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Environmental Impact of Processing Electronic Waste – Key Issues and Challenges

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Abstract

Extensive utilization of electric and electronic equipment in a wide range of applications has resulted in the generation of huge volumes of electronic waste (e-waste) globally. Highly complex e-waste can contain metals, polymers and ceramics along with several hazardous and toxic constituents. There are presently no standard approaches for handling, dismantling, and the processing of e-waste to recover valuable resources. Inappropriate and unsafe practices produce additional hazardous compounds and highly toxic emissions as well. This chapter presents an overview of the environmental impact of processing e-waste with specific focus on toxic elements present initially in a variety of e-waste as well as hazardous compounds generated during e-waste processing. Hazardous constituents/ and contaminants were classified in three categories: primary contaminants, secondary contaminants, and tertiary contaminants. Primary contaminants represent hazardous substances present initially within various types of e-waste; these include heavy metals such as lead, mercury, nickel and cadmium, flame retardants presents in polymers etc. Secondary contaminants such as spent acids, volatile/toxic compounds, PAHs are the by-products or waste residues produced after inappropriate processing of e-waste and the tertiary contaminants include leftover reagents or compounds used during processing. A detailed report is presented on the environmental impact of processing e-waste and the detrimental impact on soil contamination, vegetation degradation, water and air quality along with implications for human health. Challenges and opportunities associated with appropriate e-waste management are also discussed.

Keywords: E-waste, contaminants, hazards, environmental issues, recycling

1. Introduction

Extensive use of electric and electronic equipment (EEE) for everyday needs in a wide range of applications has led to the generation of huge volumes of electronic waste (e-waste) all

around the world. Some of the key factors responsible for the global generation of e-waste are the programmed obsolescence of EEE, rapid advances in technology and the insatiable desire for smaller/faster/up to date devices. While the electronic waste has been accumulating over several decades, keen awareness regarding their environmental impact and issues associated with e-waste management has become highlighted in recent years. Currently, only a small fraction of e-waste is being treated or recycled appropriately; most of it is either dumped or disposed of in landfills.

A wide range of substances are present in waste printed circuit boards (PCBs), the central processing unit of electronic devices. These are present as a highly complex mixture of ceramics, metals and polymers; some obsolete electronic equipment can contain more than 1000 different compounds [1]. This heterogeneous composition can include valuable constituents as well as hazardous and toxic elements or compounds. Due to inherent complexity of these devices, there is presently no standard, well-established process to treat a wide variety of e-waste. Current processing approaches are focused mainly on the recovery of copper and precious metals; the recovery of these materials is economically attractive due to their significant quantities present in e-waste as compared to corresponding concentrations in respective ores [2]. Some of the methods used to achieve these goals include open burning, manual dismantling/disassembly, mechanical processing, pyro-metallurgy, hydrometallurgy etc. Wherever the operation of these processes is inadequate or unsafe, it can lead to the generation of additional hazardous compounds, and may also release highly toxic emissions.

A significant proportion of e-waste is currently recycled using either hydrometallurgy or pyro-metallurgy. Dismantling/disassembly or mechanical sorting is generally carried out prior to the metallurgical processes to improve the recovery of materials. Mechanical processing can also be used by itself to recover materials from obsolete EEE. Some of the techniques used to separate metals and non-metals include crushing, grinding, electrostatics, gravity, shape, density-based and magnetic separation [3]. Hydrometallurgical recycling processes generally consist of leaching/dissolution of the material, a purification/concentration process and electro-winning, chemical reduction or crystallization processes for the recovery of metals. In the concentration step, methods such as precipitation, cementation, solvent extraction, adsorption, ion exchange and activated carbon have been employed [4].

The pyro-metallurgical approach to recover metals from e-waste consists of melting the material along with other substances or by itself to enhance slag formation and to concentrate and purify target metals. The steps used include smelting, converting, refining and electro refining [5]. One of the latest techniques being used to recycle e-waste is bio-metallurgy that consists of the utilization of micro-organisms to improve the leaching of metals. However, this approach has only been used on a research scale to date.

This chapter presents a brief overview of the environmental impact of processing e-waste. It focuses on toxic elements present initially in a range of e-waste as well as on the characterization of hazardous compounds generated during their processing. A detailed investigation on the composition of different types of e-waste such as large & small household appliances, IT and telecommunications equipment, light equipment, among others, is presented with an aim to provide a characterization of hazardous materials present in electronic equipment.

We also report on the in-situ generation of hazardous and toxic compounds from the reaction of base constituents present in several types of e-waste upon exposure to a range of operating conditions in various processing techniques. A comprehensive understanding of their behavior is essential to create recycling technologies that can recover valuable materials in an environmentally sustainable manner. It is also important to prevent the use of unsafe processing approaches and techniques that may create pollution and damage the environment in several different ways.

Hazardous compounds present in waste electronics can get released when these end-of-life equipment are dumped, disposed of or processed inappropriately. Such constituents have been classified in three groups based on the nature of the pollutant: primary contaminants, secondary contaminants and tertiary contaminants. A detailed report on various contaminants is presented in this section.

2. Primary contaminants

Primary contaminants are constituents present initially in e-waste that may have hazardous and/or a toxic nature. These constituents are used in the manufacture of electric and electronic equipment for their special intrinsic characteristics. Some of these hazardous constituents are listed below:

2.1. Metallic constituents

A wide variety of metals are present in electronic waste. Some of these can be hazardous when disposed of inappropriately. Key metallic constituents present in e-waste have been summarized below:

Lead

Lead metal is soft, ductile, malleable and flexible; it has high electrical conductivity and thermal expansion. As it also has a low melting point, hardness and strength, it is commonly used in a range of alloys. Some of the most common alloying elements with lead are tin, arsenic, antimony and calcium [6]. In electronic equipment, Lead is present in cathode ray tubes (CRTs), fluorescent tubes, found as solder in printed circuit boards, as well as in liquid crystal displays LCDs and batteries [7].

One of the main uses of lead in EEE is in cathode ray tubes in TVs and computers monitors. The purpose of lead in CRTs is to protect from UV and X-rays generated in the operation of CRTs. CRTs are composed of a front panel or screen, a funnel or rear part of CRTs, and the neck. The front panel contains up to 3% Pb, while the funnel contains up to ~25 wt% PbO. The neck is also made of PbO [8]. In recent years, CRTs have been replaced by LCDs, plasma or LED displays.

However, old CRTs are still being used in developing and third-world countries, and these still form a part of the old electronic waste. Waste CRTs are a major concern due to their high

lead concentrations and its toxic nature. The presence of strontium, cadmium and barium, among other metals make their recycling highly challenging and hazardous. On the other hand, printed circuit boards are one of the main constituents of EEE and most of old devices contain Pb-Sn solder. Solder is used to connect various electronic components on the surface of the printed circuit board. In recent years, the use of lead-free solders has become quite prevalent. However, most of the obsolete printed circuit boards contain hazardous lead and pose a challenge.

Tin

Tin improves the hardness and strength when used as an alloying element. This metal is generally present in EEE as a tin-lead alloy. These alloys are employed for their good melting, wetting and bonding properties with metals such as copper and steel. As lead has poor wettability with these metals, the addition of Tin gives the alloy fluidity, reduces brittleness and gives a finer structure [6]. Tin is present in EEE in printed circuit boards solders and in LCDs.

Antimony

Generally present in tin-lead alloys, the addition of Antimony is used to give additional hardness and strength in these alloys. It also makes these alloys more resistant to compressive impact and minimizes contraction upon cooling. About 2 to 5% Sb is usually used in Pb-Sn-Sb alloys [6]. Antimony, found predominantly in printed circuit boards, is known to be toxic and highly volatile [9].

Mercury

Mercury is in a molten state at room temperature, and has a tendency to volatilize due to its high vapor pressure. It can form several compounds, and is known to be highly toxic [10]. Mercury is present mainly in mercury lamps and also found in batteries, LCDs, switches, thermostats and sensors. The function of mercury in lighting equipment is to transform electrical energy into radiant energy in the UV range. Phosphor compounds then convert radiant energy into the visible spectrum [11]. Mercury lamps include fluorescent tubes, compact fluorescent lamps (CFLs), mercury vapor, sodium vapor, metal multi-vapors and mixed lamps.

The concentration of mercury in various lamps depends on the type, manufacturer and the year of manufacturing [12]. With increasingly strict regulations, the mercury content in lighting equipment has decreased considerably over time. Fluorescent tubes have been increasingly replaced by CFLs; these contain much lower levels of Hg as low as ~2.7 mg Hg per lamp [13]. However, a typical discarded fluorescent lamp can contain around 20 mg Hg on average [11].

With some manufacturers still using obsolete technologies and during the disposal of old fluorescent tubes, or mercury can get released during recycling. These lamps are likely to break when disposed of or handled inappropriately. The release of mercury depends on the quantity contained within the lamp and the temperature. The form of mercury released also depends on several factors, such as the type and age of the lamp, and whether the lamp was operated

continuously or intermittently. However, the exposure to mercury in any form is known to be toxic to humans [11].

Nickel

Nickel easily forms alloys with several metals such as copper, chromium and cadmium [6]. Nickel is predominantly found in Ni-Cd batteries as a hydroxide. This metal is also present in printed circuit boards in small amounts [14]. Ni-Cd batteries generally come in two forms: sealed or open (vented). Vented Ni-Cd batteries are generally used for industrial applications, such as for power sources in commercial applications as well as in aircraft and communications applications [6].

Sealed batteries are manufactured in button, rectangular and cylindrical forms, and are used in small household appliances, cordless tools, radios, calculators, video cameras and especially in mobile phones [15, 16]. These batteries have increasingly been replaced by nickel-metal hydride, lithium-ion and lithium-polymer batteries [17]. However, Ni-Cd batteries were used extensively over the last few decades; therefore a significant amount of spent Ni-Cd batteries are still present in e-waste worldwide.

Cadmium

Cadmium is a silvery-white, malleable and soft metal. It is used extensively in the electronics industry: ~45% of Cd is used in batteries, while 20% is used in pigments and 14% in stabilizers [6]. It is generally found as a compound in batteries, toners and cartridges [7]. This metal is also present in engineering plastics, printed circuit board solder, chip resistors, infrared detectors and semiconductors, and in the fluorescent powder coatings used in color CRTs [18]. It is present in Ni-Cd batteries as cadmium oxide. As a stabilizer in engineering plastics, it is found in the form of cadmium sulfides and cadmium salts. Various plastics can contain up to 100 mg/kg cadmium [19]. The main source of cadmium found in municipal solid waste is from NiCd batteries [20]. Due to the toxic nature of cadmium, toxic/hazardous fumes and dusts can form during waste processing and management, with serious detrimental influence on population health in surrounding areas.

Chromium

Chromium is usually used as an alloying element. One of its common applications is to prevent corrosion in steel, as it has excellent corrosion resistance properties [21]. Chromium is present in printed circuit boards, data tapes, floppy disks, pigments and polymers in the form of Cr₂O₃ pigment [7, 22]. It has a highly toxic nature, however the level of toxicity depends strongly on the valence of Chromium: Cr (0), Cr (III) and Cr (VI). Cr (VI) is considered to be 1000 times more toxic than Cr (III). However, exposure to high levels of Cr(III) can also affect the health of people living around recycling areas [23].

Copper

Copper is one of the most widely used metals in electric and electronic equipment due to its excellent conductive properties. It is the main metal present in printed circuit boards, cables, heat exchangers, among many other uses. Copper is commonly found linked with polymers.

In the informal sector, this metal is recovered through open burning and acid leaching. When combusted at low temperatures, it increases the risk of dioxin formation as well as of emissions of copper as particulate matter [24]. High exposure of copper can lead to the accumulation of excess metal into the body. This in turn can cause oxidative damage, and is known to be associated with metabolism issues and neurodegenerative changes [25].

Other metals

A number of other metals are also present in a variety of e-waste. A brief summary of these metals and potential hazards has been provided below:

Arsenic can be found in light equipment in small quantities. However As is known to be highly toxic, and exposure may lead to chronic diseases.

Barium is mainly present in CRTs. The panel of a glass CRT can contain up to 12% barium oxide and around 12% strontium oxide [18]. Ba is unstable in pure form, but can form toxic oxides when in contact with air. Even a short exposure to Ba can lead to serious health issues.

Zinc is used in the manufacture of printed circuit boards, LCDs, among others. Metals such as zinc and copper are persistent in the environment and have a tendency to accumulate in organs of the body. While these metals are essential for general health and wellbeing, excessive exposure during e-waste processing can lead to their accumulation in high levels in the human body and animals, leading to toxic and detrimental health effects [26].

Rare earth metals are mainly employed in the manufacture of CRTs, printed circuit boards, and also to improve thermal properties and toughness of alloys in batteries [27]. An exposure to rare earth metals has been to increase the risk of respiratory and lung related diseases, such as pneumoconiosis [28].

Other metals present on e-waste include americium, gallium, selenium and beryllium etc. These are generally present in ppm range. These elements are mainly found in smoke detectors, data tapes, semiconductors and rectifiers respectively. **Beryllium** is classified as a carcinogen as it can cause lung cancer, and can be inhaled as a dust, fume and/or mist. Short exposure may lead to several diseases. Exposure to **Selenium** is also hazardous as it may cause selenosis.

2.2. Organic pollutants

A range of organic pollutants are either present in-situ in e-waste or may get produced during its processing or handling. Key pollutants are described below:

Polychlorinated biphenyls (PCBs)

These belong to the family of poly-halogenated aromatic hydrocarbons (PHAHs) [29]. These organic compounds are classified as persistent organic pollutants (POPs) along with other 11 groups of chemicals, included in the Stockholm Convention. POPs are toxic, highly stable, resistant to degradation, lipophilic and bio-accumulative in organisms. These compounds can be transported through air, water as well as through migratory species. These not only can accumulate in human bodies, but also in fauna, terrestrial and aquatic ecosystems [30].

Polychlorinated biphenyls are present in transformers and capacitors as coolants, lubricants and dielectrics fluids due to their chemical inertness and high temperature stability. These can also be found as hydraulic and heat exchange fluids, such as in condensers [31-33]. Being soluble in fat, these can accumulate in humans and fauna, provoking intoxication [34]. These compounds can either be emitted or produced during the processing or handling of e-waste [35]. Being highly toxic, the use of these POPs was banned in the 1980s. However, these may still be present in old accumulated e-waste or could get formed during their processing. Therefore there still is a risk of exposure to these compounds during the recycling of obsolete e-waste.

Flame retardants

Flame retardants are compounds present in plastics due to their ability to resist temperatures high enough for a device and/or appliance to work. These are used to reduce the flammability of combustible materials such as plastics. Flame retardants are found in the form of hazardous solids. Most widely used retardants are brominated flame retardants (BFRs), which belong to the family of PHAHs [29]. Some of these have been classified as POPs due to their environmental persistence and toxicity [30]. BFRs have been used extensively due to their effectiveness and low cost.

Further details on four brominated flame retardants, namely polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol-A (TBBPA), polybrominated biphenyls (PBBs), and hexabromocyclododecane (HBCD) are provided below.

Polybrominated diphenyl ethers (PBDEs): Large amounts of PBDEs are used in the electronics industry. These have physicochemical properties similar to polychlorinated biphenyls [31]. These have low reactivity, high hydrophobicity, and as other POPs, are persistent in the environment, toxic and bio-accumulative. As these are not chemically bonded to the polymer (reactive component), there is a strong possibility for them to get released through leaching or volatilization. Even though these are a more recent development in the field, these are still highly toxic and harmful to humans. Studies have shown that PBDEs are distributed in the atmosphere, sediments as well as found in human milk [36].

Tetrabromobisphenol-A (TBBPA) is one of the most commonly used BFRs. It is used as a reactive component in epoxy resins as a flame retardant in printed circuit boards, and also in several types of polymers, such as HIPS, ABS and PET. However, this compound can get released to the environment when it is present as a reactive component or an additive component (not chemically bonded to the polymer). While TBBPA can get released into the air, soil and sediment, due to poor solubility in water, it is generally not found in water samples [37].

Polybrominated biphenyls (PBBs) are chemicals used as flame retardants in a wide variety of plastic products, such as monitors and TVs. Used as an additive component in polymers these can easily get released to the environment. Similar to other POPs, PBBs have low vapor pressure, low water solubility, and are stable and persistent in the environment and bio-accumulative due to their lipophilic properties [38]. PBBs particles mainly persist in the

atmosphere, and can also be absorbed in the soil and sediments. These can be released during combustion processes. Consequences of exposure to PBBs have been detailed in later sections.

Hexabromocyclododecane (HBCD) is generally used as an additive flame retardant in thermoplastics. As these are not chemically bonded to the polymer, HBCDs are able to volatilize and leach easily. As a POP, these are highly lipophilic and can bio-accumulate. These also have low water solubility [37].

Refrigerant gases

Refrigerant gases are mainly present in fridges, air conditioners and freezers. Three types of compounds generally used for refrigeration are: chlorofluorocarbons (CFCs), hydro-chloro-fluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). Also known as fluorinated refrigerants, these are hazardous in nature. As these exist in a gaseous state at room temperature and have low water solubility, these preferentially get released into the atmosphere and have long enough lifetimes to mix well. Emissions reported here only refer to the end of life equipment being disposed of. The most harmful compounds that can be released are CFC-12, HCFC-22 and HFC-134a, which are abundant in the atmosphere. However, they have a deleterious influence on the ozone layer and have been known to contribute to the global greenhouse effect [39].

The compounds containing chlorine have been known to contribute to ozone depletion since 1930s when CFC-12 was first developed as a refrigerant. CFCs are highly stable and easy to release to the atmosphere. The use of HCFC-22 started in 1960s, resulting in increasing emissions to the atmosphere. HCFCs are less stable than CFCs, and are called transitional substances. There has been a gradual replacement of CFCs and HCFCs with HFCs as these do not contain chlorine. HFCs are called substitution substances [39, 40]. However these also get released to the atmosphere.

3. Secondary contaminants

Secondary contaminants are the byproducts or residues generated after the processing of e-waste during the recovery of valuable materials. These are generally produced during the treatment of e-waste via pyro-metallurgical or hydrometallurgical techniques. Usually a pre-processing step is carried out to reduce particle sizes of various waste materials. Shredding is one of the most commonly used techniques to achieve this. A brief overview of secondary waste products produced during these activities is presented in this section.

3.1. Pre-processing byproducts

Two types of contaminants are likely to be produced during preprocessing steps such as shredding and crushing.

Dusts: Handling, manual dismantling or shredding of e-waste in processing workshops can generate a significant amount of dusts [41]. Even loading and/or unloading equipment can

produce fine dust particulates [42]. Manual dismantling taking place inside close environments can produce a significant amount of indoor dust as well [43]. Dusts consist of fine particulates in a range of sizes (typically in the μm range), and these can contain plastics, ceramics, and possibly heavy metals. There has been evidence regarding the release of high levels of Cd, Cr, Cu, Pb, Ni, Hg and Zn during dismantling and shredding activities. These metals are released not only during pre-processing activities, but also during inappropriate high temperature processing methods such as open burning, de-soldering or metal melting as well.

A number of researchers have investigated the levels of heavy metals present in suspended air particulates, surface dust and floor dust collected from several areas within and near e-waste workshops. High levels of these metals were found in the surface and floor dusts of an e-waste workshop dismantling area [41]. These particles have also been found to travel long distances through migrating species, winds and/or waters. Exposure to heavy metals can take place through ingestion, dermal contact and inhalation. Even when a small amount of these metals are essential for the body to function, excessive amounts of these metals in the human body can lead to high levels of toxicity.

Other particulates that may be released during preprocessing of e-waste are PBDEs, TBBPA, HBCD (described above in the Primary Contaminants section), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs). The formation of dioxins and furans is generally related to the presence of brominated and chlorinated flame retardants. The presence of chlorine can lead to the generation of chlorinated dioxins and furans PCDD/Fs, while the presence of bromine is known to form brominated dioxins and furans PBDD/Fs. Moreover, both together could lead to the formation of mixed dioxins and furans PXDD/Fs. It is however important to note that dioxins and furans are primarily formed during combustion processes.

3.2. Pyro-metallurgical byproducts

During the pyro-metallurgical processing of e-waste and recovery of valuable metals and products, several secondary and undesirable waste products are also produced. Their details are presented in this section.

Incineration of flame retardants:

When plastics containing flame retardants are incinerated, several pollutants such as PCDD/Fs, PBDD/Fs are likely to be generated. Both these products belong to the group of polyhalogenated aromatic hydrocarbons (PHAHs), and polycyclic aromatic hydrocarbons (PAHs).

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs): PCDD/Fs are also classified as persistent organic pollutants (POPs), as these compounds are highly stable in the environment, can travel long distances and accumulate in the fatty tissue of living species [44]. Unlike POPs such as PCBs or PBDEs mentioned in primary contaminants, PCDD/Fs are produced as a byproduct of manufacturing and combustion processes.

A major source of PCDD/Fs is the uncontrolled burning of solid waste. Open burning of e-waste and de-soldering of printed circuit boards in coal grills releases large amounts of these compounds during the processing of e-waste [36]. When PCDD/Fs are released into the atmosphere, these are not only transported over long distances, these pollutants can also get deposited in other environments. These compounds are present in the atmosphere in the gas as well as the particulate phase [44]. Human exposure to these pollutants is extremely likely near e-waste processing workshops. There has been evidence of elevated levels of PCDD/Fs in environmental and health analysis near recycling facilities. Exposure to chlorinated dioxins and furans is known to cause neurologic toxicity, dermal, hepatic and gastrointestinal issues in humans, and reproductive and immunologic toxicity in animals.

Polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs): These compounds have physicochemical characteristics and environmental behavior similar to the corresponding chlorinated compounds. These dioxins and furans have been found to be present as complex mixtures as PXDD/Fs in living organisms. These PHAHs are highly toxic and accumulate in the fatty tissues and food chains, leading to a wide range of adverse health and environmental effects [29]. The half-life of dioxins in humans has been estimated to be around 7 to 11 years. While the major source of dioxins is due to uncontrolled/incomplete burning activities, these are also known to be produced during natural processes such as fires and volcanic eruptions. Investigations on the effects of PBDD/Fs have shown that these may cause severe issues, such as reproductive issues, immune-toxicity and lethality. Dioxin exposure can affect breast milk, placenta and hair, and may cause cancer and other health issues [45].

Polycyclic aromatic hydrocarbons (PAHs): PAHs may be produced from natural sources as well as from human activity. Similar to other compounds mentioned above, these can be generated during combustion or incineration. PAHs can spread around in the atmosphere, and can also get disseminated in soils, water and vegetation [46]. Low weight or lighter PAHs exist predominantly in the gas phase, are volatile and are generally considered to be less toxic than heavier PAHs. However, these can react with other compounds, such as sulfur dioxide, nitrogen dioxide and ozone, and form sulfuric acid, nitro- and dinitro-PAHs and diones respectively, increasing the toxicity [47]. Heavier PAHs exist as particulate matter in the atmosphere as they have low vapor pressure [48]. PAHs can cause lung, skin and bladder diseases and may cause cancer over extended exposure [49].

Slags: Slags are a byproduct of the smelting process, and is mainly composed of oxides and heavy metals targeted to be separated from the metal to be recovered in the pyro-metallurgical process. Slags produced during the smelting of e-waste generally retain heavy metals and other hazardous elements, such as Pb, Cd, Cr, As, Sb, Bi, among others.

Gaseous emissions: A gaseous fraction is also generated during the smelting process. These are generally composed of greenhouse gases, as well as other gases. Some of the emissions are carbon monoxide, carbon dioxide and methane among others.

Particulate matter and dusts: There is a release of heavy metals as a particulate matter as well as carbonaceous particles. These are generally carried out in the generated gaseous fraction.

For example, open burning of copper wires may produce ~100 times more dioxins than burning domestic waste [50].

3.3. Hydrometallurgical byproducts

A number of secondary residues are generated during the hydrometallurgical processing of e-waste. Main byproducts are summarized below:

Spent acids: In hydrometallurgical processes, acids are the main chemicals used to treat e-waste. After leaching, concentration and electro-winning processes, spent acids are generated as a secondary waste. These are generally produced in significant quantities and can contain heavy metals, PBDEs, PCBs, and polycyclic aromatic hydrocarbons (PAHs).

Sludges: Sludges are the semi-liquid mixture that gets separated from a leaching solution. These are commonly generated after leaching e-waste and contain concentrated heavy metals removed from the solution.

Solid residues: Solid residues left after leaching processes are typically composed of plastics and other metals.

Spent activated carbon: Activated carbon is used in concentration processes to adsorb metals, and becomes a waste residue when its effectiveness becomes significantly reduced.

Volatile compounds: Hydrometallurgical processes generally use hydrochloric and/or nitric acids for metal recovery purposes. Their use can potentially emit volatile compounds of chlorine and nitrogen.

4. Tertiary contaminants

Tertiary contaminants are reagents used during the processing of e-waste either to capture target metals or to enhance the separation of various compounds. These substances have the potential to become hazardous when managed inappropriately. In this section, reagents used in the hydrometallurgical as well as in the pyro-metallurgical processes have been summarized.

4.1. Reagents used in hydrometallurgical processes

Leaching agents: Various types of solutions are used during the leaching of e-waste. These include a range of acids (sulphuric, hydrochloric, nitric, aqua regia), cyanides, halides (fluorine, chlorine, bromine, iodine and astatine), thiourea or thiosulphate etc.

Concentration substances: Dense organic liquids are usually used in the solvent-extraction processes. These include organic solvents comprising of extractants and diluents that together form an organic solution. Acid solutions are also used, where in the solvent-extraction step target metals are transferred from one solution to another. Activated carbons have also been employed in the concentration processes.

Electrowinning solutions: A range of acids are used in electrowinning for the recovery of metals. Large quantities of sulphuric acid and its solutions are generally used in this process.

4.2. Substances used in pyro-metallurgical processes

Fluxes and salts: Some approaches mix these substances with e-waste in the smelting process to either capture valuable metals or to separate and concentrate materials.

Gas injection: In smelting, oxygen bearing gases such as air are injected to the bath to oxidize metals.

Electro-refining: In the electro-refining process, electrolyte solutions composed of acids are used to capture the target metal in a highly pure form.

5. Environmental impact of processing e-waste

Most of the contaminants and hazardous materials detailed above are associated with severe environmental and health consequences. Some pollutants can be dispersed through the air, ground water and soil as well as found in the surrounding air in zones neighboring the processing areas. In other cases, by-products get dumped directly into the soil or waterways, where the subsequent leaching of pollutants could contaminate the environment and influence food chain supplies as well. Direct human exposure to these contaminants can also have irreversible short and long term health effects. These contaminants can have severe consequences for the exposed flora and fauna. A comprehensive overview on the environmental impact of e-waste is presented in this section.

5.1. Soil and vegetation

Several types of contaminants have been observed in soils and vegetation near e-waste processing areas. Various investigations have confirmed such contamination in a range of samples.

High levels of polychlorinated biphenyls (PCBs) were found in the soil and the plant samples of an e-waste recycling village in northern Guangdong province, China. *Chrysanthemum coronarium* L. from vegetable fields and *Bidens pilosa* L. (wild plant) from the e-waste open burning site were found to have higher concentrations of PCBs than other plants. Analysis of soil specimens from the burning site presented much higher concentrations than nearby zones; vegetable soils were found to have higher levels of PCBs than paddy soils [35]. PBDEs were also found present in soils and vegetation near e-waste processing areas as well as in the neighboring environment. Paddy and vegetable soils, and *Brassica alboglabra* L were contaminated with PBDEs. However, the levels of the pollutant were seen to decrease with increasing distances from the recycling sites. PBDEs entered the food chain through some vegetables [51].

17 types of PCDD/Fs, 36 types of PCBs and 16 types of PAHs were analyzed from agricultural soils near an e-waste processing site in Taizhou, China. All of these contaminants were found

to be present in the soils, and their source was determined to be the dismantling and open burning of e-waste [52]. Concentrations of ten congeners of PBDEs and nine of PBBs in soils were analyzed in three e-waste disposal sites: Removal of printed circuit board components in coal grills, acid baths, and dumping sites. High levels of both types of pollutants were found in all three soils, with the highest concentration of total PBDEs and PBBs observed in dumps (990.87 ng/g and 1943.86 ng/g, dry weight, respectively), followed by the components removal site and then the acid baths [53].

PCBs and PBDEs were also analyzed in soil samples as well as in apple snails (snails of the Ampullariidae family) within a 70 km radius from an e-waste dismantling site in southeast China. A total of 25 PCB congeners and 14 PBDE congeners were measured. Total PCB levels in apple snails ranged from 3.78 to 1812 ng/g, dry weight, which was found to be much higher than total concentration determined in soils (0.48–90.1 ng/g dry weight). PBDE content in apple snails ranged from 0.09 to 27.7 ng/g dry weight; a similar concentration was observed in soils (0.06 to 31.2 ng/g dry weight). With increasing distance from the dismantling site, concentrations of both groups of pollutants were found to decrease and were much lower. These results indicate a correlation between the dismantling activities and the release and transport of PCBs and PBDEs to surrounding regions and zones [54].

A total of 12 heavy metals were analyzed from the surface, middle and deep sediment from an acid leaching site. These were determined to be Be, V, Cr, Mn, Co, Ni, Cu, Zn, Cd, Sn, Sb and Pb. Results showed considerably high levels of Cu, Zn, Cd, Sn, Sb and Pb, especially in the middle sediments [55]. Another investigation also found high levels of Cd, Cu, Ni, Pb and Zn in sediments in Guiyu, China [56]. Analysis of the soil of Wenling, an e-waste processing area in Taizhou, China, showed it to be heavily contaminated not only with heavy metals (Cu, Cr, Cd, Pb, Zn, Hg and As), but also with POPs, including PAHs and PCBs [57].

Rice samples and paddy soils from an e-waste processing site in Taizhou, China, were analyzed for 10 heavy metals (As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni and Pb). Results showed that the agricultural soil was highly contaminated with Cd, Cu and Hg, while Pb concentrations in the rice sample were above maximum allowable levels. It was also found that heavy metals contamination occurred mainly through air migration of particulates [58]. Another study on heavy metal contamination had shown high levels of Cd, Cu, Pb and Zn in soils that were used for the open burning of e-waste. Cd and Cu were found in high quantities in soils near paddy and vegetable sites, while Cd and Pb were found in the edible tissues of vegetables [59].

Leung et al. carried out investigations on the levels of PBDEs and PCDD/Fs in soils and residues of combustion from a Chinese e-waste dismantling and processing site, Guiyu. The levels of PBDEs in combustion residues from a residential area were the highest measured in this study: 33,000 – 97,400 ng/g, dry weight. These concentrations ranged from 2,720 to 4,250 ng/g dry weight in samples from an acid leaching site. An analysis of soil samples from the acid leaching site showed the highest levels of PCDD/Fs (12,500– 89,800 pg/g). The concentrations of PCDD/Fs in the combusted residue were found to range from 13,500 to 25,300 pg/g. These results further confirm that these two informal e-waste processing activities released very high levels of PBDEs and PCDD/Fs in the surrounding areas [36].

As more strict regulations have come into force in China, the extent of these pollutants is starting to show a downward trend in their concentration over time. The PCB contents in soils of Taizhou have decreased from 2005 to 2011, while PCDD/Fs have remained fairly constant. PBDEs have shown a slight decrease as well [60]. These pollutants have also been analyzed in rice hulls over a period of time; an overall reduction was observed [61].

The situation in Bangladesh is quite similar to the ones described above. Illegal exports and informal sectors processing e-waste inappropriately have kept on increasing every year. Leaching of toxic compounds as well as pollutant emissions was seen to occur in ship yards as well as in processing areas. Investigations on pollutants released from e-waste were carried out in a ship yard in Chittagong, Bangladesh. Soil samples showed high levels of lead, cadmium, chromium, mercury, selenium, antimony trioxide, arsenic, cobalt and brominated dioxins [62].

An analysis of eleven metals (Ag, As, Cd, Co, Cu, Fe, In, Mn, Ni, Pb, and Zn) in surface and soil samples from both formal and informal processing sites in Manila, Philippines was carried out. Results showed that levels of these metals in informal processing sites were similar to those measured under similar conditions around other Asian countries. High levels of metals were recorded in both formal and informal dust analysis [63]. Another study on heavy metal levels in the soil surface of an informal e-waste processing site in Manila showed the place to be contaminated with copper, zinc and lead [64].

An analysis of heavy metals in an informal e-waste processing site in Mandoli, Delhi, India also showed their high concentration in surface soils. Concentration of lead was the highest measured, reaching 2,645.31 mg/kg, followed by zinc (776.84 mg/kg), copper (115.50 mg/kg), arsenic (17.08 mg/kg), selenium (12.67 mg/kg) and cadmium (1.29 mg/kg). Heavy metal content was also high in the local groundwater as well as in native plants [65].

5.2. Air quality

A number of studies have been carried out on the air pollution caused by the informal and inappropriate e-waste processing activities. A brief description of these is presented in this section.

An analysis of PCDD/Fs, PCBs and PBDEs were carried out in ambient air samples of Taizhou, an e-waste dismantling area. The concentrations of total PCDD/Fs, PCBs and PBDEs were found to range from 2.91 to 50.6 pg/m³, from 4.23 to 11.35 ng/m³ and from 92 to 3086 pg/m³ respectively. The levels of these three pollutants were found to be directly associated with the dismantling activities. The chlorinated dioxins and furans were mainly observed in the particulate phase, while PCBs were found only in the gas fraction [44]. Levels of PCBs and PBDEs were also measured in air of houses in an e-waste processing area in Vietnam. The concentrations of these two pollutants were observed to be much higher (1000–1800 and 620–720 pg/m³, respectively) than in the control areas [66].

Chlorinated and brominated dioxins and furans were analyzed in Longtang, China, and two other villages in the vicinity. The levels of PCDD/Fs were observed to be ~17 times higher than those observed in the distant neighborhood. However, high measured levels in these two

vicinity sites were mainly attributed to dismantling activities in Longtang; as these particulates are known to be persistent and can be transported over long distances through air [67]. Chlorinated and brominated dioxins and furans contamination in air was analyzed in the e-waste dismantling area of Guiyu, China. Levels of PCDD/Fs were found to be among the highest in the world ranging from 64.9 to 2365 pg/m³. PBDD/Fs concentrations in air were also determined to be very high [68].

Total suspended particles (TSP) and particulate matter 2.5µm were analyzed from the air of Guiyu. PAHs related to TSP and PM2.5 was found to range from 40.0 to 347 and 22.7 to 263 ng m⁻³ respectively. The levels of Cr, Cu and Zn in PM2.5 were observed to be between 4 and 33 times of values typically measured in other countries of Asia. Such an exposure was inevitable for the people living in the dismantling area [69]. Another study in Guiyu showed that all congeners of PBDEs analyzed in air were ~58–691 times higher than in other cities and were more than 100 times higher than recorded in previous studies [70].

Air samples from the Agbogbloshie market located in Accra, Ghana, were analyzed to assess levels of metals and corresponding exposure of workers and people moving around in different areas of the market. The site is known to be a dismantling and trading place for end of life electronic items, as well as an informal processing and dumping site. Both air and soil in these and surrounding regions were found to be heavily polluted. Air samples had high levels of aluminium, iron, zinc, copper and lead [71].

5.3. Water quality

Water tables have also been found to be contaminated by the crude e-waste processing activities. Some of the studies on water pollution are described as follows.

An analysis of heavy metals contamination in ponds and well waters was carried out in the vicinity of a former e-waste processing site in Longtang, China. Results showed acidification and contamination with Cd and Cu of the pond water used for the irrigation of paddy soils. Well water was less contaminated with heavy metals, however it was observed that the surface soil showed high concentrations of these metals which were transported to other areas such as pond water [72]. Concentration of lead in the groundwater of an e-waste processing site was found to be elevated. Such a contamination has a high potential for producing cancer [26]

Rivers Lianjiang and Nanyang in Guiyu, China, were both found to be highly contaminated with a range of metals. Lianjiang river showed high levels of As, Cr, Li, Mo, Sb and Se, while Nanyang river had high contents of Ag, Be, Cd, Co, Cu, Ni, Pb and Zn. Sediments of these rivers had concentrated levels of Cd, Cu, Ni, Pb and Zn [56, 73].

PCBs levels in fish from two ponds near a solid waste site in Kolkata, India, were analysed. Results showed levels of 33,000 pg/g lipid weight in fish from a pond located 2 km away from the site. 4,400 pg/g lipid weight was found in fish from the pond located 3 km away. These levels are extremely higher compared with a reference sample taken, which was 1,900 pg/g lipid weight [74].

5.4. Human health

A number of investigations have been carried out to show the impact of inappropriate processing of e-waste on human health and associated consequences. A brief overview of these studies is presented in this section.

Human breast milk was analyzed for PCBs and PBDEs in three e-waste processing sites of Vietnam. PBDEs concentration was significantly higher in two of the processing sites (20–250 ng/g lipid weight) than in the reference city, Hanoi. PCBs levels were much lower than PBDEs (28–59 ng/g lipid weight). Exposure to these pollutants was believed to have occurred through inhalation and the ingestion of dust [33]. Both PCBs and PBDEs levels were analyzed in two e-waste processing villages in China. While recycling facilities in Luqiao process PCB containing e-waste, PBDEs containing e-waste is processed in Wenling. Dual exposure and associated burdens were found to be significantly high at both processing sites [75].

Samples of human milk were taken from women living nearby a solid waste dump in Kolkata, India. Average levels of PCBs reached 1700 ng/g lipid weight, while in the reference site the concentration was as low as 60 ng/g lipid weight [76]. PCDDs levels obtained were 610 ± 280 pg/g, while PCDFs reached 44 ± 20 pg/g in mothers giving birth for the first time [74]. Hair samples were also analyzed for PBDEs as well as for PCDD/Fs in Taizhou, China. PBDEs levels ranged from 22.8–1020 ng/g dry weight, which was three times higher than the reference samples. PCDD/Fs levels were found to be 126–5820 pg/g dw, which was 18 times higher than reference samples. This study has shown evidence of the high level of exposure to persistent organic pollutants from e-waste [77]. PCB concentrations as well as PBBs and PBDEs were also analyzed in people diagnosed with cancer living in an e-waste disassembly site in Zheijiang, China.

Levels of these three pollutants were found to be high enough to relate with high incidences of cancer in this e-waste processing site [78]. The concentrations of PCBs, PBDEs and dioxins and their correlation with thyroid stimulating hormone in children from Luqiao were assessed. The levels of all pollutants were much higher in children from Luqiao than in the control area, while levels of TSH were found to be lower in children from the e-waste processing site, as well as the distribution of TSH in their bodies was affected [34].

PCBS, PBDEs and HBCDs were analyzed in human milk samples in Ghana. Even when the levels of these were lower than measurements in Chinese e-waste processing sites PBDEs (0.86–18 ng/g lipid weight) and PCBs (15–160 ng/g lipid weight), Ghana is much less industrialized. The source of these pollutants is believed to have come from the informal handling and disposal of e-waste [31]. PAH metabolites were analyzed in the urine of the workers from an e-waste processing site in Agbogbloshie, Ghana. These were found to be significantly higher than a control group. Two thirds of the workers had cough, while one quarter had chest pain [79].

Serum of workers of an e-waste processing site in India was analyzed to study the presence and levels of PBDEs. Results showed an average of 340 pg/g wet weight, higher than a control site [80].

In regions where the exposure to POPs was high, there was also an evidence of correlations between the accumulation of POPs and DNA lesions and dysregulation of DNA damage repair mechanisms [81]. Exposure to metals released from informal e-waste processing has been also analyzed. High concentrations of Fe, Sb, Pb, As in urine were found for workers of an e-waste processing site in Ghana [82]. Trace and heavy metals were also analyzed from the scalp hair samples from people living near an e-waste processing site. Lead and copper were found to be the highest compared to control areas [83].

Various studies on the exposure of children to metals have been reported in the literature. Analysis of chromium, nickel and manganese and their relation to lung function was assessed in children living in an e-waste processing site in China. Levels of Mn and Ni were found to be comparatively higher than for children from the control areas. These two metals can be responsible for lower pulmonary function as well as oxidative damage [84]. Levels of lead and cadmium were analyzed in children of Guiyu, China. Both metals had much higher concentrations in children from Guiyu than from Chendian (control area). These enhanced levels were associated with significantly lower height of Guiyu children [85].

Lead exposure and their correlation with physical growth, bone and calcium metabolism in children from Guiyu, China were investigated. The exposure to lead was found to affect growth and increased bone resorption that may lead to osteoporosis. [86]. Lead levels in blood of children of Guiyu, China, were also analyzed and correlated to temperament alterations. Authors found evidence of significant differences in activity levels, approach withdrawal, adaptability and mood of Guiyu children and a control area (Chendian, China). The main risk factor was the absence of hand washing prior food consumption [87]. Lead concentrations were measured in children from Luqiao, China. 6.97 $\mu\text{g}/\text{dL}$ of lead were found in children from Luqiao, compared to 2.78 $\mu\text{g}/\text{dL}$ of a reference area. Some consequences of lead levels were lower calcium, and a negative relationship between lead levels and intelligence quotient [88].

Levels of lead in cord blood were measured in Guiyu, China. Analysis showed that Pb concentrations in Guiyu children were much higher than in the control area, Xiamen 10.78 $\mu\text{g}/\text{dL}$ vs 2.25 $\mu\text{g}/\text{dL}$. These levels were related to adverse birth outcomes, such as stillbirth (four times higher risk than in Xiamen), lower birth weight and lower Apgar scores (test related to the tolerance of birth and the requirement of medical attention) [89].

Ha et al. analyzed the levels of zinc, copper, lead and manganese contained in the hair of workers of an e-waste processing site in Bangalore, India. Zn content was 141 $\mu\text{g}/\text{g}$ dry wt., while Cu, Pb and Mn reached 22.8, 9.07 and 1.16 $\mu\text{g}/\text{g}$ dry wt, respectively [90]. A similar situation was observed in Pakistan. Activities to extract metals generally comprise dismantling, open burning or acid leaching. Informal sector receives end of life equipment from illegal imports. Typical age of workers ranges between 6 and ~50 years, with children doing the same work as adults. Exposure to toxic compounds present and released from the informal processing directly affects their health with severe consequences. Breathing problems, cuts, burns, fever and body aches were reported from workers in this sector [91, 92].

Open burning is used in Lima, Peru, for the removal of polymer from copper wires. The scale of these operations is far smaller than the ones reported in Asia and Africa, but carried out under similar conditions. There is generally little processing of e-waste in Peru, only collection and dismantling, a common practice in Latin America. Printed circuit boards and valuable parts are exported to China and Europe for final recovery processing. However, if gold content is high, local workers recover the metal by using hydrometallurgical methods, such as acid or cyanide leaching, or amalgamation with mercury. Residues such as cathode ray tubes glass or secondary leftovers are generally dumped, leading to severe environmental and health issues [93]. An analysis of the health of workers of an informal e-waste processing site located in Santo André, Brazil, has shown the workers to suffer from pain in the back, shoulders, arms and legs, and respiratory diseases such as flu and bronchitis [94].

6. Challenges and opportunities

As described in this chapter, there are a range of hazardous and toxic compounds that may be present in significant quantities or can be formed during the processing of e-waste. All these different types of contaminants are associated with severe environmental and health consequences. Some pollutants can be dispersed through the air, water and soil. In other cases, by-products are dumped directly into the soil or waterways, where the subsequent leaching of pollutants could contaminate the environment and influence food chain supplies as well. Direct human exposure to these contaminants can also have irreversible health effects. There is evidence of dermal, gastrointestinal, hepatic, neurologic toxicity and breath issues in humans, immunologic toxicity and reproductive issues in animals, high levels of lead, copper and chromium, especially in children, changes in milk, placenta, hair and thyroid hormone levels, and even lung cancer and leukemia cases.

The identification of various hazardous substances present in a range of e-waste, toxic compounds generated during processing, as well as the public awareness regarding the severe consequences to health and environment caused by improper handling and processing of e-waste is crucially important. This knowhow will lay the foundations of sustainable processing of e-waste, and prevent the release of toxic pollutants during the recovery of valuable resources. This chapter has presented an overview on the nature and associated impact of a number of harmful compounds that could be produced by a range of recycling approaches.

Better practices in collection, handling and processing of e-waste are needed, especially in the developing countries where e-waste is mostly processed informally and inappropriately, with huge consequences on environment and health. While stricter regulations have improved and reduced the toxic emissions to the environment, however, there has been an accumulation of hazardous compounds over time. There is an urgent need to improve current approaches towards developing environmentally friendly waste recycling and material recovery.

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