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A review on various electronic waste recycling techniques and hazards due to its improper handling.

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Abstract:- The growing use of electrical and electronic equipment and their early obsolescence has resulted in generation of a large quantity of electronic waste (e-waste). This ever piling waste, if not handled properly, can have various detrimental effects on biotic as well as abiotic components of the ecosystem.Proper handling of this waste requires good recycling designs and improved machineries. In developing countries like India, China, Indonesia, Brazil, commercial organizations tend to focus more on economic aspects rather than environmental regulations of waste recycling. So, for the profitable recovery of reusable materials and sustainable environment, the efficient recycling of this waste has been rendered indispensable, and is considered as a challenge for today's society. In this literature study, first we have briefly introducedseveral toxic components present in e-waste or generated during recycling processes and their detrimental effects. This is followed by various commercial techniques used for recycling of metallic and non-metallic fractions of e-waste.

Keywords: Electronic waste (e-waste), health hazards, metallic fractions (MFs), non-metallic fractions (NMFs), recycling techniques and wastes printed circuit boards (WPCB).

I. INTRODUCTION

An end-of-life equipment, whose working depends on electric current or electromagnetic field is referred to as electrical and electronic waste (e-waste) [1]. In recent years, the amount of consumers and business of electronic equipment has increased enormously. According to the recent studies by researchers[2], the production of Electrical and Electronic Equipment (EEE) is growing very fast, i.e. about 3-5% per year [3,4]. Also the advances in information and communication technologies, resulting into increasing versatility of most electronic devices together with the ever decreasing electronics prices have led to a drastically reduced lifespan for most electronic equipment. The growing use of such equipment, together with their early obsolescence has contributed to the generation of e-waste, to a large extent.

There has been a significant increase in quantity of generation of e-waste in the USA, the EU and developing countries like India and China, over the past decade[5]. As reported by US Environmental Protection Agency [6], each household in the USA uses about 34 electronic devices and electrical appliances, on an average, resulting in generation of more than 5×10^6tons of e-waste per year [6]. For the EU, it was estimated that, on an average, each citizen generates about 15 kg of electronic waste per year, to give an approximate total of 7×10^6tonnes[6].About 8% of the total municipal waste originates from waste of electrical and electronic equipment (WEEE) [5]. In developing countries, like China and India, e-waste generation per capita is still only about 1 kg per year [5], but this is increasing rapidly. Due to the huge population, it would not take long for the total e-waste generation, in these two countries to surpass that produced in the western countries. In addition, the amount of e-waste in the newly industrialized and developing countries [5] is also growing because of the import of e-waste from developed countries. According to the recent studies, up to 50– 80% of the WEEE, that generated in developed markets is being shipped to developing countries for reuse and recycling [5], often against the international laws.

E-waste, if not managed properly, can have very fatal effects on the environment as well as the living beings in the vicinity. In most of the developing and under-developed countries, e-waste is dumped directly into the soil without any treatment; often due to weak environmental regulations and financial problems. This can induce toxicants into the soil, making it barren and often leaching into the ground water and contaminatingit.Hence, management of this ever piling WEEE is a big matter of concern in developed as well as in developing countries. For profitable recovery of materials and sustainable environment, the efficient recycling of electronic waste is very necessary, and is still regarded as a major challenge for today's society. Recycling of

PCB is an important subject not only from the treatment of hazardous waste point of view but also from the recovery of the valuable materials [7, 8] point of view. PCB recycling is difficult particularly because of its heterogeneity in organic materials, metals and glass fibers [8, 9]**.** Hence, in this review, major focus is onhazards caused by such e-waste, followed by various recycling and recovery techniques of metal and non-metallic fractions of waste PCB and their reusability.

This paper is structured as follows: In the first section, the health hazards caused by various components in e-waste are discussed. It is then followed by several physical and chemical recycling techniques for e-waste management. In the final section, some modern profitable applications for the reuse of the recovered materials have been discussed.

II. HEALTH HAZARDS CAUSED BY EXPOSURE TO E-WASTE.

E-waste not only includes house-holdand industrial electrical appliances but also includes their components such as, batteries, capacitors, castings, cathode-ray tubes, glass, etc[10]. Recycling of such waste has been carried out both formally and informally in several countries like China, India, Ghana, Thailand, Vietnam, etc. [11, 12]. Formal recycling techniques use well designed techniques and machineries to safely separate the required fractions from the waste, but are expensive to build and run. Such recycling techniques do not have much impact on the environment.In various underdeveloped and developing countries, where finance is a major issue of concern, cheap informal recycling methods are implemented. This may release several pollutants in the environment, on exposure to which, might result in several detrimental effectson various biotic and abiotic components in vicinity of such informal recycling plants [12-14].

Most common ways of exposure to hazardous components of e-waste is by ingestion, skin contact and inhalation, through mediums like contaminated soil, water, food and air [15-27]. Pregnant women, workers in the informal e-waste recycling plants, children, and other vulnerable populations come acrosscomparatively more risks of exposure. Children are at maximum risk because of additional mediums of exposure (eg, maternal feeding), excessive dermal contact behaviors (eg, hand-to-mouth activities in early years and care less behaviors while growing ages), and their changing body requirements (eg, more intake of water and food, and low rates of toxin elimination)[28]. The effect can also transfer from workers in informal recycling plants to other family members through dermal contact, clothes, etc.

Hazardous chemicals or compounds from e-waste can come either from the components of that electronic equipment itself or form during recycling process. Pollutants those are difficult to break down due to long half-lives, known as persistent organic pollutants (POPs), are major hazardous pollutants in e-waste. Some of the most common POPs that are found during recycling are brominated flame retardants (BFRs) (poly-brominated di-phenyl ethers), polychlorinated biphenyls, hexa-bromocyclododecanes, poly-brominated di-phenyls, di-brominated di-phenyl ethers, poly-chlorinated or poly-brominated dioxins and di-benzo furans dioxins, and per-fluroalkyls. POPs formed during dismantling and smelting consists of polychlorinated di-benzofurans, polychlorinated biphenyls and dioxins like polychlorinated dibenzodioxins.Poly- cyclic aromatic hydrocarbons get generated due to incomplete combustion of fuels like coal, gas, oil, etc.[16, 29]. These hydrocarbons get releasedinto environment during the combustion of e-waste materials.[30]Heavy metals like lead, cadmium, chromium, mercury, copper, manganese, nickel, arsenic, zinc, iron, and aluminum can also impose several hazardous threats [31].Table 1 shows a brief account of various hazards caused by exposure to different components of e-waste, vulnerable population section and medium of exposure.

Table 1.Brief account of major e-waste toxicants, their source, medium of transfer and Major hazards on long term exposure.

Major toxic component	Source of exposure	Medium of exposure	Major health hazards on sufficiently high exposure	Reference(s)
Polybrominated di-phenyl ethers.	Fire retardants	Air, water, food and soil	Thyroid disfunction	[32, 33]
Polychlorinated Bi-phenyls.	Capacitors, lubricants dielectric fluids, motors, coolants, etc.	Food (may result into bio-accumulation), dust and soil	Thyroid disfunction	[32, 34]
Polychlorinated di-benzodioxins, polychlorinated di-benzofurans,	Combustion byproduct	Air, soil, dust and vapors	Thyroid disfunction	[32, 34]
Chromium	Corrosion resistant films, memory tapes, disks, etc.	Soil, water, air, dust.	Lungs dis-function, reproductive health and DNA damage.	[32, 35, 36]

Lead	PCBs, computer monitors, bulbs, Televisions.	Dust, air, water, soil	Reproductive health, growth, mental illness, DNA damage.	[32, 34, 37, 38, 39, 40, 41]
Nickel	Batteries	Dust, air, water, soil, food	Lungs disfunction and growth	[32, 42, 43]
Copper	Wires, PCBs, etc	Dust, air, water, soil	Headaches, dizziness, irritation in eyes, nose, mouth, etc.	[41]
Cadmium	Switches, connecting components, PCBs, semiconductor chips, xerox/photocopy machine, batteries, computer monitors, cell phones, etc.	Dust, water, soil, air, food.	Reproductive health, DNA damage.	[32, 43, 41, 44]
Mercury	Thermostats, computer monitors, cell phones, PCBs, sensors, etc.	Food (bio-accumulative), water, soil.	Reproductive health, growth, mental illness, DNA damage.	[32, 45]
Polycyclic aromatic hydrocarbons	Combustion byproducts	Air, water, soil, dust	Reproductive health	[32, 46]

It can be concluded from table 1 that, on long term exposure of many of the e-waste toxicants, may result into extremely fatal effects. Hence, proper management of this large amount of ever piling e-waste is very important. Due to this, recycling of this huge e-waste is being practiced all over the world on a large scale. In the next section, several recovery and recycling techniques for metallic and non-metallic fractions of e-waste have been discussed.

III. RECYCLING TECHNIQUES

Printed circuit boards (PCBs) is one of the most important component of electronic equipment. These PCBs encompass majority of the valuable metals and also most of the toxic components in the e-waste. PCB waste recycling includes three processes namely, pretreatment, physical recycling and chemical recycling [47]. Starting with pretreatment stage, it includes disassembling of the reusable and toxic parts using shredding or separation and followed by physical recycling process. Finally material is recovered by chemical recycling process that includes gasification and pyrolysis [47]. There are various traditionaland some modern methods to recover the valuable metallic and non-metallic fractions from printed circuit boards (PCBs). The following section will consist of various physical and chemical recycling processes for recycling of metallic and non-metallic fractions from waste PCBs.

3.1 Pyrolysis method.

Pyrolysis is a chemical recycling technique, extensively used for recycling synthetic polymers including polymers that are mixed with glass fibers. Pyrolysis of such polymers gives gases, oils and chars. These products can further be used as chemical feedstock or fuels [48]. The printed circuit boards are heated to a temperature, high enough to melt down the solder, used to bind the electrical components to the circuit board, in the presence of oxygen. After pyrolysis blackish metal substance is left behind [49]. This blackish metal (Fig 1) substance on leaching gives good yield of copper. Also, small quantity of iron, calcium, nickel, zinc and aluminum could also be recovered [49]. Table 2 shows the mass composition of the pyrolysis gases produced by PCBs from different equipment in wt. % [8]. Also Table 3 and Table 4 shows the composition of metals present in the char produced by pyrolysis of each of the PCBs and quantification of the major products in the oil resulting from the pyrolysis of PCBs in a fixed bed reactor (%) [8].

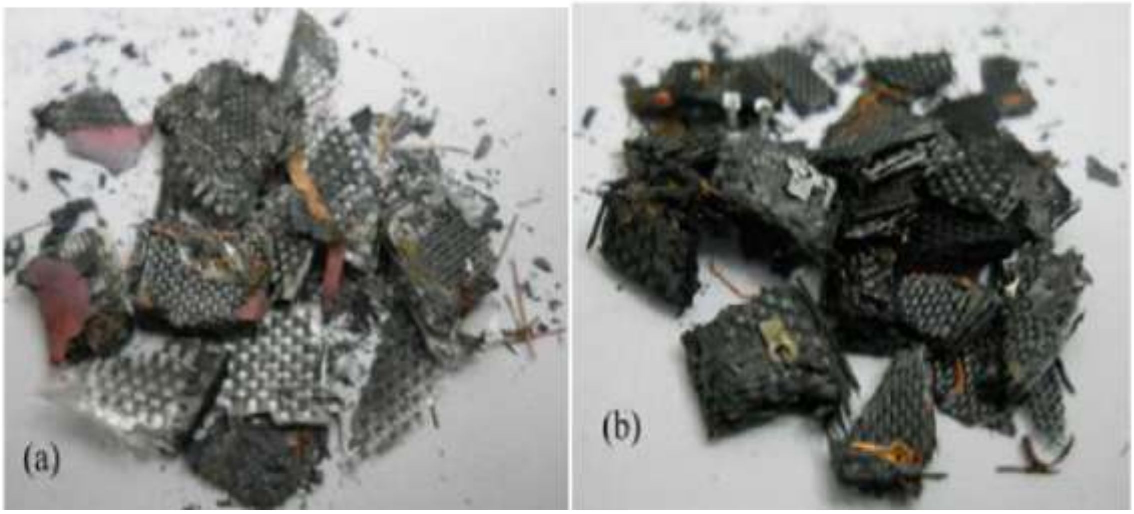

Fig 1.Photographs of PCBs scraps(a) Burned (b)Pyrolysed [49].

Table 2. Mass composition of the pyrolysis gases produced by each of the three printed circuit Board types on a nitrogen free basis (wt%) [8].

Component	Computers	Television	Mobile phone
H_2	4.6	3.2	5.7
CO	27	21.8	36.1
CO_2	51	51.5	45.8
Methane	10.3	14	6.4
Ethene	0.6	1.1	0.5
Ethane	1.9	2.7	0.6
Propene	2	1.1	2.7
Propane	1	1.6	0.4
Butene	0.8	1.8	1
Butane	0.5	1.2	0.2
Cl	0	0	0.1
Br	0.3	0.1	0.5

Table 3. An analysis of the metals present in the char produced by the pyrolysis of PCBs in a fixed bed reactor (mg/kg) [8].

Element	Computers		Television		Mobile phones	
	>600μm	<600μm	>600μm	<600μm	>600μm	<600μm
Li	6	13	<5.6	<5.6	13	15
Na	474	1206	140	554	897	1197
K	151	519	1332	697	236	347
Mg	448	1317	414	4315	635	947
Ca	25167	50647	2578	24905	33901	40984
Sr	185	685	<5.6	20	334	372
Ba	618	8050	41	285	10739	6786
Cr	42	268	118	787	1792	139
Mn	372	177	674	592	654	569
Fe	69729	11355	159671	31461	15089	5366
Co	12	<5.6	93	56	64	39
Ni	10660	1331	24388	1863	13454	6870
Cu	242986	167105	260404	185190	333228	323163
Zn	13139	700	14695	10149	1011	960
Ga	45	27	94	29	210	184
Al	10479	21618	3215	6426	14949	18333

In	**<5.6**	**<5.6**	**<5.6**	**<5.6**	**<5.6**	**<5.6**
Bi	**301**	**77**	**75**	**68**	**<5.6**	**<5.6**
Pb	**128242 21466**		**76900**	**91577**	**1405**	**2495**
Cd	**8**	**<5.6**	**13**	**<5.6**	**<5.6**	**<5.6**
Ag	**6458**	**800**	**15020**	**1164**	**8118**	**4125**
Sb	**<5.6**	**7**	**<5.6**	**12**	**44**	**8**
Au	**6**	**211**	**<5.6**	**<5.6**	**18**	**28**
Hg	**7**	**6**	**6**	**<5.6**	**12**	**7**
Pd	**<5.6**	**<5.6**	**<5.6**	**<5.6**	**<5.6**	**<5.6**
Ti	**19**	**70**	**90**	**1508**	**1508**	**708**

Table 4. Quantification of the major products in the oil resulting from the pyrolysis of PCBs in a fixed bed reactor (%)[8].

Component	**Computers**	**Television**	**Mobile**
Phenol	**25.23**	**10.06**	**38.49**
2-Methylphenol	**1.04**	**1.60**	**1.07**
4- Methylphenol	**1.45**	**2.20**	**0.31**
2,6-Dimethylphenol	**0.27**	**0.50**	**0.15**
2-Ethylphenol	**0.22**	**0.20**	**0.24**
4- Methylphenol	**0.47**	**0.26**	**0.61**
4-(1- Methylethyl)phenol	**8.61**	**1.26**	**16.11**
p-Hydroxydiphenyl	**1.47**	**0.08**	**2.87**
Bisphenol A	**1.38**	**0.11**	**0.67**
Triphenyl phosphate	**0.92**	**4.25**	**0.09**
o-Cresyl phosphate	**0.55**	**0.00**	**0.00**
m-Cresyl phosphate	**0.10**	**0.00**	**0.00**
2,4-Dibromophenol	**0.03**	**0.35**	**0.01**
2,6-Dibromophenol	**0.34**	**0.56**	**0.10**
TBBPA	**0.0006**	**0.0013**	**0.000**

3.2 Hydrometallurgical method

This process is majorly used for profitable recycling of metallic fraction [50]. In this method, metal contents are dissolved into leaching solutions such as strong acids and alkalis. This is followed by electro-refining of desired metals [50, 51].This technique is considered to be more flexible and energy saving, hence cost effective. Widely used leachants are aqua regia, nitric acid, sulfuric acid and cyanide solutions [51]. In case of nonmetallic substrates, metals leach out in the resulting solution, from the substrate [52]. Electrochemical processing can be done to recover metals, in case of metallic substrates [52]. Thus, a pure metal recovered is sold without any further processing while the remaining nonmetallic substrates still need to be treated thermally prior reusing or dumping in landfills. The major disadvantage of this method is the corrosive and poisonous nature of the liquid being used [51].This process also leaves high totally dissolved solids [53].

3.3 Mechanical recycling

It is a physical recycling method. In this method, the disassembled samples are first cut into specific sizes depending upon the milling needs. Then the pieces are put through a milling process resulting into fine pulverized PCB powder. This powder is subjected to eddy current separators that separates the metal by their eddy current characteristics [54]. Finally the pulverized samples are subjected to density separation process [55]. Depending upon the density and particle size, stratification can be seen in the liquid column [56].

3.4 Air classification method

In this method, the separation of dispersed solid particles takes place on the basis of the particle sizes and their density. The principle of separation is based on the fact that the particles suspended in the gas, mostly air, move to different sections under the influence of different forces. Hence they get separated from one another. PCB particles experience drag and gravity force in opposite directions [57]. Heavy particles possess terminal settling velocity larger than the velocity of air whereas lighter particles have terminal settling velocity smaller than the velocity of air. Hence heavy particles move downwards against the air stream, while the light particles rise along with the air stream to the top of the column [57]. Fig 2 shows the schematic drawing of an air classification set up.

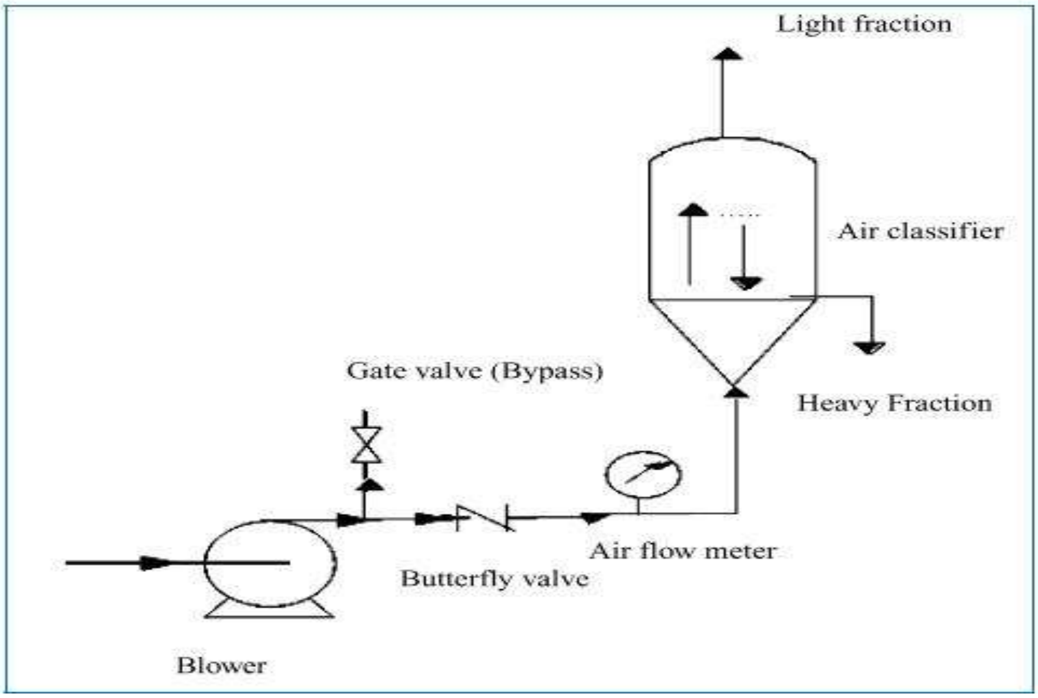

Fig 2. The schematic drawing of a air classification experiment set up [57].

3.5 The separation of waste PCBs by dissolving bromine epoxy resin using organic solvent (DMSO)

Dimethyl sulfoxide (DMSO) is a non-aqueous solvent that act both as a soft base (sulfoxide sulfur) as well as a hard base (sulfoxide oxygen). Various organic and inorganic chemicals are soluble in DMSO also it does not corrode metal. It has a high thermal stability at low temperatures and hence can be recycled many times [58].

The waste PCBs are composed of glass fiber, bromine epoxy resins and metals. The separation process of waste PCB involved its treatment with DMSO in presence of nitrogen environment. The bromine epoxy resin concentration in DMSO was determined by measuring the amount of bisphenol-A, which is a component of bromine epoxy resin [59]. Fig 3 shows the schematic diagram of the reactor for treating waste PCBs in DMSO solvent [59].

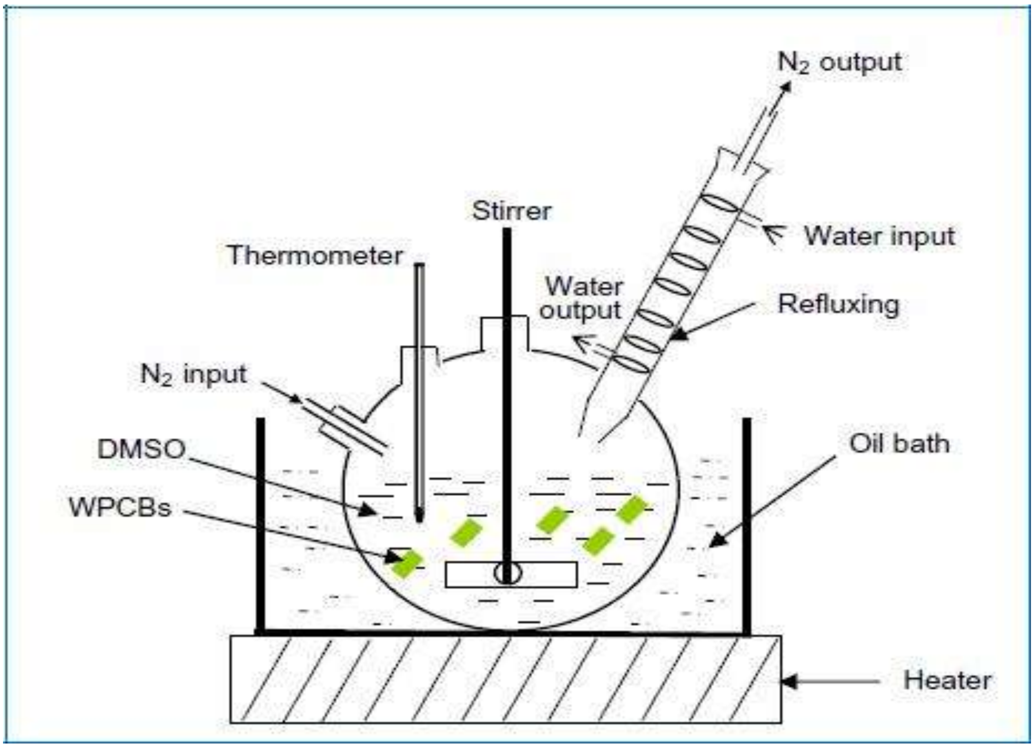

Fig 3.Schematic diagram of the reactor for treating waste PCBs in DMSO solvent [59].

Fig 4 shows a flow diagram of the entire separation process[59]. The used DMSO was continuously stirred and vapored under the decompression. Further the regenerated DMSO and residues can be obtained by cooling down the vaporing substance to room temperature, from which the bromine epoxy resin in DMSO is separated out [59].

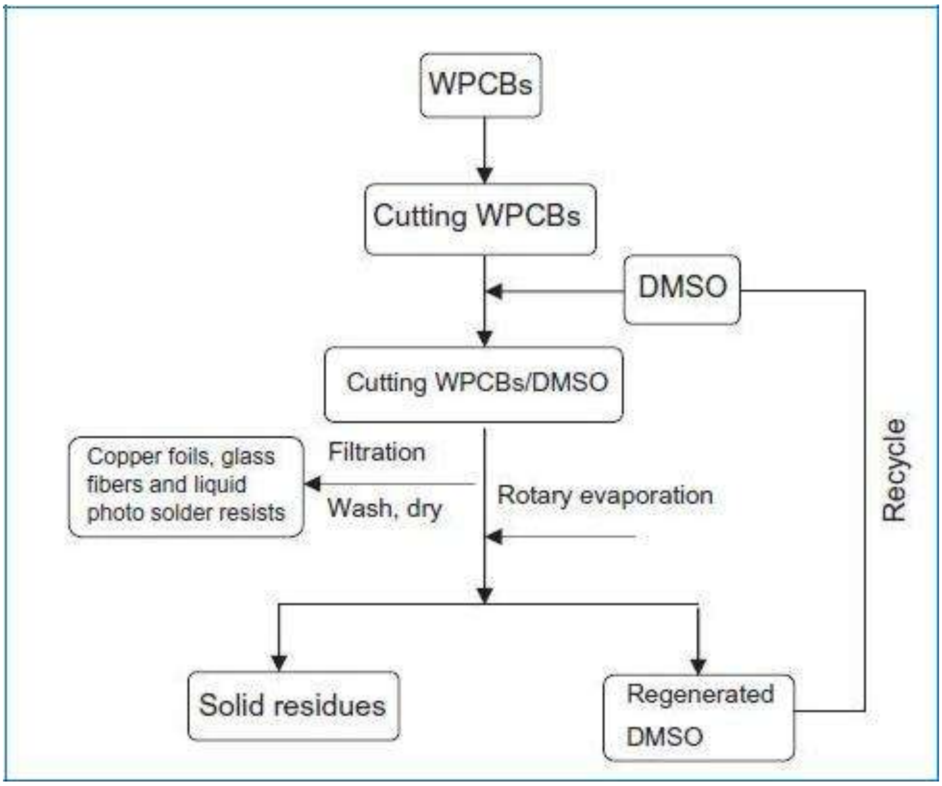

Fig 4. Flow chart of separation process [59].

3.6 Recycling of metals from waste PCB by electrostatic separation method

In electrostatic separation technologies, electric force acting on charged or polarized bodies is used for the separation of granular materials [60]. These technologies have been applied for recycling of metals and plastics from industrial wastes [61]. Electrostatic separation technologies can be used to recycle Cu, Al, Pb, Sn and iron, certain amount of noble metals and plastic from scrapped printed circuit board (PCB) [62].

3.7 Biometallurgical separation method

This method has been used for recovery of precious metals and copper from ore [63, 64]for many years but still the process is not well developed. Biological micro-organisms transfer metal ions into the cells for their intracellular functions by binding metal ions present in the external environment on their cell surface. Every type of microbe has a characteristic tendency to bind with a particular metal in a particular environment. This process could promote selective or non-selective in recovery of metals. Bioleaching and biosorption are broadly the two main areas of biometallurgy for recovery of metals. Bioleaching has been successfully applied for recovery of precious metals and copper from ores for many years[63]. Same methodology can be applied for extracting copper and other precious metals from waste PCBs.

3.8 Magnetic separation method

Magnetic separators with low intensity drum separators are widely used for the recovery of ferromagnetic metals from non-ferrous metals and other non-magnetic wastes [65]. The disadvantage of magnetic separation is agglomeration of the particles. This agglomeration causes the magnet to also pull the non-metal materials which agglomerate with the ferrous materials [47].Hence efficiency of separation lacks.

3.9 Recycling of non-metallic fractions by gasification process

The main application of the gasification process is in the generation of synthesis gas (CO, H_2). Gasification is roughly performed at a temperature of 1600^oC and about 150 bar pressure. The hydrogen rich synthesis gas is the most significant product of gasification. It is a valuable feedstock for methanol synthesis. After proper processing, certain fractions of this gas could be used for generation of heat and electricity [66].

Yamawaki studied gasification recycling of plastic, containing brominated flame retardants, from non-metallic fractions in waste PCBs [67]. He developed a gasification model by which gasification can be achieved at a low decomposition rate, of brominated flame retardants (BFRs), including polybrominated biphenyls (PBB) and polybrominateddiphenyl ethers (PBDEs), which on combustion gives toxic gases, the dibenzodioxins and polybrominateddibenzofurans and dioxins and furans. Hence due to the low decomposition rate of BFRs, the toxicity level drops to a large extent [66]. A model of gasification experimental setup is shown in Fig 5. For detailed process, refer literature [67, 4].

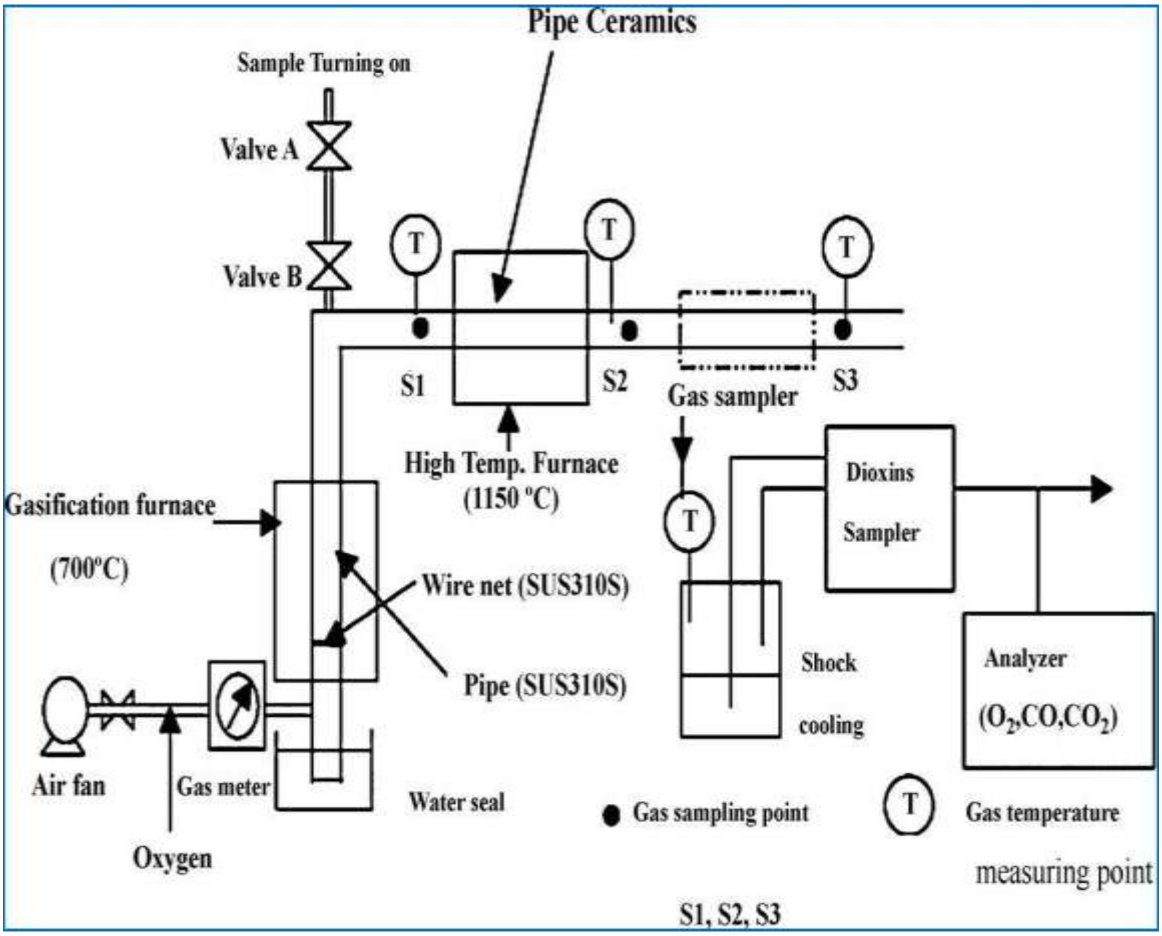

Fig 5.Gasification experimental model [67].

Most of the processes mentioned above are for the recovery of precious metals from waste PCB and reuse it for commercial purposes. After metal recovery, remaining is the non-metallic fractions that usually end up in a landfill [68-70]. Hence there is a strong need for new methods that can make use of these redundant non-metallic fractions from PCB waste. In the next section we will discuss methods for reuse of non-metallic fraction from waste PCBs.

IV. REUSE OF RECOVERED MATERIALS FROM WASTE PCBS

After the recovery of metallic fraction from the PCB waste, what is left behind is the non-metallic fraction. Traditionally the remaining nonmetallic substrates are hazardous (due to presence of brominated flame retardants and heavy metals like lead, cadmium, beryllium, etc.) [68, 69], and have been dumped into landfills after proper treatment. This has caused large soil toxicity problems and contamination of ground water [68-70]. Hence, measures to make use of the non-metallic fractions have been in demand. Recently, there has been some success in better management of non-metallic fraction. In the following section few potential recycling methods and reuses of non-metallic fraction is discussed.

The non-metallic fractions recovered from waste PCB powder are lighter than cement and sand, the granules are much finer comparatively, hence, more reliable microstructure. Mechanical strength of the material is improved by the presence of coarse glass fibers. Hence due to above stated properties, non-metallic fraction can be successfully used as filler material, concrete, for other framing applications, adhesives and decorative agents [47, 71].

A technique had been developed that utilizes the nonmetallic PCB materials in production of Nonmetallic Plate (NMP) [72, 73]. Unsaturated Polyester Resin (UPR) can be used as the bonding agent [7]because of its excellent chemical resistance, fast cure and low viscosity. Also it is cost effective [74]. Fig 6 shows specimens of a NMP.

Fig 6.Specimens of NMP [75].

Further, the NMP was used to produce composite boards. Composite boards find applications in many fields including automobiles, furniture, amusement equipment and decorative materials [47, 76]. Nonmetallic fractions from waste PCBs can also be used to make products which results in greater bending stress due to their excellent flexural strength [47, 76].

Phenolic molding compounds (PMC) are majorly used in the production of radios, kitchen utensils and electronic switches. Increase in production of PMC has led to rise in demand for wood flour, which is used as organic filler in molding compounds. Due to decreasing timber resources and increase in their price, there was need for an alternative for wood floor. The nonmetallic fractions from paper-based waste PCBs seemed a good alternative for wood floor [75, 77]. The process of producing filler material from PCBs is as follows: Starting with pulverization, including coarse-crushing and fine- pulverization, using a shearing machine and a hammer grinder, followed by an electrostatic separation for separating the metallic fraction from non-metals and finally, screening by a vibrating screen, to get the filler for PMC. Fig7 shows metallic and non-metallic fractions after pulverization of waste PCBs [72].

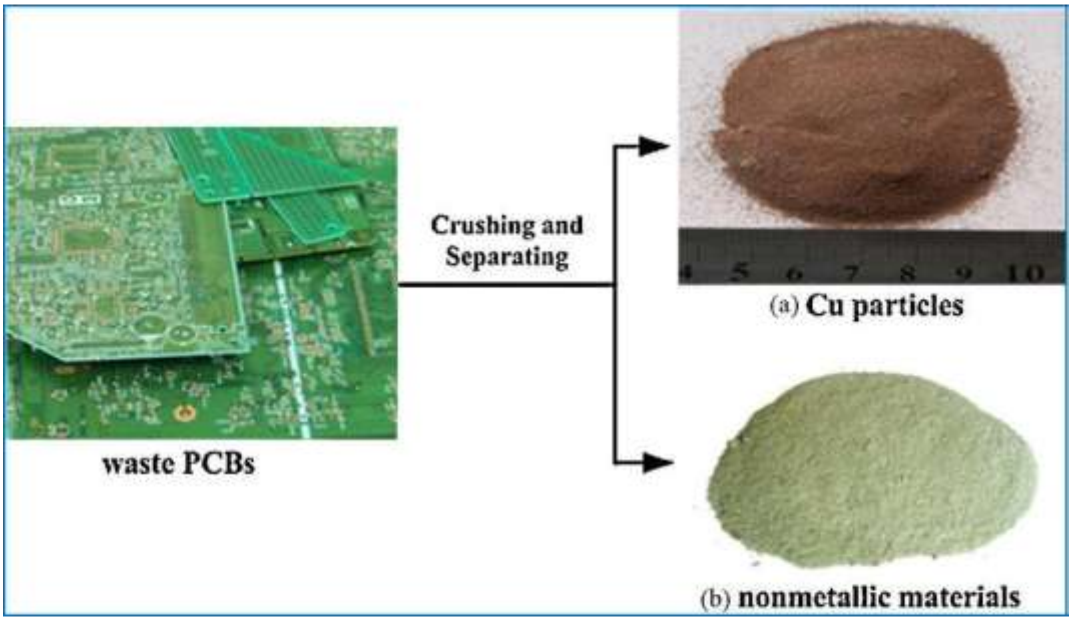

Fig 7.Metallic fractions (MFs) (a) and the NMFs (b) of pulverized waste PCBs [72].

Apart from the above methods, non-metallic fractions of the waste PCBs can also be used to produce reinforcing fillers for thermoplastic resin metal composites [78]. Nonmetallic fractions of PCB has been effectively used as reinforcing fillers in polypropylene as it provides increased strength and rigidity, with particles size between 0.178-0.104 mm [73].

V. CONCLUSION

The advantage of physical recycling methods like magnetic separators, density separators, etc. over chemical recycling is that, they require low financial investment in instruments; they are relatively simple, convenient, less environment polluting and require less energy to operate. Metallic fractions obtained from physical recycling can be commercially used without much treatment but non-metallic fractions need to go through proper chemical recycling procedure for commercialization. Hence, physical recycling methods are more economical for recycling of metallic fractions than non-metallic. The main purpose of chemical recycling methods like pyrolysis is to convert the polymers contained in the non-metallic fractions to chemical feedstock or fuels. Chemical recycling methods have the advantages in converting bromine fire retardants to monomers and in taking out the heavy metals left in residue, over physical recycling methods.

As discussed earlier, combustion of the redundant non-metallic fraction obtained after recycling of waste PCBs, in municipal solid waste causes the formation of highly toxic polybrominateddibenzodioxins and dibenzofurans, while land filling of the non-metallic adds to secondary pollution caused by heavy metals and brominated flame retardants leaching to the groundwater, resulting in contamination of soil, water, food and air in nearby region. This can have detrimental effects on living beings in the vicinity. Hence, it is the non-metallic fractions that have to be recycled from waste PCBs, environmental soundly.

Lot of research is going on in the field of recycling of both metal fractions and non-metallic fractions but with more emphasis on metallic fractions. There is still a lot of room for research in the direction of development of economical processes for recycling of non-metallic fractions from waste PCBs.

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