Chapter- 1

Introduction

1. Introduction

Growing population, techno-economic advancement, and increased consumer need for comfort have led to rapid increase in per capita utilization of electronic gadgets (e-gadgets) all over the world. All e-gadgets (domestic, industrial etc.) possess certain life-span and after completion of it, they are discarded. Many e-gadgets are discarded even before the end of their intended life due to factors like malfunctioning, outdated technology, newer available versions etc. A huge quantity of such trash is being generated globally and it joins a waste stream known popularly as Waste Electrical and Electronic Equipment (WEEE) or Electronic Waste (e-waste).

1.1 Composition of WEEE

Domestic and industrial user generated wide spectrum of e-waste form household, warehouse, plant, office etc. The WEEE comprises of rejected e-gadgets like,

a. Refrigerators, air conditioning units, vacuum cleaners etc.

b. Computers, laptops, mobile phone, iPods, tablets etc.

c. Computer monitors, televisions, other display devices etc.

d. Domestic and industrial lighting (FLs, CFLs, LEDs, Halogen, etc.)

e. Speakers, earphones, electrical motors, other magnetic devices etc.

f. Hard discs, jumpers, electrical connectors, circuit breakers etc.

g. Memories, RAM, card reader, pen drive, flash memories etc.

h. Other consumer durables, military and sensing equipment, industrial equipment etc.

1.2 Promoting factors for e-waste generation

In last few decades, the e-waste generation has become a hot issue all around the globe due to humongous generation. The generation of e-waste is influenced by factors like-

a. Rapid economic growth (advancement in living standard)

b. Quick transforming and customer oriented electronic market

c. Increase in the production and sales of electronic devices due to high demand

d. Rapid upgradation of technology and features (continuous launch of newer version)

e. High demand for sophisticated and modern equipments

f. Better appeal and ergonomics made the consumer market more competitive.

Advancement of the global economy of developing and developed countries during last decade has increased the per capita income of the population. This resulted in increased purchasing power of the consumer and hence consumption and rejection of e-gadgets boosted. For instance, in India, per capita annual income was projected to be Rs 103,007 in fiscal 2016-17. Earlier it was Rs. 93,293 in 2015-16, Rs 67,839 in 2012-13 and Rs 61,564 during 2011-12 [1,2].

Per capita income represents the living standard of person and improved living standard involves more electronic instruments for higher luxury and comfort. As the decade passed and human being stepped into the 21st century; the e-gadgets (smartphone and computer) became the essential part of routine life. The utility and dependency upon internet have also been motivating factors towards the routine involvement of e-gadgets in modern lifestyle. A World-Bank report says that at present ~ 40% of the global population has access to the internet and more than 4 billion Google searches are being

performed daily [3]. In developing countries, ~ 80% individual owns a mobile phone. It is a fascinating fact that growth rate of global smartphone subscriber is ~31% per annum and nearly 21% of the world population is switching to smartphone each year [4].

Further, as the economy has advanced, the product-oriented market has turned into a customer-oriented market. Thus, rapid technology and feature upgrade of existing e-gadgets in accordance with consumer needs have become a common marketing trend. This led to the frequent launching of newer models of existing gadgets and boosted the rejection of old ones. Thus, modern civilization resulted in the generation of e-waste amounting million tons which seeks attention towards its proper handling and disposal.

1.3 Importance of WEEE

In early 1990, WEEE was not given much attention due to its very less generation [5]. Later, the globalization resulted in a rapid boom in the WEEE generation and its handling became a global issue. In the last decade, the e-waste generation increased six times and reached to 54 million tons in the year 2014 [6] with an annual growth rate of 5-10% [7]. Forecast projects that developing countries like, India will produce 200-400% more e-waste in the year 2020 from levels of the year 2010 [8]. Another forecast indicates that nearly 25-80% of the computers being used all around the world will be discarded by the year 2030 [9]. Thus, more e-waste generation is expected in the upcoming years. The humongous pile of WEEE often comprise of working/repairable e-gadgets due to their non-applicability for the intended application. Thus, they possess more intrinsic values as compared to non-repairable fractions. Hence, e-waste is considered highly important and may be handled as follows:

a. The damaged component may be replaced and repaired to restore it in working conditions.

b. Non-repairable fraction also contains fully function parts and that can be added to the supply chain of the respective manufacturers.

c. Recyclable and easily detachable components as plastic, rubber, metal sheets etc. may be recycled directly.

d. Un-recycled and complex components like, 'waste printed circuit boards' (WPCBs) etc. may contain metal, nonmetal, resin etc. and thus it must be recycled by a special technique.

e. Non-recyclable fractions may be checked for inherited hazards and should be disposed off carefully.

Recycling and handling of WEEE are essential as it comprises good salvage value, high amount of valuable metal and precious metals (even more than respective ore). It is also notable that most of the WEEE generating habitats are localized in the urban area. Thus, WEEE is often termed as 'Urban ore' and seeks the high attention of the recyclers. Reports state that the precious metal content of WEEE is 10-250 times more than their respective commercial ores [10,11]. WEEE comprises of 30-40% metal along with 70% nonmetal (65% glass fibre, 32% epoxy resin substrate and others) [12–17]. The non-ferrous, plastic and other fraction of WEEE contains heavy metals, toxic compounds and thus adds hazardous value [18].

1.4   Valuable and hazardous contents of WEEE

The WEEE contains various valuable metals, non-metals, plastic, and other materials. The metal comprises of copper, tin, zinc, aluminium, iron, nickel, rare earth metals etc. along with precious metals *viz.* gold, silver, palladium etc. [19,20]. The content of the

copper and gold from printed circuit boards of WEEE is 20-40 and 25-250 times more than their respective commercial ore [11]. Apart from these metals, various kind of recyclable plastics and glasses are also there in WEEE which adds value during its recycling [21,22]. E-waste also comprise of numerous toxic metals and compounds as arsenic, bismuth, beryllium, cadmium, chromium, lead, mercury, lithium, Poly Chlorinated Biphenyls, Poly Brominated Biphenyls (PBB), Tetra Bromo Bisphenol- A (TBBA), Poly Bromo Diethyl Ether (PBDE) etc. [18,23,24]. In spite of a high intrinsic value of WEEE and years of research orientation towards recycling; any commercial, efficient and promising recycling technique has not been developed. Thus, most of the WEEE recycling is carried by the illegal units which implement layman technique such as incineration, open-air burning, hot acid bath dipping etc. This unsystematic recycling process leads to consequences *viz.,* inefficient recovery of valuables, release of toxins into the atmosphere, soil and water pollution, adverse effect on human health and ecosystem etc.

1.5   Indian e-waste generation scenario

India is one of the fastest growing economies in the world as well as among the largest electronic market. World Bank's recent forecast says that by 2017 India will become the fastest growing economy with 7% GDP (Gross Domestic Product) rise [25].

In India, the e-waste generation statistics are not very clear due to the involvement of unorganized e-waste collectors and recyclers. A United Nations University report states that in the year 2014, India generated 1.7 million tons of e-waste (**Figure 1.1**) which is only 4% of global e-waste generation [26]. Although, the current WEEE generation rates of developing countries are lesser than developed countries. But, forecast estimates that the e-waste generation of developing countries will increase by 2-4 times in near

future [27]. By the year 2030, developing countries will dispose of around 400-700 million computers while developed countries are discarding around 200-300 million computers annually [28,29]. India is the 2nd largest telecom market in the world with 1198.89 million subscribers [30] and studies indicates that in year 2020, the amount of rejected computers and cell phone will increase by 5 and 18 times, respectively compared to year 2007 [31]. It is clear from data analysis and forecasts that in near future, India will turn into a massive e-gadget consumer as well as WEEE producer. This situation is appreciating in context to the development and technological advancement but discouraging in environmental aspects and habitat's health. At present, there are 178 registered WEEE recyclers in India, with annual processing capacity of 4.4 lakh tons [32]. The current WEEE recycling rate is ~ 5% and yet, more 50,000 tons of e-waste is being imported in India each year [33]. A report says that nearly 60 % of total e-waste generated in developed countries has been illegally imported in the developing countries e.g., India [14]. The imported and non-recycled e-waste is either being stockpiled due to their intrinsic values or recycled by illegal units running across the country. Present statistics of WEEE generation and handling shows that India's e-waste generation is 3-4 times more than e-cyclers capacity [26]. This situation will become even worst in near future if the e-waste handling and recycling capability are not expanded tremendously in order to handle huge upcoming volume of e-waste. Thus, development of a novel recycling technique for proper handling, cost-effective recovery and safe disposal of the hazardous fraction is essential before the alarming situation is faced.
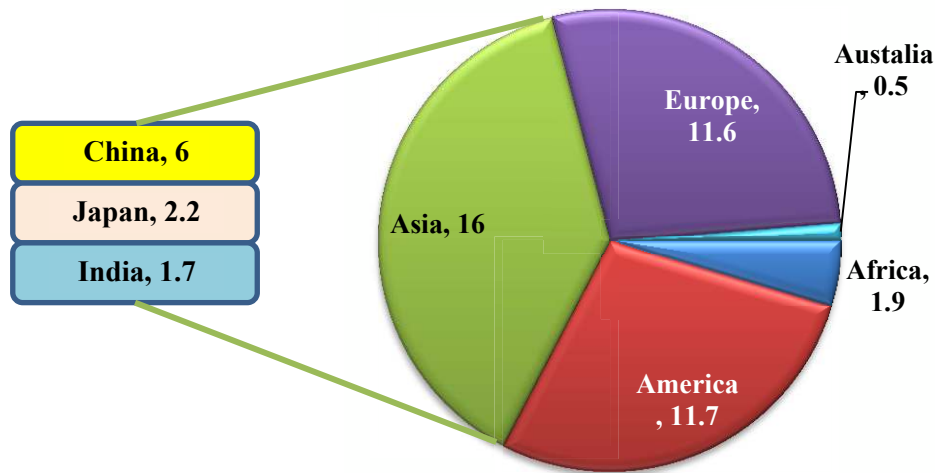
Figure 1.1- E-waste generation of world and India (in million tons) [26]

1.6 Consequences of improper handling of WEEE

Most of the illegal recycling activities are concerned about the recovery of precious metals and copper [34]. The harmful content of WEEE and adverse consequences of improper handling are not considered during the illegal operations [35]. The essential steps followed by the improper e-waste handlers are shown in **Figure 1.2**. Open air burning and incineration leads to conversion of PBB, TBBA, PBDE etc. into toxic dioxins and furans gases [36–38]. Dioxins and furans refer to the group of ~ 75 gases of the Poly-Chlorinated Di-benzo-p-Dioxins (PCDD) family and 135 gases of Poly-Chlorinated Di-benzo Furans (PCDF) family, respectively [39]. Dosage of these gases are extremely lethal to human health and leads to damage to skin, lungs, eyes, liver, nervous system and long-term exposure leads to cancer, genetic changes and reproductive disorders [17,40–43]. Further, the hot acid bath treatment also leads to formation of harmful acid vapor, poor recovery of valuable metal and disposal of waste acid to ground severely affects the quality of soil and ground water due to leaching of heavy metals [44–46]. **Table 1.1** represents a number of hazardous constituents of 500 million computers and these quantities are significantly high [47].
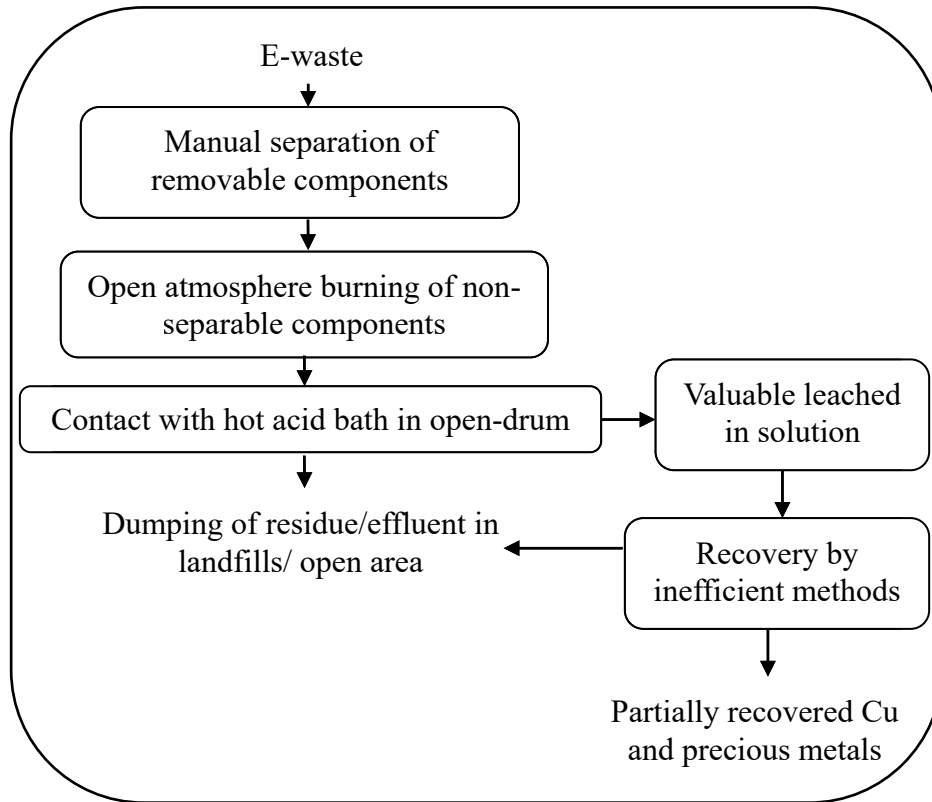
Figure 1.2- General flow sheet of illegal WEEE recycling [34,35,48]

Table 1.1- Hazardous content of 500 million computers [47]

Substance	Quantity
Plastic	2.86 Million tons
Lead	0.716 Million tons
Cadmium	1360 tons
Chromium	861 tons
Mercury	287 tons

The hazardous emissions that may be generated during the WEEE handling and recycling are classified into three categories *viz.,* primary, secondary and tertiary emissions. The primary emissions released into habitats and atmosphere due to direct contact with the hazardous content. The secondary and tertiary emissions are released as

a precursor of decomposition and transformation of the hazardous content of WEEE during recycling techniques such as burning, smelting etc. The ill effect arising due to contact with the toxic content of WEEE are listed below-

Lead is a neurotoxin which adversely affects the proper functioning of kidneys and reproductive systems. Its regular and high dosage can be extremely lethal to human beings. Lead intake retards the mental development of children's and its leaching to ground causes severe soil and water pollutions [49].

Plastics content of WEEE majorly contains Brominated Flame Retardants (BFR), Bis-Phenol A (BPA), PBB, TBBA, PBDE etc. Direct intake of BFRs and BPA is not health friendly as it leads to breathing problems, damage to lungs, liver, skin and eye. Prolonged dosage may lead to cancer and permanent reproductive and genetic disorders. There are 5-10% of halogenated flame retarding plastics in PCBs [13,50]. Now a days, many countries have banned BPA containing bottles for water and food storage purpose. The plastic content emits carcinogens like dioxins and furans once exposed to high temperature. Additionally, these contents can be leached to ground leading to soil and water pollution.

Chromium which is used as a preventive coating against corrosion can damage liver, kidney, lungs etc. In severe cases, it may cause bronchial maladies, asthma and lung cancer [51].

Mercury is a well-known heavy and toxic metal possessing the ability to affect kidney, nervous and immune system of human being. It is easily transported to infants by mother's milk and its transportation through water and vegetable entraps it in the food chain [49].

Long-term exposure to **Cadmium** promotes heavy pain in joints and spinal cord. It softens the bone density and continued exposure may lead to cancer [49].

Acidic fumes of sulphuric and hydrochloric acids are highly corrosive and exposure to human causes irritation in eye and skin. Continuous exposure severely affects the respiratory system and damages the skin.

Other metals and compounds as bismuth, arsenic, lithium, barium cobalt etc. also adversely affect the human health and long-term exposure leads to carcinogenic effects, reproductive disorders, damage to lungs, liver, kidneys etc. [49].

There is a high risk of exposure to ecosystem and habitats to toxins present in e-waste and thus an efficient handling and management system is demanded. It will ensure economical recovery of valuables and minimal toxin emission to the environment.

1.7 WEEE Recycling Statistics

The global recycling statistics show that only 15-30% of generated e-waste is being recycled while rest is either landfilled or stockpiled due to high intrinsic value [52,53]. Further, only 13-16% recycling is carried by formal sectors and rest volume of e-waste is being handled by either informal recyclers or landfilled illegally [26,54]. Improper recycling and illegal landfilling attributes to consequences such as loss of valuables, water and soil-pollution, eco-system degradation because of exposure to the hazardous content, increases the load on mines, poor recovery yields etc. It is noticeable that proper recycling of various components of WEEE saves 20-95% energy than their commercial production [55]. Thus, proper handling and recycling of WEEE is essential to recycle the valuable content and minimize the contact of hazardous to the ecosystem. Among the different components, the Printed Circuit Boards (PCBs) are most attention

seeking because of their complex structure, metal-rich content, associated risks and difficulty in recycling. The fraction of PCBs in the WEEE is varying from 3-6 wt% [8,56].

Development of the advanced manufacturing processes and technology has reduced the size of the e-gadgets considerably. Modern e-gadgets comprise of advanced electrical circuits and electronic assemblies which has replaced the conventional wiring and electrical circuits. Electrical and electronics circuits of modern e-gadgets are etched by electrolytic grade copper on a hard reinforced resin board (substrate). The substrate comprises of multiple layers of circuits interconnected together. Thus, the PCBs are the essential component of all modern electronic devices. Due to this structure, the normal recycling techniques are not applicable to WPCBs. The proportion of PCBs in WEEE is reported approximately 3% [57,58]. Among all kind of municipal waste, the e-waste seeks greater attention due to the presence of precious metals concentration nearly 10 times higher than their respective ore [59,60].

1.8 Structure of PCBs and its composition

PCBs are the core of any electronics devices on which capacitor, resistor, diode, resistance, triode etc. are mounted by precision soldering. The circuit connecting the various components is also etched on the surface, and inner laminates of PCBs by electrolytic grade copper (onto a non-conductive substrate). The structure of PCBs is similar to a multilayered sandwich having 2-8 layers of glass fibre matrix and metal laminates/clads. The sandwiched structure of PCBs is reinforced by using suitable resin to provide the requisite strength and electrical insulation properties [56]. The most common reinforcing agent is halogenated compound blended epoxy resin (HER) which exerts good flexure strength (60 MPa), high temperature and moist atmosphere

operation (moisture absorption 0.15%), flame retardant capabilities up to the temperature of 130 ^{o}C [61,62]. Generally, the epoxy resin substrate of PCBs is blended with 5-20 % of halogenated flame retardants [63]. The schematic view of a cross-section of PCBs is shown in **Figure 1.3**. The electrical circuit etched on the outer surface and inner layers are connected together by drilling '*through hole'*, and '*buried via'*. The walls of '*through holes*' and '*buried via*' are also coated with electrolytic grade copper for providing good electrical connectivity. An inert coating of solder mask (blue, green, purple, magenta colour etc.) is usually spread over the top and bottom surface of PCBs to protect copper circuit form corrosion, short circuit and current leakage.
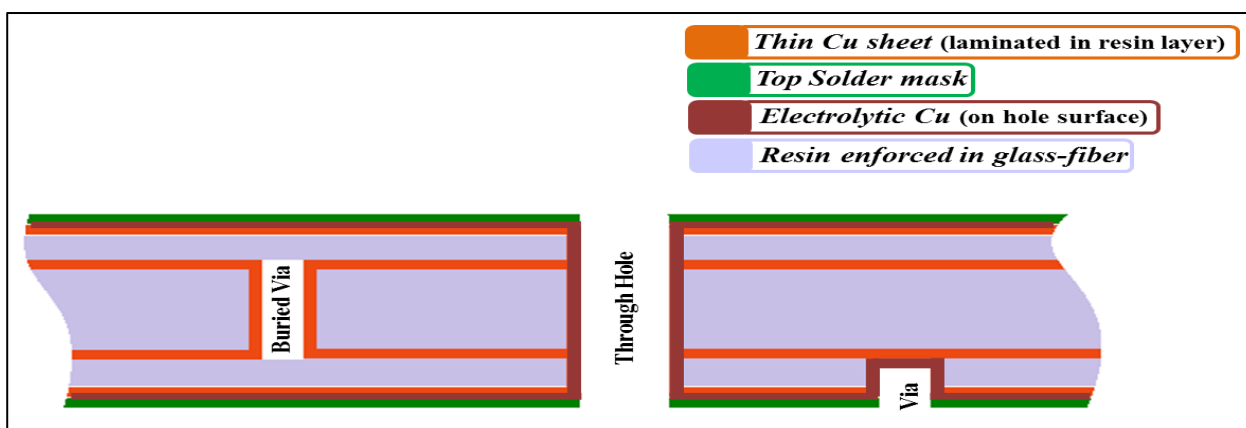

Figure 1.3- Schematic view of cross-section of PCBs

The composition of PCB is generally different from WEEE. It is composed of 15% halogenated epoxy resin (HER), 30% glass fibre, 22% copper, and remaining other metals (tin, lead, iron, nickel, gold, silver etc.) and nonmetals along with solder mask [64]. The composition of WPCBs varies depending upon the manufacturer and the origin of its generation. The different compositions of WPCBs reported by various researchers have been listed in **Table 1.2**.

1.9   Conventional recycling techniques

The early research for recycling of valuable from e-waste started back in the year 1990. Later, the research work throttled with a high pace and numerous methods have been thoroughly investigated. The different techniques may be broadly subdivided into three categories *viz.,* preprocessing followed by mechanical processing and ultimately the end recycling. The overall conventional processing of WPCBs is represented in **Figure 1.4.**

1.9.1   Preprocessing

It includes the collection, sorting, segregation, separation of easily recyclable parts i.e. plastics, glass components, metal cabinets, wires and electrical cables etc., storage and transportation of non-recyclable parts (waste PCBs, intricate electronic components etc.). It also includes removal, storage and transportation of intact (reusable) and toxic components (batteries, liquid colour display, cathode ray tubes, etc.)

Table 1.2- The composition of WPCBs reported in various literature

Metal		Reference									
		[65]	[66]	[67]	[15]	[68]	[66]	[69]	[70]	[71]	[72]
Weight %	Cu	23.4	23.47	20	20	26.8	10	15.6	22	14-18	18.5
	Al	4.7	1.33	5	2	1.9	7			5-8	1.33
	Pb	4.48	0.99	1.5	2		1.2	1.35	1.55	2-4	2.66
	Zn	0.75	1.51		1	1.5	1.6	0.16	0.32		
	Ni	3.32	2.35	1	2	0.47	0.85	0.28	3.6	1-2	0.43
	Fe	7.47	1.22	7	8	5.3	12	1.4	2.6	1-3	2.05
	Sn	3.65	1.54		4	1		3.24		4-6	4.91
	Sb	1.82			0.4	0.06					
	Au	0.08	0.057	0.025	0.1	0.0008	0.028	0.042	0.0350	0.02-.05	0.086
	Pt		0.0003					0			
	Ag	0.08	0.33	0.1	0.2	0.33	0.0011	0.124		0.1-.2	0.694
	Pd	0.02	0.03	0.001	0.005			0.0001		0.01-0.005	0.097

1.9.2   Mechanical processing

The mechanical processing of WPCBs is carried out after pre-processing followed by, end recycling (using hydrometallurgical and/or thermal techniques). Mechanical processing covers various aspects *viz.* separation of recyclable, reusable and magnetic components; primary and secondary crushing; grinding; enrichment of metal content; liberation and separation of metal and nonmetal etc. [73,74]. It includes multiple processing stages by utilizing various manual and automated equipments [75]. Mechanical processing ensures proper size reduction, removal of a the soldered component, liberation of interlocked metals, and separation of the metallic fraction, etc. [76–78]. These are the most influential factors for successful, economical and efficient end recycling [79]. The main advantage of mechanical processing is that it neither leads to the moderate emission of toxins nor requires usage of any corrosive and harmful reagents.
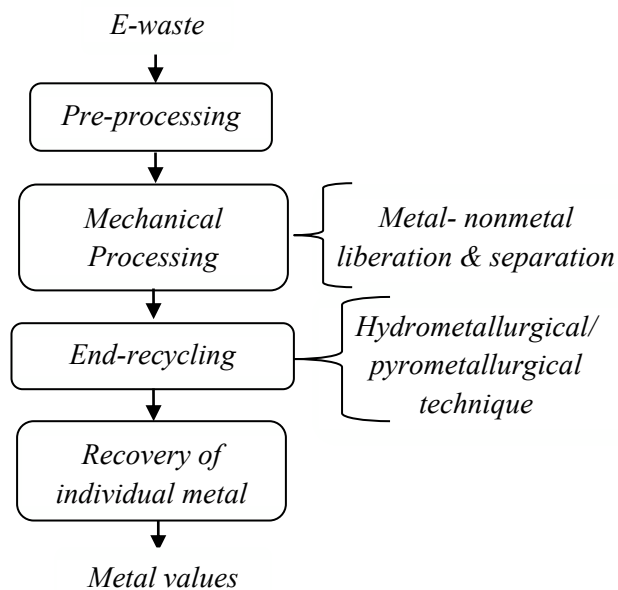

Figure 1.4- Unit processes in conventional recycling of WPCBs

Mechanical processing is quite similar to the mineral processing as it comprises of 3 intermediate steps *viz.,* (i) Disassembly, shredding and sorting; (ii) Crushing, grinding, and liberation of metal and nonmetal; (iii) concentration of metal content. Initially, the disassembly of the intricate component and WPCBs takes place and then different components are sorted into groups. After successful sorting, the primary and secondary crushing of WPCBs is achieved by using shredders having high impact forces [80]. The complex and heterogeneous structure of PCBs encapsulates the metal inside the layers of nonmetallic components. Thus, application of special equipment for crushing and grinding is essential to overcome the barrier to the successful liberation and separation of metal values [81,82]. Application of machines having high impact forces during operation ensures demolition of rigid and high strength structure of WPCBs [80]. After requisite size reduction, WPCBs are ground to fine sizes as it is highly essential for the most efficient liberation of metal and nonmetal and subsequent enrichment of metallic values. Zhang and Forssberg (1999) investigated that successful liberation of metals is achievable only when the WPCBs are crushed to –3 mm. Yet any crushing and grinding technique suitable of producing this size doesn't guarantee the effective liberation and enrichment of metal values. In order to find the most efficient crushing, the applicability of techniques namely knife mill, cryogenic mill, ball mill, stamp mill and hammer mills have been investigated by researchers.

Veit and Bernardes (2015) reported that knife mills are not suitable for waste PCBs due to its very hard and tough structure. These mills are better suited for elastic and relatively soft materials because size reduction is dependent on inter-blade spacing. On the other hand, Cryogenic milling requires liquid nitrogen to developed cracks followed by an increase in crack tip length resulting in rupture of WPCBs. It results in the

generation of relatively coarser product, having non-uniform size distribution. Yoo et al. (2009) investigated grinding of WPCBs of -10 mm size by using stamp mill. The study revealed that 80% nonmetallic fraction was concentrated in -1.2 mm size, while 70% metals were condensed in +5 mm size. This is because unlike brittle nonmetal, the ductile metal elongates during stamping. The concentration of metal in large size range adversely affects the post-treatment operation and thus this process is also discouraged. Applications of ball mills for grinding of WPCBs have also been investigated but fruitful and encouraging results were not found [85,86]. The more energy consumption and rapid wear of grinding media might be the cause behind it. Koyanaka et al. (1997) investigated hammer milling of WPCBs to –1 mm and achieved spherical and non-homogenous copper particles at higher circumferential speeds. Other materials such as glass fibre and resin attained fibrous and angular shape, respectively. Size distribution study revealed that copper possesses coarser size and non-copper is having smaller size due to inherent brittleness. High-speed camera analysis of fracture of material during hammer milling showed that hard resin material exerts brittle fracture initially and later copper foils are peeled off [88]. At the same time, the reinforced glass fibre structure collapsed [88]. Cui and Forssberg (2003) reported 96 % liberation of metals when WPCBs were crushed to –5 mm size. Further crushing to –2 mm size resulted in 99 % liberation of metals [90]. The hammer mill found wide applications in the grinding of WPCBs because of faster milling rates, excellent liberation and narrower size range distributions of product.

After successful liberation, concentration of metals is exercised by using various unit operations: corona discharge separation [91–95], magnetic separation [86,96,97], eddy current separation [98–100], vibrating screen [101,102], air classification [103–106],

flotation [50,107–109], gravity separation and density based separation [50,84,108,110], flotation in liquid media [111], sink-float technique [112] etc. The various techniques which have been exercised for the mechanical processing of WEEE are shown in the flow sheet (**Figure 1.5**) and the summary of the individual concentration techniques investigated for e-waste treatment is shown in **Table 1.3**.

All these operations exploit variation of physical shape and size, magnetism, electromagnetism, conduction, density and other properties of components of WEEE for the separation of metals and non-metals. Selection of individual techniques for active metal liberation and separation is highly dependent on each other e.g.: prior to electro-static separation of metal, crushing of PCBs to -1 mm size is essential [87]. Flakiness, toughness, cohesion between the metals - base materials, the toxic gases generated during the crushing process are the inherent characteristics of PCBs. Thus, in spite of the availability of numerous mechanical processing methods, the maximum yield of metal liberation and separation from the non-metallic fraction is limited to 75–80% [113]. Further, these unit operations are highly energy intensive, noisy, dusty, associated with loss of precious metals in the dust, contamination of grind PCBs due to mechanical wear etc. [8,77,114–118].
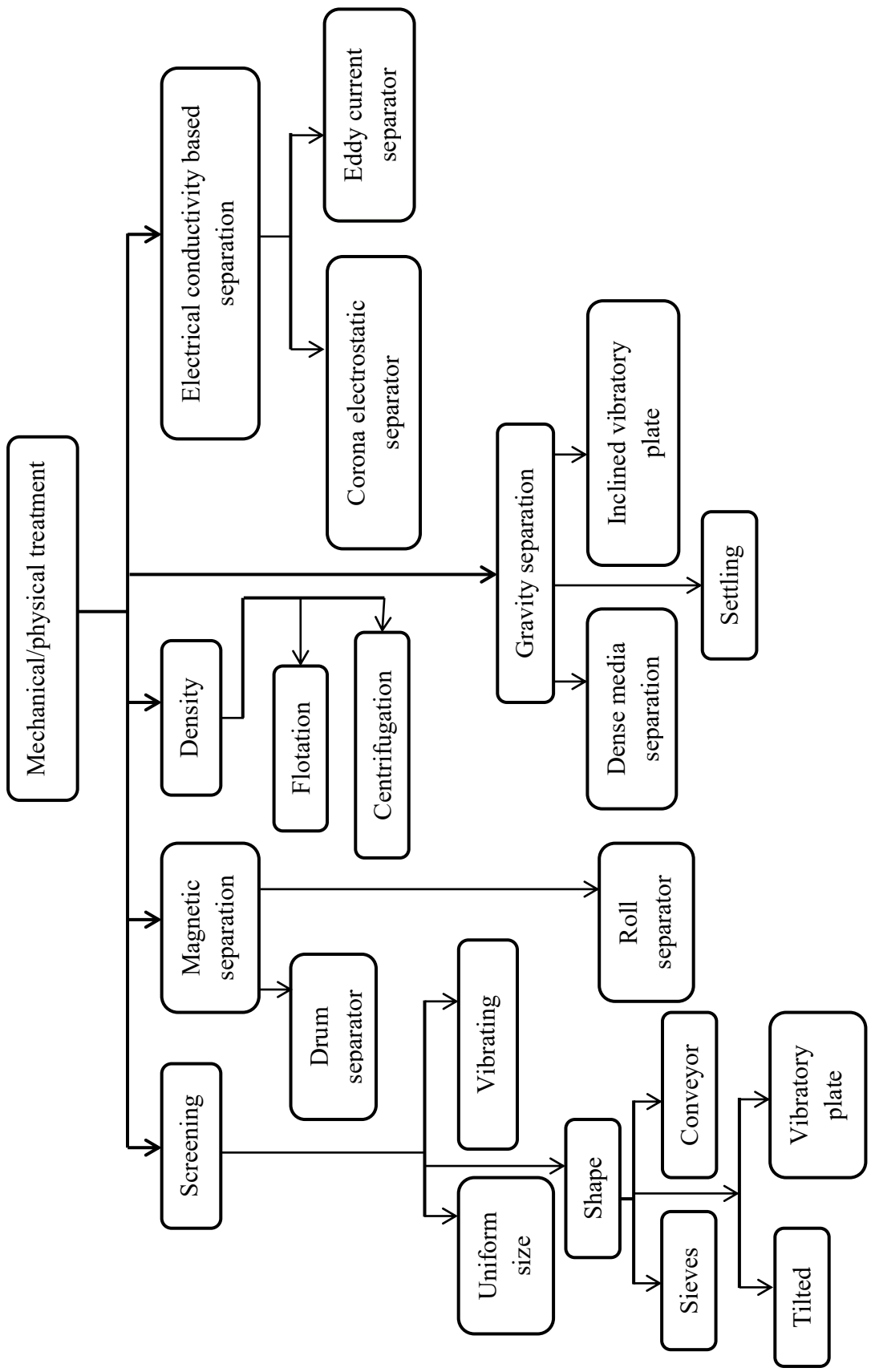
Figure 1.5- Various techniques exercised for the mechanical processing of WPCBs

Table 1.3- Detailed summary of various mechanical treatment techniques investigated for WPCBs recycling

S. No	Process	Input	Parameters	Output	Results/ remarks	Ref.
		Physical/ mechanical treatment (metal–nonmetal separation)				
1.	Roll type corona electrostatic separator	Size- 0.3- 0.45 mm; Composition- 25% metal	25 °C, 55-70 RH, 25-30 kV, 60-80 rpm, Corona electrode at 25-35° with gap 60-70 mm, electrostatic electrode at 65-75° with gap 90 mm.		$\eta_{separation}$ depends on parameters and particle interaction	[91]
2.	Roll type corona electrostatic separator	Size: - 1 +0.32 mm; Composition: 28% metal	Room temperature		$\eta_{separation}$ max for +0.6 - 1.2 mm size fraction	[93]
3.	Stamp mill	Size: -10 mm	35 strokes·min⁻¹, 60 min time, 1.5 kg feed	5 batch: -0.6 mm, +0.6 -1.2 mm, - 2.5 +1.2mm, -5 +2.5mm, +5 mm	80% non-metal below 1.2 mm, metals distributed in all size fraction, Inefficient metal separation	[84]
4.	Zig-zag air classifier	5 batch-	Feed rate 100 g·min⁻¹		95% metallic components separated for size -0.6 mm	[84]
		+0.6 mm	1.4 m·s⁻¹			
		-1.2 +0.6mm,	1.7 m·s⁻¹			
		- 2.5 +1.2 mm	2.6 m·s⁻¹			
		-5 +2.5mm,	3.5 m·s⁻¹			

Physical/ mechanical treatment (metal- nonmetal separation)

S. No	Process	Input	Parameters	Output	Results/ remarks	Ref.
5.	Magnetic separation	2 batch: +5 mm and -5 mm	1st - 700 Gauss by hand magnet 2nd stage- 3000 Gauss by Drum separator	2 stage application of a magnetic field	1st step- 99% recovery of Fe and Ni content 2nd stage- 55% Fe and Ni content	[84]
6.	Eddy current separator	+7 mm -7 mm	feed rate- 0.3 kg·min^{-1}	90% of Al recovered with purity of 85%.	Lower recovery for size -7 mm	[99]
7.	Sink- float technique	-2 mm	Saturated $ZnCl_2$ solution	**Sink**- 1.1% Plastic, 96.7% **Cu, 94.8%** Al, 95.9% other	**Float- 98% plastic,** 3.2% Cu, 4.93% Al, 4.085% other	[103]
8.	Flotation	Flotation (water) (-1500μm +75μm)	Air flow rate: 5 m^3·h^{-1}, Metal recovery - 81.9%, Agitation 1500 rpm	75% metal recovery (grade 88%)	Highest metal fraction in +500 -850μm range	[119]
9.	Pneumatic separation	WPCBs size (-1500μm +75μm)	Air flow: 20 m^3·h^{-1}	65% metal recovery (grade 78%)	Highest metal recovery in (-250μm +150μm)	[119]
10.	Post pyrolysis mechanical treatment	-0.28 mm +4 mm	Crushing then air classification, -0.45+ 4 mm 100% Cu recovery by air classifier	Copper content: 22% in-0.45+0.9mm 54% in -2 +0.9mm, 23% in -4+2mm	-2+4 mm Cu rich (97%); 0.1- .45mm mostly non-metallic	[120]

1.9.3   End recycling

After the successful mechanical processing, the End recycling of WPCBs is carried out. These processes mostly fall in the domain of either thermal or hydrometallurgical processes.

1.9.3.1 Thermal processes

The most common thermal process is pyrolysis in which heating of e-waste is carried out at elevated temperature in absence of oxygen. It results in disintegration of the organic matter to gases, liquids (pyrolysis oil, char), and soft solid residue (metal-rich phase). During the processing, toxic gases containing dioxins, furans, halides and acid vapours are also emitted due to the decay of flame retardants [36–38,121]. Char is produced due to the presence of oxygenated and aromatic organic compounds present in PCBs [122]. Pyrolysis in nitrogen, air, argon and vacuum has been extensively investigated by researchers [40,120,123–132]. Comparative study of these results showed that vacuum results in lower activation energy, improved outcome and relatively lower and narrower temperature range of dissociation (**Table 1.4).**

Table 1.4- Effect of gaseous atmosphere on decomposition temperature of organic

compounds during pyrolysis

S.N.	Atmosphere	Temperature range (^{o}C)	Reference
1	Air	297- 400	[127]
2	Nitrogen	270- 350	[126,133][134]
3.	Vacuum	270-300	[132]

The high-temperature pyrolysis of WPCBs has also been carried out by various researchers expecting faster decomposition of organic compound to low molecular weight products [40,128,135]. But, Oleszek et al. (2013) found that high-temperature

pyrolysis may result in loss of ~ 50% of copper and silver content in form of respective bromides (CuBr and AgBr). Further, release of more oxygenated, halogenated and ozone reacting gaseous emissions are also experienced (**Table 1.5**).

The analysis of gases and liquid oil generated during pyrolysis showed that gases are mainly composed of carbon dioxide, carbon monoxide and different hydrocarbons and halogenated gases [137,138]. In pyrolysis oil phenol, phenol derivatives, styrene etc. were the primary constituents [40,64,131,139–141] with other brominated and organic compounds. de Marco et al. (2008) reported that content of phenol and its derivative in the pyrolysis oil derived from PCBs may exceed than 60%.

Table 1.5- Composition of gases emitted during pyrolysis at different temperature [133]

S. N.	Compound	Quantity ($\mu g \cdot g^{-1}$) *vs.* Temp.		
		300 ^{o}C	400 ^{o}C	500 ^{o}C
1	Tetrachloromethane	738	973	5269
2	Dichloromethane	533	1190	1231
3	Bromophenol	67	117	919
4	Cis-1,2 dichloroethylene	89	365	515
5	Dibromophenol	61	134	426
6	Trans-1,2 dichloroethylene	89	112	131
7	Methanol	1965	2708	2538
8	Acetone	898	1487	1543
9	Ethyl Acetate	1064	1830	1532
10	Acrylonitrile	333	589	846
11	Methyl methacrylate	68	184	102
12	Others (including oxygenated and halogenated compounds)	264	648	1732
13	Ozone-depleting gases	2479	4015	6180

Kinetics study of pyrolysis process revealed that decomposition of PCBs is highly dependent on the applied temperature. During pyrolysis process at the temperature lower than 297 ^{o}C only gases like H_2O, CO_2 etc. are evolved and as the temperature increases to 400 ^{o}C, HER decomposition took place leading to various toxic emissions [63]. These studies revealed that the organic fraction of WPCBs decomposes at an elevated temperature range (260-400 ^{o}C) and results in the release of toxic dioxin, furans gases and acid vapours [96,137,143]. Pyrolysis treatment results in very easy separation of metal, glass fiber, and ash from the obtained residue thus, offers added advantage of non-requirement of special metal-nonmetal liberation. Other benefits are- by-product generation as gases and liquids having potential utility as fuel and derivative for chemical synthesis; the presence of Fe, Co, Ni in PCBs promotes its easy cracking [118,120,129,131,144,145]. Contrary, the generation of toxic and gaseous emission are the most important and attention seeking drawback of the pyrolysis process.

Thus efforts have been made to minimize the toxic emissions by implementing different techniques. The most common way is the trapping of condensable matter from the off-gases by passing it through the ice-bath cooler (Temperature < 4 ^{o}C) [125,130]. Lin and Chiang (2014) found that ionic species (Na^+, PO_4^{3-}, K^+, NH_4^+, SO_4^{2-}, Br^- etc.) present in non-condensable emissions can be absorbed by water contact. Application of Fe-Al_2O_3 as a catalyst for treatment of flue gases generated by pyrolysis process has also been reported [133]. The brominated emission can be reduced in the gases by trapping them it in the pyrolysis oil by pyrolyzing PCBs with fir-sawdust of the wood processing plant. But increase in the bromine in the oil (14.84 wt% from 6.51 wt%) adversely affects its utilization as fuel or by-product [130]. Co-pyrolysis of WPCBs:coal in a ratio of 6:4 results in bromine free emission and lower activation energy but the risk

associated with coal has to be considered [137]. Co-pyrolysis of WPCBs with lime and calcium based waste product such as calcium carbide, red mud etc. also results in increased solid product yield and improved absorption of hydrogen bromide content [146].

Pyrolysis of WPCBs at 1200 ^{o}C with sodium hydroxide in argon atmosphere results in melting of PCBs and evolution of reducing gases. These gases once passed through the molten metal pool of pyrolysis reside causes the reduction of metals as well as cleaning of gases too [147]. Compounds such as sodium hydroxide solution, sodium bicarbonate, lime and other alkali have also been used to absorb aerosols, formic acid, acetic acid, hydrogen bromide etc. being generated during pyrolysis [63,130]. All these efforts have proven to be helpful in lowering the quantity of toxins in the emission. Yet due to highly lethal nature of emission, release of even a small amount of these toxins is restricted and thus, requires further investigation.

Apart from pyrolysis, there are other pyrometallurgical processes which have also been practised for recycling of e-waste. In one of commercial Cu production process *viz.,* Noranda process, WEEE along with mined copper concentrates are directly immersed in a molten copper bath, and vigorous air churning is done [148]. The iron, lead and zinc etc. present in WEEE gets oxidized and trapped in slag while copper and precious metal joins the copper matte. Similarly, Kaldo furnace treats blended feed of e-waste with copper scraps and lead concentrates [149]. E-waste as 10% of the feed has been used to treat several industrial wastes with Isasmelt furnace, where impurities get concentrated in a lead slag and precious metals (Ag, Au, Pd, Pt etc.) gets in a copper bullion [150,151]**.**

Alternatively an environment-friendly route *viz.,* Plasma Arc Processing has been investigated [6] as it offers high energy density, ionic and excited species atmosphere [152]. This results in better slag metal separation, decomposition of exhaust gases, faster reaction kinetics and short processing time [153]. Post-processing analysis of metal phase showed presence of ~ 90% copper along with precious metals [6] while emissions were found close to the pollution limits set by Central Pollution Control Board of India (CPCB) [154].

The overall approach of the thermal process can be represented in a flow sheet shown in **Figure 1.6**. The summary of various thermal processes in the context of WEEE treatment is shown in **Table 1.6**.
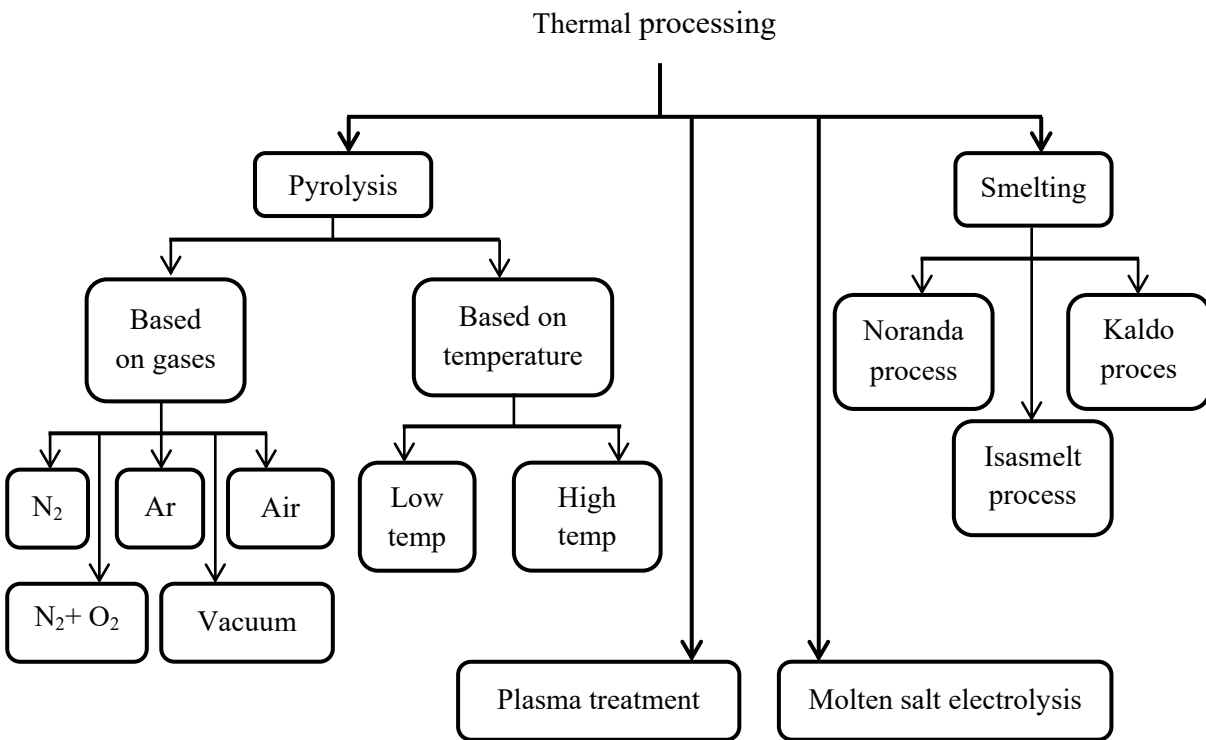
Figure 1.6- Overall flow sheet of pyrometallurgical processes investigated for WPCBs recycling

Inspite of numerous efforts to recycle WPCBs economically, efficiently and eco-friendly; any thermal process couldn't come into the picture without considering emission within limits, post-treatment of slags and pyrolysis by-products (gases and oil), recovery of copper and precious metals etc. Thus, processes like pyrolysis have been flayed by the environmental policymakers while newer process needs further investigation to understand their full-scale potential for WEEE recycling. Further, a metal-rich fraction having a heterogeneous mixture of copper, silver, gold, iron, nickel, lead, tin etc. is obtained after the thermal treatment. To ensure cost-effective recycling of individual metals from that it is must to recover them in form of respective metallic salts which requires hydrometallurgical processing. All these factors motivated researcher to look for a better alternative to the thermal processing. Thus, extensive efforts have been made by researchers to investigate non-thermal process *i.e.,* hydrometallurgical processes. Studies revealed that the non-thermal processes offer a cleaner emissions, efficient recovery, separation of individual metals etc. and thus these are more attractive.

Table 1.6- Detailed summary of various thermal techniques investigated for WPCBs recycling

S. No	Process	Input	Parameters	Output	Results/ remarks	Ref.
				Pyrolysis		
1.	Pyrolysis (reductive atmosphere)	12wt% NaOH+ PCB	1200 °C,	Slag- Al, Ca, Si Metal- Cu, Ag, Au	Smelting of metallic phase with slag in air resulted in 95% pure Cu and most of the precious metal in slag.	[147]
2.	Pyrolysis (Air)	WPCBs of 36×16 mm	700 °C	17.8wt% liquid, 5.4wt% gases, 76.8wt% solid	1. Pyrolysis oil converted to phenolic resin. 2. L*- phenol, benzene, methyl etc. 3. S*- 67% glass fibre, 28% metal	[141]
3.	Pyrolysis (N$_2$)		700 °C, 10 °C·min^{-1}	64.18% solid residue	Max. degradation- 314 °C, E$_{a}$- 149.28 kJ·mol^{-1}	[155]
4.	Pyrolysis (N$_2$)	50×50 mm, 2:1 PCB:Ca waste	10 °C·min^{-1}, held for 30 min	84% solid by using- CaO, 3.1% liquid by using sintered red mud	1. Additive addition lowered the liquid product yield (Max- 10.5%) 2. Gases not influenced by addition (Calcium based products- Sintered red mud, Bayer red mud, Ca-carbide dust, CaO)	[146]

Pyrolysis

S. No	Process	Input	Parameters	Output	Results/ remarks	Ref.
5.	Pyrolysis (N_2)	PCBs	500 °C, 30 min	16% liquid, 7% gas, 77% solid	L*- phenol and phenolic derivative (63%)	[142]
6.	Pyrolysis (N_2)	Nonmetal fraction of PCBs	500 °C, 30 min	1. 39wt% S*, 37wt% L*, 24wt% G* 2. L*- 73% carbon, 14% hydrogen, 5% nitrogen, 0.05% sulphur	L*- phenol group compound having heat value- 37.5 MJ/kg,	[125]
7.	TGA analysis	PCBs	Heating rate- 5, 10, 20 $K \cdot min^{-1}$ N_2:O_2- 4:1 and 9:1	Product yield 76%, maximum wt loss 630 K 4:1 ratio- 85% product yield at 10 $K \cdot min^{-1}$	Heating rate- no effect on decomposition Inert atmosphere result in no oxidation of metallic thus higher wt loss	[135]
8.	Pyrolysis (products)	PCBs	600 °C, 30 min,	20.1 wt% L, 63wt% S, 10.8wt% G	Pyrolysis oil was used for synthesis of carbon nanotubes	[64]
9.	Thermal treatment	Cu, Ag with TBBPA; Cu, Ag with TTDE	100-1300 °C, He atmosphere		>50% Cu and Ag evolve as respective bromides.	[136]
10.	Centrifugal separation + vacuum pyrolysis	PCBs	Pyrolysis- 600°C, 40°C·min⁻¹, 30 min	76wt% S*, 20wt% L*, 4wt% G*	Heating in Diesel at 240°C- solder removal Centrifugal furnace- 240°C, 6 min, 1400 rpm.	[118]

Pyrolysis

S. No	Process	Input	Parameters	Output	Results/ remarks	Ref.
11.	Thermal treatment	~ 1 cm^2 sized PCBs	1150 °C, 20 min, 1 L·min^{-1} Ar flow	Red droplet of Cu- 92% Cu, White droplet of Sn- 47% Sn, 34% Cu	Slag phase contains carbon and carbonaceous compounds	[143]
12.	Plasma Processing	PCBs 10-15 mm	1400-1600 °C, 20 min,	Plasma furnace- 60% wt loss, 80:20 = metal: nonmetal (wt%)	Product- 30wt% metal of feed, 25wt% ash of feed, Gas within CPCB limits, only acidic content was higher.	[154]
13.	Plasma Processing	PCBs	1350°C	Product- 7:3 metal: nonmetal, 61% wt loss	Treatment rates- 0.55 Kg E-waste·min^{-1}	[6]
14.	Recovery using molten salt	20×10 mm PCB, molten salt	300 °C, 1 h, 2 L·h^{-1} Ar flow, Wt$_{PCB}$/Wt$_{salt}$ = 0.3	After treatment- metal phase- Cu, Ni, Ag, Au Brown powder- CaCO$_3$, Ca-silicate	Molten salt (41 wt% NaOH, 59wt% KOH)	[156]

*L- liquid product
S- solid product
G- gas product

1.9.3.2 *Non-thermal process*

Hydrometallurgy is one of the most important areas in the domain of non-thermal processing of e-waste. Valuable metals present in the WEEE are selectively leached out by using reagents. These processes essentially require crushing of WEEE and separation of metal content to avoid excess reagent consumption during leaching. The major steps followed in hydrometallurgical processing of WPCBs are shown in **Figure 1.7** in form of a flow sheet.

E-waste

```
          Pre-processing (grinding)

          Metal- nonmetal separation

          Selective leaching

          Recovery of individual metal
```
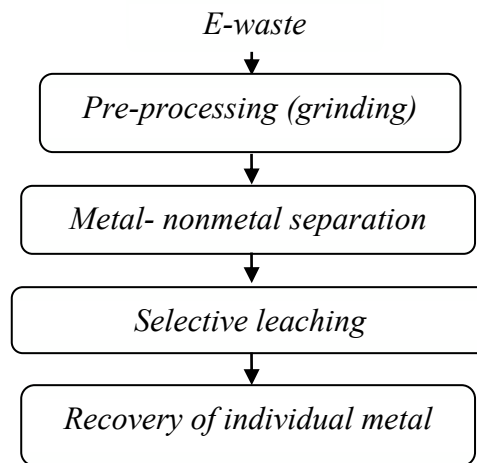
Figure 1.7- Steps of hydrometallurgical processing of e-waste

In general various leachants suitable for selective dissolution of specific metals are as follows:

   I. *Copper* - Sulphuric acid, aqua regia, ammonia-ammonium salt solution, HNO_3, H_2SO_4 with H_2O_2 [145,157–166]

  II. *Solder* - Fluoboric acid (HBF_4), sodium chloride, NaOH, HCl, HNO_3, H_2SO_4, [114,145,160,166–172]

 III. *Gold, silver* - aqua regia, thiourea, thiosulfate, cyanide [60,161,165,172–182]

 IV. *Palladium*- Hydrochloric acid, sodium chlorate [72,161,181,183,184]

Among all the metals present in WPCBs, copper content is high and thus, many researchers investigated the recovery of copper by its selective dissolution. Ping et al. (2009) found that electro-oxidation process offers lower processing time. Among different acid solutions, HCl + HNO$_3$ mixture shows highest copper leaching compared to other acids like H$_2$SO$_4$, H$_2$SO$_4$ + HCl, HCl and HCl + HNO$_3$[185]. In an investigation, it was found that HCl leaching of copper is hindered due to enveloping of the copper particle by copper chloride (CuCl) layer [186]. The study also revealed that addition of chloride ion promotes dissolution of CuCl thus enhance leaching of copper. Further, Havlik et al. (2011) reported that initial thermal treatment also enhances copper leaching in HCl media. The oxidization of copper from WPCBs in ammonical-alkaline solution as Cu(II) results in lower oxidation-reduction potential and thus enhances leaching rate [188]. Ammonical sulphate showed better selectivity for copper leaching and post-leaching purification by using LIX 26 compared to ammonical chloride solution [189]. Kinetics study of leaching of copper in HCl in electro-generate chlorine showed that empirical surface layer diffusion model controlled by logarithmic law controls the copper leaching [160]. Ionic liquid, 1-butyl-3-methyl-imidazolium hydrogen sulphate resulted in 100% copper leaching. Investigations showed that particle size has pronounced effect on leachability in ionic liquids as the leaching mechanism was governed by shrinking core model controlled by diffusion [190].

In a two-stage leaching process of WPCB followed by solvent extraction by LIX984, nickel and copper were recovered along with 99% gold in form of flakes [182]. Sheng and Etsell, (2007) reported a two-stage leaching process in which base metals were leached out by HNO$_3$ followed by precious metal leaching in aqua-regia. Economic feasibility of hydrometallurgical routes to claim recovery of Ag, Au, Pd from waste

mobile phone was investigated [192]. Once the most of the metallic fraction is dissolved, the extraction of the individual is a tedious and demanding process. Copper leaching has also been reported by using nitric acid and it was found that thermal treatment enhances leaching rates considerably and Mankhand et al. (2012) found 30.4%, 92.5% and 96.2% copper recovery for untreated, pyrolysed and air burned PCBs, respectively.

Apart from copper, the amount of precious metals in e-waste is considerable and its recovery has also been studied. Cyanide is most common lixiviant for precious metal recovery but it is capable of leaching gold present at the surface of PCBs only. Petter et al. (2014) found that leaching of precious metals in aqua regia is low (8%) due to the formation of insoluble silver chloride which is stable at all pH. Thiourea leaching of precious metal resulted in 91% gold and 60% silver recovery from PCBs [193].Jun et al., (2009) reported 91.4% gold and 80.2% silver leaching from PCBs using acidic thiourea. Thiourea leaching of gold is fast, less-toxic, highly efficient, eco-friendly but possess high cost, large consumption, lack of recovery after leaching [195]. Using ammonium thiosulfate it was possible to recover 78.8% gold under optimized leaching conditions [176]. Comparative study of leaching of precious metals by using thiosulphate and thiourea revealed that sodium thiosulfate is more suitable for leaching of gold compared to ammonium thiosulfate and the leaching can be further enhanced by the addition of small concentration of $CuSO_4$ [173]. Heath et al. (2008) investigated the kinetics of the electrochemical reaction of thiosulfate in ammonia medium and found that leaching enhances as the concentration of thiosulfate, Cu^{2+} ion and ammonia increases. During thiosulfate leaching consumption of regent is more because of copper dissolution [197]. Halide leaching has also been reported for recovery of gold from e-

scrap. Xu et al., (2010) reported 95% gold leaching by using iodide leaching. Hydrometallurgical treatment of gold from its ore is universal practice commercially, but from e-waste precious metals are recovered as a by-product from existing plants where copper from e-waste is recovered *via*. thermal processing.

Apart from copper and precious metals, a considerable amount of solder containing tin and lead, is used in electronic gadgets to join the electronic components with the printed circuit boards. Thus, an effort has been made to recover tin and lead from the e-waste. Jha et al. (2012) reported 96% tin recovery by using hydrochloric acid from waste PCBs after organic swelling by using dimethylformamide. Kinetic study revealed that chemical reaction control dense constant size cylindrical particle model was best suited the leaching behaviour of tin. Almost 100% lead present in the solder material was further leached by HNO_3 [167]. Castro and Martins, (2009) leached 98% tin and 93% copper from metal concentrate from PCBs by using aqua regia solution. Further by sodium hydroxide precipitation resulted in 86% tin and 34% copper recovery from leach liquor.

Aluminum and iron present in the metallic fraction are mostly separated by using eddy current separator and magnetic separators, respectively. New techniques such as supercritical extraction and recovery by molten salt have also been investigated. Supercritical water-based extraction of copper and lead has been carried out because under supercritical conditions water has a high solubility for organic compounds, oxygen as well as rapid oxidation of organic components present [200]. For this, WPCBs (–0.1 mm) with water and hydrogen peroxide were subjected to 440 $^{\circ}$C, 30 MPa and 1 h time. It resulted in oxidation of copper and lead to CuO, Cu_2O and β-PbO_2 and decomposition of ~ 98% organic matter.

In another process, copper along with precious metals was recovered by molten salt treatment [156]. This was achieved by heating WPCBs in KOH-NaOH eutectic at 300 ^{o}C in argon atmosphere. The metals present were recovered in the metal phase while organic and glass content was recovered as a brown powder (composition- calcium carbonate and calcium silicate). The highly basic nature of salt probably dissolved all the organic and glass content of WPCBs leaving a cleaner emission having the majority of hydrogen, carbon dioxide and carbon monoxide.

Based on the literature review of non-thermal processes, a flow-sheet may be proposed summarizing the application of different techniques (**Figure 1.8**). The application of hydrometallurgical techniques without thermal treatment has been studied extensively as it offers a cleaner environment, negligible hazardous gaseous emission and relatively low energy consumptions. Yet, the generation of large quantity of effluent, need of additional crushing and metal non-metal separation stage, non-utilization of the intrinsic value of resin and generation of the heap of non-metal fraction (having 60-70% of total PCB content) are the major drawbacks of non-thermal processes. These factors again limit their applicability to scale up to a commercial process.

A summary of various non-thermal processes investigated for recovery of metallic values present in WPCBs has been shown along with details in **Table 1.7.**
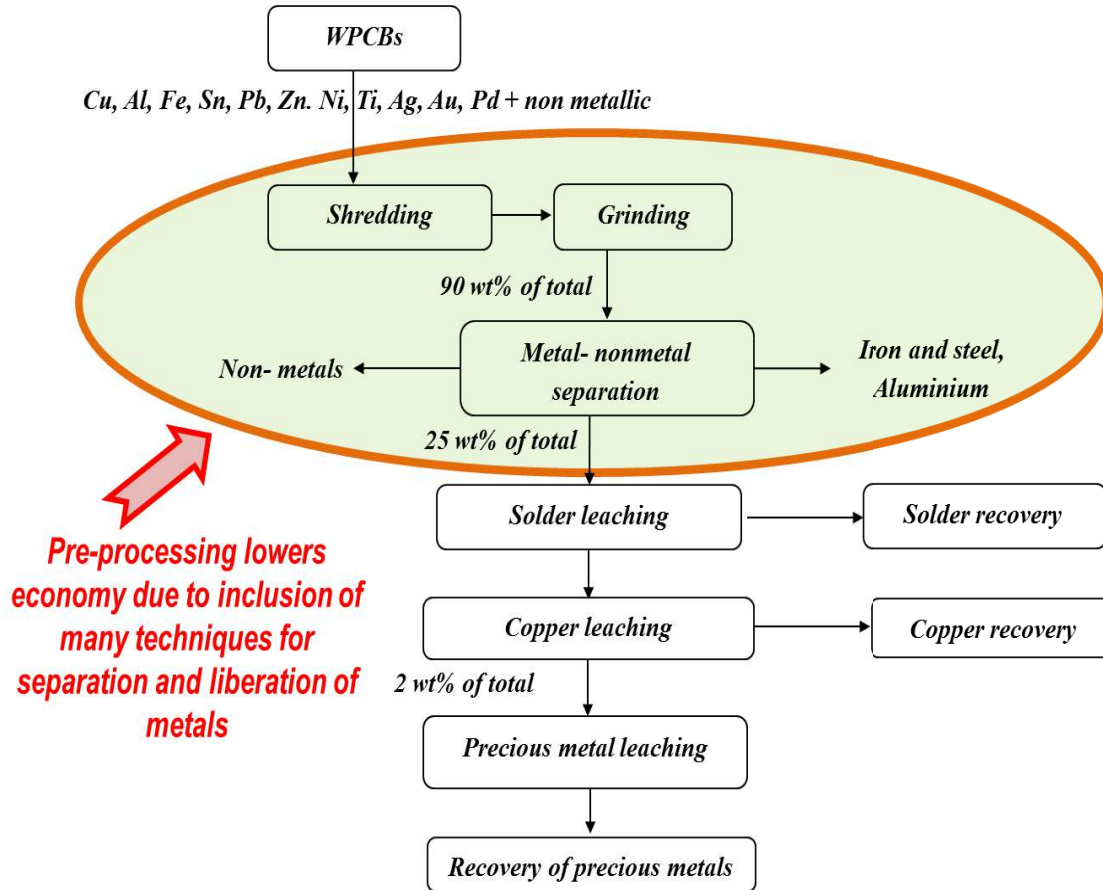
Figure 1.8- Flow sheet of hydrometallurgical recycling of WPCBs

Table 1.7- Detailed summary of various hydrometallurgical techniques investigated for WPCBs recycling

S. No	Process	Input	Parameter	Output	Results/ remarks	Ref.
			Hydrometallurgical processes			
1.	Thermal treatment and leaching	- 8mm	Thermal treatment- 300, 700, 900 °C for 15, 30, 60 min. Leaching- 1M HCl, 80 °C, 180 min, 3/400 g·mL⁻¹	1. Highest wt loss- 900 °C, 18 min, 2. 90% Cu leaching for 900 °C treated sample 3. Higher Sn recovery at 300 °C	35%wt loss at 900 °C, higher temp expose the Cu laminated inside and oxidation of Sn present on the surface	[187]
2.	Leaching with Cl⁻ ion	25 cm² Cu plate	1M HCl (600 mL), 25°C, 400-100 A·m⁻²	Mass transport controlled kinetic model, E_a= 4.3 kcal·mol⁻¹	Leaching rate of Cu with Cl is higher than cupric ions	[201]
3.	Leaching, Solvent extraction	10×20×2 mm PCB,	Leaching- 1st stage: 0.1M HNO₃, 21 g·L⁻¹, 72 h, 90°C 2nd stage- 1M HNO₃, 21 g·L⁻¹, 6 h, 90°C Solvent extraction: 2 pH, 100g·L⁻¹ LIX984 diluted in kerosene Stripping-4M HNO₃	Leaching- 98% Ni, 94% Au, 97% Cu Solvent extraction - 99.8% Cu extraction Stripping- 99% Cu	2 stage leaching resulted higher dissolution, gold flakes recovered directly. High extraction, distribution ratio of Cu in LIX 984	[182]
4.	Leaching, Solvent extraction, Electrodeposition	0.5- 3mm size PCBs (Ammonia-ammonium sulphate/ chloride)	1. At pH 10, Cu, Zn, Pb, Mn leached and Al, Ni, Fe forms passive layer. 2. LIX26 used for SX	1. Pb, Mn, Ni, Al, Fe, Zn extracted 2. Electro-deposition- Cu with 24 ppm impurity from Sulphate medium	Chloride system- more impurity leached, lower extraction.	[189]
5.	Leaching	PCB swelled by n-methyl-2-pyrrolidone	1. Pb - 0.2M HNO₃, 90°C, 45 min, 10 g·L⁻¹ 2. Sn- 3.5M HNO₃, 90°C, 120 min, 50 g·L⁻¹	99.9% Pb and 98.7% Sn leached out.	Pb leaching followed chemically controlled model with E_a= 26.94 kJ·mol⁻¹	[167]

Hydrometallurgical processes

S. No	Process	Input	Parameter	Output	Results/ remarks	Ref.
6.	Leaching with Oxidant	PCB particle crushed -2mm	100 mL 15wt% H_2SO_4, 10 mL 30wt% H_2O_2, 10 g crushed PCB, 3 h, 23 °C	96% Cu leached out in 5 cycles	1. -1mm size showed good leachability, 2. -0.5 mm size no improvement in leaching	[163]
7.	Leaching with oxidant	Plasma processed metal phase (-150μm +500μm)	32% HCl sol, 4.2% H_2O_2 solution, 1h, 500 rpm	92% Cu, 95% Ni, 93% Co, 26% Fe, 40% Al leaching		[154]
8.	Leaching (Ag, Au)	Zinc refining residue (- 75 μm)	Pre-treatment- 90°C, 2h, 250g·L^{-1} S/L, lime- 100 kg·t^{-1} Leaching (cooled sol^n) - 1M NaCN,, 40°C, 5.5- 8.5 mg·L^{-1} dissolved O_2	68.17% Au, 90% Ag leaching, Shrinking core model,	Size fraction +75 μm showed poor leaching	[180]
9.	Leaching	Ball mill crushed PCBs <0.2mm	3M HCl+1M HNO$_3$, 60 °C, 100 g·L^{-1}, 120 min	93% Cu leaching, 3M HNO$_3$ showed similar results	H_2SO_4, HCl, HNO$_3$ mixed in different proportion were also tested	[185]
10.	Recovery using ionic liquid	Ionic liquid- 1-ethyl-3-mrthylimizadolium tetrafluoroborate [EMIM][BF$_4$$^-$]	1:5= PCB:[EMIM][BF$_4$], 1st stage- 5°C·min^{-1} to 240°C, 10 min, 2nd stage- further heated to 260°C, 20 min	1. At 240°C solder removed, 2. At 260°C PCB's delamination	At 260°C, epoxy resin started to dissolve into ionic liquid and delamination of PCBs achieved	[202]
11.	Ionic liquid leaching	Crushed PCBs -0.5mm	Particle size- 0.1-0.25mm, 10 mL H$_2$0$_2$, 70 °C, 1/25 S/L, 2 h	99% Cu leaching. Shrinking core model with E_a= 25.36 kJ/mol	Ionic liquid- 1-butyl-3methyl-imidazolium	[190]

1.10 Modern approach to the recycling of WPCBs

In spite of extensive research to process WPCB for the recovery of metals, no commercial recycling process has been developed. This is because of the complex composition, structure of WPCBs and presence of Halogenated Epoxy Resin (HER). The high-temperature process is limited due to HER content because its decomposition releases the toxic dioxin, furans gases and acid vapours [96,137,143]. On the other hand, the non-thermal process ensures relatively higher metal recovery yield and negligible lethal emissions but requires mechanical pre-processing. Mechanical processing ensures liberation and concentration of metal content of milled WPCBs leading to high metal recovery, quick processing, small lixiviate consumption and lower effluent generation [145,167]. The inclusion of pre-processing methods highly increases the economy of the entire non-thermal process thus commercial viability is compromised [86]. Thus, it is essential to explore an alternative technique which may result in the complete liberation and separation of metal values present in the WPCBs. It will also overcome the drawbacks of existing uneconomical recycling techniques.

In recent years, the researchers have investigated a new technique of dissolution and separation of the HER from the PCBs by using different solvents. The dissolution of HER destructs the reinforced multilayered WPCB's structure, and thus enveloped metals are liberated. It results in the liberation and separation of metal clad of PCBs and hence the overall economy is also improved considerably [203]. This process reduces the concentration of toxic gas precursors (especially HER) and also delaminates the layers of WPCBs thus revives the applicability of conventional thermal and hydrometallurgical recycling techniques.

Various novel techniques investigated featuring exploitation of this phenomenon are dissociation of HER in supercritical water, carbon dioxide, methanol etc. [63,113,204,205], separation of HER by ionic liquid treatment [202,206] and dissolution in an organic solvent [207].

Xing and Zhang (2013) found that supercritically heated water at 400 ^{o}C and 40 Mpa results in complete decomposition of brominated flame retardants in hydrogen bromide (HBr) which readily gets dissolved into the water due to its higher solubility at elevated temperature. Analysis of solid and liquid obtained after treatment showed that only 2.3% of total bromine content of PCBs was left into solid residue and no bromine compound in the liquid product. Chien et al., (2000) also found that at 520 ^{o}C and 25.3 MPa, 90% of the HER of WPCBs decomposed into carbon dioxide and water within 10 min. During the process, bromine was distributed as HBr, NaBr and Br_2 in gas and liquid products. Sanyal et al., (2013) found that at 180 ^{o}C and 13.8 MPa, supercritical carbon dioxide with a small amount of water may result in successful delamination of WPCBs. Methanol can be used as a supercritical fluid under conditions 350 ^{o}C, 22 MPa. Under these conditions, almost 58% pure phenol based oil was recovered without any bromine contamination. Most of the bromine was distributed in gas product and recovered in form of HBr solution (41 vol%) [204]. Although the results of supercritical treatments were quite appreciating yet its commercial viability is argumentable. Due to high temperature and elevated pressure operation, initial cost and energy requirement are quite discouraging in view of commercialization [85].

Alternatively, successful dissolution of HER using ionic solvent 1-ethyl-3-methylimizadolium tetrafluoroborate at 260 ^{o}C for 20 min followed by its regeneration has been reported [202]. The reported solvent is quite stable up to 300 ^{o}C thus requires

extremely high vacuum and temperature during the regeneration making the process vastly energy consuming. The operating temperature is also very close to the HER decomposition temperature range thus chances of decomposition of HER is also there. High cost and toil in the synthesis of ionic liquid attracted attention towards cheaper solvents. Organic solvent dimethylsulfoxide (DMSO) [209] resulted in complete separation of WPCBs of area 15-20 mm^2 in 30 min contact time at 170 ^{o}C. Comparative study of the dissolution of HER in DMSO and N, N-dimethyl pyrrolidone (NMP) showed that NMP is relatively better solvent as it results in delamination of 4 mm (16 mm^2) size WPCBs within 90 min at 100 ^{o}C [207]**.**

These techniques exploit the phenomenon of rupture of van der Waals' bonds of HER chain under influence of elevated temperature. The researcher found that once WPCBs are heated above the glass transition temperature (T_g) reversible breaking of internal *Van der Waals'* bonds occurs and bonds starts vibrating with higher energy [210,211]**.** This promotes the bonding of broken resin chains with the solvents resulting in the dissolution of HER. Since, T_g for WPCBs is 135 ^{o}C and thus operation near to this temperature does not lead to any decomposition of HER (resin decomposition range 260- 400 ^{o}C) [125,127,134], during dissolution neither HER stability is compromised nor pollutant emission occurs.

However to obtain the WPCBs of 15-20 mm^2 size by the simple cutting tool is quite tedious and often requires the use of special equipment (hammer mill/crusher) that makes the process quite costly. On the other hand, the physical and chemical properties of DMSO and NMP are also discouraging in view of commercial viability. **Table 1.8** shows the properties of solvent DMSO and NMP. The DMSO is a highly hygroscopic solvent having high specific heat and high viscosity, ability to penetrate human skin and

its vapors are heavier than air [212]. Conversely, NMP also possesses high specific heat and moderate viscosity [213] and its exposure leads to cancer and reproductive disorders [214]. The hygroscopic nature, difficulty in usage and regeneration, excessive energy consumption in heating, hindrance in mass transport are the major drawback of these solvents. Also, special ventilation and stringent safety measures are required to prevent the exposure of these solvents to a human being. Contrariwise, the studies involving DMSO and NMP were mainly focused on the delamination of WPCBs rather than optimization of parameters governing the dissolution of HER.

Table 1.8- Comparison of properties** of DMSO and NMP [207,215–217]

Solvent	DMSO	NMP
Specific heat $(J \cdot K^{-1} \cdot mol^{-1})$	153	308.9
Viscosity (cP)	1.990	1.65
Vapor pressure (mm Hg at 20 ^{o}C)	0.42	0.29
Evaporation Rate (BuOAc =1)	0.026	0.03
Cost (relative to DMF)	~ 1.5 times	~ 3 times
Other features	Ability to penetrate human skin	Carcinogenic and reproductive disorders

*** All properties at 25 ^{o}C*

1.11 Objectives and scope of the present work

The literature survey showed that after a long research in the domain of e-waste recycling, neither thermal nor hydrometallurgical processes could have been commercialized. All the thermal processes lead to some toxic emissions and thus flayed by the governments and environmental policymakers. On the other hand, the hydrometallurgical processes ensure no toxic emission, but essentially require the mechanical processing prior to final leaching. The mechanical processing result in liberation and separation of metal values from WPCBs that ensures improved metal recovery with low effluent generation. Most of the mechanical processing operations are highly energy consuming. Thus, the economy of the hydrometallurgical process is debatable due to the inclusion of mechanical processing. Considering these facts in mind researchers investigated an alternative to the mechanical processing step. It features the dissolution of halogenated epoxy resin (HER) in solvent(s) and thus in a single step, the removal of HER and liberation of copper laminate from parent WPCBs is achieved. Ionic liquids, supercritical fluid, organic solvents (Dimethylsulfoxide and N, N-dimethyl pyrrolidone) are the few such solvent systems and among them, NMP was found to be relatively advantageous due to the economy, ease in operation and better dissolution of HER. Contrary, the carcinogenic nature and other properties of NMP is not highly encouraging in view of commercial viability.

Thus, present work focuses on the dissolution and separation of HER from WPCBS in relatively cheaper, eco-friendlier and superior organic solvent(s). The solvent systems chosen are *Dimethylformamide* (DMF) and *Dimethylacetamide* (DMA).

The DMF and DMA are polar, colorless and ammoniacal/fishy odor possessing aprotic (cannot donate hydrogen) solvents. These anhydrous solvents are readily miscible in

water and many organic compounds due to their strong dipole moments. The DMA and DMF, both belong to amide group-containing organic compounds. Due to their remarkable properties as excellent safety, stable operation near boiling point, low evaporation rates, capabilities to dissolve a wide variety of organic compounds and polymers; they are highly appraised and utilized in numerous commercial applications. As compared to DMSO and NMP, these are less hygroscopic and widely used due to possibility of prolonged usage and easy regeneration

The DMF is widely used in the dissolution of the hydrophobic organic compounds such as orlon, polyacrylic fibers, vinyl resins, acetylene, butadiene and it penetrates into a wide variety of plastics too. Its stability is quite appreciable up to its boiling point (153 ^{o}C) with low evaporation rates. At temperature more than 350 ^{o}C, it may decompose into dimethylamine and carbon monoxide [218,219]. DMF gets hydrolyzed in the presence of strong acids and alkalis but remains stable in aqueous solutions.

The DMA is versatile reagent used as a solvent and reagent also in many applications. It is commonly used as a solvent for production of fibrous material (polyacrylonitrile, polyurethane, spandex etc.). In adhesive industries, film and coating industry, agrochemicals, and dyes its application are very popular. DMA is also used as a solvent for production of X-ray contrast media. In some popular drugs like, teniposide, busulfan, cephalosporins etc., it is intentionally added as an excipient. The polycarbonate, polyimide resin and Acrylonitrile Butadiene Styrene (ABS) based material are easily dissolved in DMA and it is used as solvent and reagent during the production of pharmaceutical and plasticizers products. This is an ideal solvent used during the production of dialyzer membranes, cellulose fibres etc. The polar nature of this solvent enables its dual characteristics to act as solvent as well as reaction catalyst

46

Delamination of Waste Printed Circuit Boards (WPCBs) by using Organic Solvents for hydrometallurgical Recovery of Copper

[220]. Thus, it is also having many catalytic applications. DMA gets easily hydrolyzed in acid media but shows remarkable resistance in basic media. Unlike DMF, DMA also decomposes to gaseous products containing NO_x etc. [221].

The objectives and the scope of the present study are as follows:

- The dissolution of HER and subsequent delamination of WPCBs in solvent DMF and DMA

- Study of the effect of parameters governing the dissolution of HER in solvent(s) and their optimization.

- Comparative study of the dissolution of the HER in both solvent systems and investigation of the mechanism responsible for the dissolution of HER.

- Investigation of the mechanism responsible for the dissolution of HER in the solvent(s)

- Optimization of the conventional mechanical processing technique i.e. hammer milling of WPCBs for the effective enrichment of copper content.

- Comparative study of the leachability of the copper from the WPCBs after hammer milling as well as organic solvent treatment.