustion, including CO, NO_x, various hydrocarbons, and particulate matter (PM). These products and byproducts span the range from innocuous chemicals (N₂ and H₂O) to greenhouse gases and to highly toxic brominated dioxins and furans (PBDD/PBDF) (Weber and Kuch, 2003).

Methods

Technologies using high temperatures to destroy FRs include incineration (including waste-to-energy), pyrolysis, gasification, plasma treatment, and supercritical water oxidation (SCWO). Some are commercial, whereas others need additional research and development (Stockholm Convention, 2015a). Converting demonstration and laboratory-scale units into industrial systems has proven difficult (Altarawneh *et al.*, 2009).

These technologies share significant issues, including byproducts and ash, greenhouse gas emissions, waste transportation, siting, and environmental justice, and process monitoring. Halogens introduce the potential for toxic byproducts, including halogenated dioxins and furans. The amount and type of FRs in the waste alters the destruction processes, so FRs cannot simply be added to existing processes.

Foams and plastics have high calorific values, so energy recovery is viable (WEEE polymer energy content is slightly below 40 MJ/kg (Tange and Drohmann, 2005); for PUR it is 25.6 MJ/kg (Brunner *et al.*, 2000).

There are numerous reviews, journal articles, and government and nongovernmental publications describing thermal treatment methods (Addink and Olie, 1995; Tuppurainen *et al.*, 1998; McKay, 2002; Stanmore, 2004; Shibamoto *et al.*, 2007; Weber, 2007; Karstensen, 2008; Altarawneh *et al.*, 2009; Bosmans *et al.*, 2013; Quicker *et al.*, 2015; Zhou *et al.*, 2015; Peng *et al.*, 2016; Zhang *et al.*, 2016).

Waste incineration and waste-to-energy. Incinerators are mainly divided into three types: municipal solid waste (MSW), hazardous waste, and medical waste (not discussed in this study). Hazardous waste incinerators handle material deemed hazardous by regulations, and have more stringent operating requirements. They often share combustion and pollution control technologies with MSW incinerators.

Municipal and hazardous waste incinerators vary widely in their size, design, pollution control, and waste type and pre-treatment (Niessen, 2010; Klinghoffer *et al.*, 2015).

Temperature. While high temperatures are favorable to the complete waste destruction, there are practical and material and energy issues to consider. The carbon–bromine bond is less stable than the carbon–chlorine bond (270 vs. 330 kJ/mol),

TABLE 1. TEMPERATURE RECOMMENDATIONS FOR HFR MATERIALS

<i>Material</i>	<i>Halogenated FR content</i>	<i>Recommended combustion temperature</i>
WEEE plastics	3–20% bromine	1100°C
WEEE plastic shredder	1.7–5.2% bromine/ 0.1–4.4% chlorine	1100°C
PUR: molded seating, arm, and head rests	0.5–1.0% BFR	850°C
PUR: carpet padding	2–5% BFR	1100°C
EPS	0.5–0.7% HBCDD	850°C
XPS	0.8–2.5% HBCDD	1100°C

BFR, brominated flame retardant; HBCDD; WEEE, waste electrical and electronics equipment.

so lower temperatures might effectively destroy brominated compounds (Yang *et al.*, 2012). The EU Waste Incineration Directive⁴ mandates the following incineration temperature for various materials (Table 1).

Cement kilns. Portland cement is typically made in large rotary kilns, with temperatures of ~1,500°C and residence times of seconds. Kilns can be as large as 6 m in diameter, and over 200 m long. They are very energy intensive, and use a variety of fuels, including MSW and hazardous waste, tires, and biomass. The raw material enters the high end of the kiln, with alternative fuels (including FR materials) fed in at the bottom (LeHigh Hanson, 2016).

Conversion technologies. Gasification, plasma gasification, and pyrolysis are closely related and often referred to as “conversion technologies.” They involve heating waste in an oxygen-controlled environment to avoid combustion (Seltenrich, 2016). Their primary differences relate to heat source, oxygen level, and temperature, from ~300°C for pyrolysis to >11,000°C for plasmas (Stringfellow, 2014). Conversion technologies differ from conventional combustion by their production of syngas (mainly hydrogen and carbon monoxide), which is burned or converted into other fuels (GSTC, 2016). There employ a wide range of system designs and operating conditions. These technologies are currently not proven destruction technologies for PBDE-containing materials (Stockholm Convention, 2015a).

Pyrolysis. Pyrolysis is the thermal breakdown of waste in the absence of oxygen or steam. Waste is heated to temperatures >300°C by an external energy source (Lamers *et al.*, 2013).

Gasification. Gasification converts carbonaceous materials into CO, CO₂, and H₂ at temperatures >700°C with controlled amounts of oxygen and/or steam. The resulting syngas (or producer gas) is burned or used to produce other chemicals. Normally, the first stage is oxygen deficient in staged combustion processes. The syngas is oxidized completely downstream in a secondary combustor (Quicker *et al.*, 2015).

⁴European Commission 2000, Directive 2000/76/EC of the European Parliament and of the Council.

Technically, these processes are classified as combustion processes with lower energetic efficiency than classic waste incineration (Lamers *et al.*, 2013).

Plasmas. Plasmas use an electric arc with inert gases in the absence of oxygen to heat materials to >11,000°C. Organic waste converts to syngas, and metals and inorganics fuse into slag.

Supercritical water oxidation. SCWO uses water at supercritical conditions ($T > 374^\circ\text{C}$ and $P > 3,200$ psia). 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. Organics yield CO_2 and water; halogens, phosphorus, and sulfur are converted to inorganic acids or salts; and metals produce metal oxides. The technology cannot treat solid waste such as WEEE plastic or polyurethane foam.

Base-catalyzed decomposition. Base-catalyzed decomposition (BCD) 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 breaks bonds in toxic chemicals (Vijgen and McDowall, 2009). Also BCD cannot treat solid wastes such as WEEE plastic.

Health and environmental impacts

Besides the toxic FRs themselves, the primary health and environmental concern for thermal technologies is the formation of PXDD/PXDFs with incomplete combustion or improper cooling (Weber and Kuch, 2003).

Regulations

The U.S. EPA regulations on dioxin compounds and dioxin-like compounds include TSCA, CERCLA, SDWA, and the CAA. The World Health Organization has established total equivalency factors (Van Den Berg *et al.*, 1998).

The EPA regulates thermal treatment methods based on the health and human risks. They require that an incinerator destroy and remove at least 99.99% of each harmful chemical in the waste. When hazardous waste is treated, incinerators must destroy or remove at least 99.999% of the contaminants.

Two ash streams are products in thermal processing. Bottom ash is the heavier material remaining on combustor grates. Fly ash is PM that mixes with the flue gases. All ash from hazardous waste systems is considered hazardous; ash from thermal treatment of MSW contains nonhazardous bottom ash and hazardous fly ash (EPA, 2015). Modern cement kilns incorporate ash and cement kiln dust into their product.

The National Emission Standards for Hazardous Air Pollutants (NESHAP) 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), 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 pollutants, including dioxins and furans, HCl and Cl_2 , particulates, 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.

TABLE 2. EPA MACT AND NESHAP RULE LIMITS FOR PORTLAND CEMENT EXISTING AND NEW SOURCE STANDARDS

<i>Pollutant source standard</i>	<i>Existing source standard</i>	<i>New</i>
Mercury	55 lb/MM tons clinker	21 lb/MM tons clinker
THC	24 ppmvd	24 ppmvd
PM	0.07 lb/ton clinker (3-run test average)	0.02 lb/ton clinker (3-run test average)
HCL	3 ppmvd	3 ppmvd
Organic HAP (alternative to total hydrocarbons)	12 ppmvd	12 ppmvd

Most cement kilns are not permitted to burn hazardous waste in the United States. There are 14 hazardous waste certified kilns in the United States, and 94 kilns that are not. The kilns not permitted to burn hazardous waste are subject to the Portland cement MACT/NESHAP rule⁵, and not the combustor MACT rule. Current NESHAP rule limits are in Table 2.

Halogenated dioxins and furans. Dioxins and Furans, including polychlorinated PCDD/PCDFs, polybrominated PBDD/PBDFs, or mixed halogenated PXDD/PXDFs are a major concern for many scientists, engineers, government agencies, and environmental groups. Currently in most regulations only PCDD/PCDFs are covered. In thermal processes, their formation can be viewed as being representative of unintentionally formed POPs.

Dioxins are produced through two main mechanisms: precursors and *de novo* synthesis (Addink and Olie, 1995; Liu *et al.*, 2012). Precursors include species such as chlorobenzene and chlorophenol, PCBs, PBDEs, or other brominated aromatic FRs (Addink and Olie, 1995; Weber, 2007). Precursors are also produced through incomplete combustion, or heterogeneous catalytic reaction on the surface of fly so as (*De novo* synthesis) to form chlorinated biphenyls and naphthalenes, and benzenes through degradation of macromolecule carbon and chlorine (or bromine) in fly ash at $200\text{--}600^\circ\text{C}$ (Addink and Olie, 1995; Weber *et al.*, 2001). Complicating factors are the heterogeneous nature of the waste streams and the usually unknown input conditions. Zhang *et al.* (2016) recently published a review of this subject.

For BAT incinerators it is not the chlorine content but the combustion quality that controls dioxin formation. The hypothesis that fuel chlorine content and combustor flue gas PCDD/F concentrations are related was not confirmed 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, 2000, 2001; Weber and Sakurai, 2001).

⁵See the EPA Air Quality fact sheet for Portland cement: www3.epa.gov/airquality/cement/pdfs/20121220_port_cement_fin_fs.pdf

TABLE 3. WASTE-TO-ENERGY AS A % OF TOTAL DIOXIN EMISSIONS (G TEQ/YEAR)

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 ^a

Source: Dwyer and Themelis (2015).

^aThe 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% (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.

Air emissions of dioxins from 53 U.S. Waste-to-energy (WTE) plants were reduced significantly over the past 25 years (Table 3), and most of these emissions now are from fires and open burning (Dwyer and Themelis, 2015). The major dioxin release from BAT incineration and other thermal facilities is normally from ash, often not accounted in dioxin release inventories. Ash with high dioxin and heavy metals needs strict management and control.

FR-containing materials have reduced flammability, which can result in increased incomplete combustion and increased halogenated dioxin/furan formation in non-BAT combustion facilities (Weber and Kuch, 2003). Materials containing brominated aromatics (PBDE; brominated phenols; Firemaster 550) are excellent precursors of PBDD/PBDF; evaluating the formation of more toxic compounds is crucial in these systems (Melber *et al.*, 1998; Sakai *et al.*, 2001; Vehlow *et al.*, 2002; Weber and Kuch, 2003; UNEP, 2010). Because chlorine is normally present in PBDE-containing materials (WEEE plastic, ASR, PUR foam), formation of mixed halogen PXDD/PXDFs can comprise the highest share of dioxin-like compounds (Hunsinger *et al.*, 2002; Zennegg *et al.*, 2009). The measurement of only PCDD/PCDF in such operations is not sufficient and rather misleading.⁶

Well-designed and controlled combustion systems can effectively destroy dioxins and precursors, but some conditions could produce dioxins, including:

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

While these conditions may last only for short periods, significant dioxin emissions could happen during these periods.

Even when combustion conditions are optimized, *de novo* synthesis of dioxins can occur. This happens postcombustion, and can be minimized by cooling gases quickly to tempera-

tures of ~400–250°C, and minimizing certain metals (e.g., copper) and PM known to facilitate dioxin formation.

Dioxin/furan congeners and TEQ. When bromine and chlorine are present, there are >5000 congeners of PXDD/PXDFs, with several hundred 2, 3, 7, 8-substituted congeners. A complete chemical analysis is currently not possible. At present, mixed (PXDD/Fs) congeners have not been assigned a toxic equivalency factor (TEF) value and for brominated (PBDD/Fs) it is suggested by the WHO expert group to use the TEF of the corresponding PCDD/PCDFs. For many compounds insufficient environmental and toxicological data exist. Monitoring with accredited bioassays measuring total dioxin-like toxicity, such as CALUX, DRCALUX, or EROD, is recommended (Stockholm Convention, 2007). Their ability to assess dioxin-like toxicity in complex mixtures was demonstrated at open e-waste recycling sites (Yu *et al.*, 2008).

Corrosion. Halogens will corrode metals, with Br especially corrosive (Ozturk and Grubb, 2012). If Br is considerably lower than Cl, corrosion is mainly caused by Cl (Rademakers *et al.*, 2002). Operators of facilities with boilers are often reluctant to burn large amounts of bromine-containing waste (Rademakers *et al.*, 2002). Close monitoring is required, and the economic benefits and drawbacks assessed for different facilities, including maintenance and repair costs (Stockholm Convention, 2015a).

Removal of HBr and Br₂. Bromine is present in the flue gas as HBr and Br₂, and the ratio is influenced by the sulfur level. HBr, HCl, and other acid gases can be removed by the conventional technologies (dry/semidry scrubbing with basic adsorbents, NaOH scrubbing, etc.). However, Br₂ in the flue gas needs a reductive wet scrubber stage with the addition of sulfite or bisulfite (Stockholm Convention, 2015a).

Discussion

In the United States, there are 84 facilities that recover energy from combustion of MSW in 23 states, but few facilities have opened in the United States since 1995 (the newest opened in Florida in 2015). In 2013, they handled ~12% of MSW. It is difficult to site and construct new WTE facilities due to expense, rigorous environmental

⁶The addition of bromine can result in reduced levels of PCDD/PCDF, partly by bromination of the chlorinated aromatics and formation of PXDD/PXDF.

considerations, and public resistance. Currently, there are 34 states that consider WTE renewable.⁷

Historically, incinerators and/or hazardous waste facilities were in low-income communities, communities of color, and tribal land, which poses significant environmental justice concerns.⁸ The lack of transparency and inconsistency in the reporting from some facilities led to distrust between the public and developers. Despite efficient technologies in modern facilities, some fail tests, are cited and have been fined.⁹

Thermal treatment covers a wide range of technologies, but when treating XFR foam and plastic they share a set of common advantages and problems. Toxic species can be greatly reduced, and the overall toxicity of the waste and byproducts lowered. Problems include collection, storage, pretreatment, transportation, cost, energy consumption or generation, atmospheric and water emissions, solid waste produced, and environmental justice issues. Each technique has different parameters, and any ranking methodology would include many subjective determinations. Table 4 includes some of the major attributes of these technologies.

MSW incinerators. The formation of mixed brominated/chlorinated PXDD/PXDF in relation to PCDD/PCDF strongly depends on the Cl/Br ratio of the waste mixture¹⁰ (Stockholm Convention, 2015a). PCDD/PCDFs and PXDD/PXDFs were efficiently destroyed, resulting in moderate PCDD/PCDF and PXDD/PXDF levels in the raw gas and low levels in the clean gas (Vehlow *et al.*, 2002; Nordic Council of Ministers, 2005; Tange and Drohmann, 2005). These tests demonstrated that BAT incineration can cope with BFR-containing polymers and unintentionally formed halogenated dioxins are largely destroyed in the secondary combustion zone with sufficient residence time (2 s), temperature control (>850°C), and turbulence. To meet an emission limit of 0.1 ng TEQ/Nm³ further air pollution control devices are necessary (Integrated Pollution Prevention and Control, 2006; Stockholm Convention, 2007).

Cement kilns. Controlling the halogen input is important when treating FR/BFR/POP-containing waste in cement kilns, particularly with BAT cement kiln types with preheaters. Preheater kilns (with or without a precalciner) was

the main kiln type considered in the Stockholm Convention BAT/BEP guidelines (Stockholm Convention, 2007) (they are also the main type in the United States). The average total chlorine input should be <0.03% by mass to avoid clogging without chlorine bypass (Stockholm Convention, 2015a). As bromine has similar physicochemical properties as chlorine, it will probably react in a similar way. However, the detailed behavior of bromine in cement kilns has not been investigated.

Cement kilns with preheaters normally have PCDD/PCDF emission levels <0.1 ng TEQ/Nm³ (Karstensen *et al.*, 2006), but levels as high as 136 ng TEQ/Nm³ were reported (Stockholm Convention, 2007; Karstensen, 2008). Wet and long dry kilns can have emission >1 ng TEQ/Nm³ for high chlorine levels. With increased input of bromine in waste, the risk of brominated and brominated-chlorinated PXDD/PXDF and other brominated emissions needs to be assessed for all kilns, but in particular for wet and long dry kilns.

Gasification. Only limited data on operation experiences, energy efficiency, emissions, costs, and long-term operation are published (Lamers *et al.*, 2013). Challenges include the quality of the product gas, the need to characterize and pretreat waste, high tar, and dust levels that require extensive gas purification, and high maintenance.

Pyrolysis. While pyrolysis was suggested as an alternative for incineration of WEEE plastic (Alston and Arnold, 2011; Wang and Xu, 2014), conclusions are based on laboratory-scale studies (Alston and Arnold, 2011). Pyrolysis should not be considered as the BAT/BEP for treatment of BFR-containing materials until long-term full-scale applications are shown to be environmentally and economically sound. For BFR waste, elevated concentrations of PBDD/PBDF can be expected from pyrolysis when aromatic BFRs are present (Ebert and Bahadir, 2003; Weber and Kuch, 2003). Thus, for feedstock recycling of BFR and PVC-containing waste using pyrolysis, the formation of PBDD/PBDF, PCDD/PCDF, and PXDD/PXDF can be problematic (Weber and Sakurai, 2001; Weber and Kuch, 2003).

During pyrolysis/gasification significant debromination of decaBDE to lower-brominated PBDEs occurs (Hall and Williams, 2008). Another issue is the halogen content of the resulting oil. Pyrolysis oil used as fuel should have halogens <50 ppm (Stockholm Convention, 2015a), whereas Wajima *et al.* (2015) suggest a 2,000 ppm limit.

In addition to technological issues, regulations and acceptance by governments, environmental groups, and the general public need consideration. Thermal treatment is not widely accepted in the United States, especially compared with Europe. Concerns about incineration, raised by many environmental organizations, focus on byproduct emissions, and the perception that thermal treatment reduces the need for reuse and recycling. Older MSW plants did not always have advanced pollution control equipment, and gained a reputation as highly polluting.¹¹ These concerns must be addressed so that meaningful changes in regulations and disposal programs can be explored and implemented.

⁷Energy Recovery Council. 2014. Directory of Waste-to-Energy Facilities. Available here: http://energyrecoverycouncil.org/wp-content/uploads/2016/01/ERC_2014_Directory.pdf

⁸Recently, strong opposition in the Curtis Bay, Baltimore area, halted incineration facility construction. The Baltimore Brew's special series "Curtis Bay Incinerator" is available here: www.baltimorebrew.com/special-series/curtis-bay-trash-incinerator.

⁹Detroit 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: www.detroitnews.com/story/news/local/detroit-city/2016/10/18/detroit-incinerator-faces-suit-safety-violations/92351000

¹⁰In 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).

¹¹EPA FAQ "Energy Recovery from the Combustion of Municipal Solid Waste." Available: www.epa.gov/smm/energy-recovery-combustion-municipal-solid-waste-msw#pane-5

TABLE 4. SUMMARY OF THERMAL TREATMENT TECHNOLOGIES

<i>Technology</i>	<i>Major advantages</i>	<i>Major disadvantages</i>	<i>Other advantages</i>	<i>Other disadvantages</i>	<i>Comments</i>
Hazardous waste incinerators	Well regulated High DRE Mature technology Less pretreatment 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 wastes	No energy recovery No resource recovery Halogen levels must be monitored Corrosion issues	Suitable 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	Suitable for foams and plastics
Cement Kilns	High DRE Waste energy offsets other energy sources Mature technology Large capacity	No CEM for all toxic byproducts Halogen levels must be monitored to keep cement quality Byproducts: Ash (old kilns), PXDD/PXDF congeners	Long residence time, high temperatures	Not all operators handle toxic materials No resource recovery other than cement	
Gasification	High DRE possible Energy recovery	Gas produced must be cleaned/processed Need data on brominated/mixed halogen wastes		Cost data for XFR waste processing needed Corrosion issues	Not considered a proven technology for FR waste
Pyrolysis	High DRE possible Energy recovery	Gas produced must be cleaned/processed Need data on brominated/mixed halogenated wastes Byproducts: VOCs/SVOCs		Complex system engineering Corrosion issues	Not considered a proven technology for FR waste
Plasma	High DRE Small plants in operation	Large capacity systems needed Treatment data for XFRs needed		Energy intensive Needs significant pretreatment	Could be viable for plastic wastes.
SCWO	High DRE Low gas emissions Low solid byproducts	Small capacity Pretreatment required if treating solid waste must be a slurry	SCWO systems have small footprints and can treat wastes at the source, eliminating transportation		Requires liquids and cannot treat large volumes of solid plastic or polymer waste

DRE, destruction and removal efficiency; SCWO, supercritical water oxidation; VOCs/SVOCs, volatile and semi-volatile organic compounds.

A major concern is the lack of effective monitoring of PXDD/PXDFs, as described previously. In state-of-the-art incineration facilities that continually comply with an emission limit for PCDD/PCDFs of less than 0.1 nanogram/Nm³, it can be assumed that brominated and mixed halogenated dibenzodioxins and furans are also adequately captured.

Classification of wastes. The U.S. EPA excludes certain solid wastes from its definition of hazardous waste, even if the material technically meets a listing or exhibits characteristics that would normally meet this definition. Note that household hazardous waste is not considered a hazardous waste by the EPA¹² (including foams and plastics that contain chemical FRs that are regulated or removed from the market due to their toxicity).

Recommendations

Research needs.

- More complex waste streams need investigation, as limited data exist on mixed halogen PAH and dioxin emissions from laboratory studies (Yu *et al.*, 2008).
- Faster and more comprehensive diagnostic methods for toxic species, especially real-time methods and continuous monitoring, allowing detection/reporting of upset conditions.
- Chemical modeling aimed at developing markers to provide quantitative feedback for emissions control.
- Standardized TEF values or other integrative approach for capturing brominated and mixed halogen dioxins and furans.
- Alternative technologies, such as plasma processing, pyrolysis, and gasification need fundamental studies on how XFRs and materials react, which could lead to new materials, coatings, or protective measures.
- Research on basic chemical mechanisms involved with dioxin/furan formation, including *de novo* synthesis, the formation of toxic byproducts in the postflame region, and the role of metals.
- Fundamental research on the formation and health effects of other toxic species in thermal processes (e.g., environmentally persistent free radicals that form reactive oxygen species in a catalytic cycle).
- Rigorous schemes for needed to quantify toxicity reduction.
- Better understanding of chemistry/fluid mechanics to properly scale treatment methods.
- Pilot- and full-scale tests of different technologies with different types and concentrations of FR wastes.

Summary and Recommendations

Until more responsible methods are developed for managing waste products containing FR foams and plastics, hazards to humans and ecosystems will exist after these products reach the end of their useful life. Chemicals no longer used (such as PBDEs) will remain a human and ecological health hazard as “legacy” products enter the waste stream. Long-term solutions

require the destruction of toxic FRs and their byproducts. As outlined in this study, scientific, engineering, regulatory, and political challenges must be addressed to improve waste management. Research should be prioritized at the laboratory scale and larger pilot scale to identify best practices. We identified a variety of opportunities where basic science and engineering research can contribute to improved waste management, but these problems must be addressed soon to limit continued harm from hazardous FRs.

Unfortunately, existing market-scale waste management facilities 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 *et al.*, 2010). Addressing this injustice should be a priority.

Improved policies and regulations

Regulators play a key role in establishing policies for waste management. Changes are difficult due to costs and the political environment in much of the U.S. Opportunities exist to improve policies and regulations in both the short- and long-term for the hazards from FR wastes, ranging from reducing potential emissions from waste treatment facilities to improving siting, and reporting requirements and establishing new funding mechanisms.

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 HFRs, poses a significant problem for reuse or recycling. It will be critical to develop methods to process waste so that hazardous chemicals are identified and removed before recycling (Kral *et al.*, 2013; Stockholm Convention, 2015a). 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 reuse. The United States lags other countries in considering a circular economy approach (The U.S. Chamber of Commerce Foundation, 2015), but would benefit from adopting such principles.

Below is a list of opportunities for policy changes:

- Explore funding mechanisms that enable separate handling and treatment of wastes containing FRs. Funding could initially support smaller pilot-scale programs and research that could be scaled up. Current funding mechanisms in states and other countries should be considered.
- New waste facilities should not be located in already-disadvantaged or marginalized communities.
- Improve monitoring and disclosure for waste facilities. This is important to both improve operation of new and existing facilities and create more trust between communities and waste management facilities. Increased transparency would also improve acceptance of existing and new technologies.
- Encourage development of manufacturer-sponsored product stewardship policies and programs for FR materials.
- Limit the use of hazardous additives in new products. In some cases, product redesign or substitution with greener alternatives can eliminate unnecessary uses of

¹²EPA excludes household hazardous wastes from hazardous waste in the U.S. Codes of Federal Regulation §261.4(b)(1). See www.epa.gov/hw/criteria-definition-solid-waste-and-solid-and-hazardous-waste-exclusions

harmful chemicals. In other cases, regulations and standards need to be improved.

- Labeling or other waste designation methods could improve separation and recycling, allowing for better diversion of hazardous materials from waste streams, and provide important information to consumers.
- Products that contain FRs could be designated as a separate waste category (such as “universal waste”¹³), handled separately from standard MSW and diverted from MSW landfills. Research is needed to support the economic and health/environmental case for such a designation.
- Increasing public awareness of product contents and how waste is processed would support improved siting and other policies.

Recommended areas of research

Responsible disposal of products mixed with FRs presents numerous challenges, and will require engagement and interaction between diverse sectors. We identified four major areas where research is needed. Each technology section presents a more exhaustive list of recommendations.

Major crosscutting areas for research:

- Practical and cost-effective methods to identify, categorize, and quantify FRs in existing products that are not clearly labeled.
- Assessment of occupational exposures at all stages of handling or processing products with toxic FRs.
- Evaluate exposures and hazards to human health and the environment near existing waste processing, treatment, and storage facilities.
- 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.
- Assessment of how technologies can be combined for the most effective management of high-volume mixed waste with low concentrations of toxic FRs.

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¹³40 CFR 273.9 defines “Universal Waste”; also see EPA descriptions here: www.epa.gov/hw/universal-waste

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