

Recovery of Metals from Electronic Waste by Physical and Chemical Recycling Processes

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Abstract—The main purpose of this article is to provide a comprehensive review of various physical and chemical processes for electronic waste (**e-waste**) recycling, their advantages and shortfalls towards achieving a cleaner process of waste utilization, with especial attention towards extraction of metallic values. Current status and future perspectives of waste printed circuit boards (**PCBs**) recycling are described. E-waste characterization, dismantling/disassembly methods, liberation and classification processes, composition determination techniques are covered. Manual selective dismantling and metal-nonmetal liberation at $\sim 150\ \mu\text{m}$ at two step crushing are found to be the best. After size reduction, mainly physical separation/concentration processes employing gravity, electrostatic, magnetic separators, froth floatation etc., which are commonly used in mineral processing, have been critically reviewed here for separation of metals and non-metals, along with useful utilizations of the non-metallic materials. The recovery of metals from e-waste material after physical separation through pyrometallurgical, hydrometallurgical or biohydrometallurgical routes is also discussed along with purification and refining and some suitable flowsheets are also given. It seems that hydrometallurgical route will be a key player in the base and precious metals recoveries from e-waste. E-waste recycling will be a very important sector in the near future from economic and environmental perspectives.

Keywords—E-waste, WEEE, PCB, recycling, metal recovery, hydrometallurgy, pyrometallurgy, biohydrometallurgy.

I. INTRODUCTION

E-WASTE contains lots of valuable resources together with plenty of hazardous materials, which are considered both an attractive secondary source and an environmental contaminant. E-waste represents a rapidly growing disposal problem worldwide. Therefore, recycle of valuable metallic and/or non-metallic materials from them are necessary and compulsory today in many developed and developing countries. With the phenomenal technological advancement and growth in electronic industries, the number of consumer and business electronic products per capita has been raised manifold in the last three decades in tandem with the downward price of newer products. At the same time, the average lifetime of electronic products has also been reduced drastically, resulting in massive generation of **End-of-Life (EoL)** electronic goods, popularly known as **waste electrical and electronic equipment (WEEE)**. The UN estimate of the global WEEE production was 20–50 million tons per year and growing at an exponential rate.

Printed circuit boards represent the most economically attractive portion of WEEE and account for the weight for

about 3%. Waste PCBs constitute a heterogeneous mixture of metals, non-metals and some toxic substances. By containing many electronic components, such as resistors, relays, capacitors, and integrated circuits, Waste PCBs have a metal content of nearly 30% (copper (Cu): 10–22%, lead (Pb): 1–5%, nickel (Ni): 1–3%), especially the purity of precious metals in PCBs is more than 10 times that of content-rich minerals.

Besides all the hazards originating from e-waste, manufacturing mobile phones and personal computers (PC) consumes considerable fractions of the Au, Ag and Pd mined annually worldwide. 43% of total production of gold in the world is used in electronics. A large fraction of the WEEE precious metals is found on the PCBs. Since PCBs as becoming more complex and smaller, the amount of materials is constantly changing. 1 mt of circuit boards can contain between 80 and 1500 g of Au and between 160 and 210 kg of Cu. To put this number into context, it should be stated that these concentrations are 40–800 times the amount of gold in Au ore, and 30–40 times the concentration of copper in Cu ore mined in the United States. It has been proved that it is worthwhile to recycle electronic scrap in spite of the fact that the content of precious metals (Au, Ag, Pd) steadily decreases.

E-waste, in particular waste PCBs, represents a rapidly growing disposal problem worldwide. Considering that the lifetime of a mobile phone is approximately 1 year and of a computer 2–5 years, it is estimated that about 100 million mobile phones and 17 million of computers are discarded annually in the world due to malfunctioning equipment or because technologies become obsolete. There are several factors to consider in developing a new recycling technology for waste PCBs driven by innovations, social and environmental impact, an integrated waste management policy and economy of the process. Some of the key factors are:

- The waste PCBs are diverse and complex in terms of type, size, shape, components and composition. With time, the composition of PCBs is continuously changing, making it more difficult to obtain a stable material composition.
- The presence of plastics, ceramics and metals in PCBs in a complex manner leads to great difficulty in liberation and separation of each fraction.
- Presence of numerous metallic elements leads to very complex recovery process. The recovery process becomes more complicated when the elements are available in minute concentration.
- The driving force for recycling is the recovery of metal values, which is nearly 30% of the total weight of waste

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PCBs. The non-metallic materials (~70%) have rather less economic value.

- The objective of the most recycling processes is to recover maximum metallic values from waste PCBs but sometimes these processes are not very environment-friendly.

II. PRINTED CIRCUIT BOARDS (PCBs)

PCBs are used to mechanically support and electrically connect electronic components using conductive pathways, tracks or signal traces etched from Cu sheets laminated onto a non-conductive substrate, employed in the manufacturing of business machines and computers, as well as communication, control, and home entertainment equipment. PCBs are essential parts of almost all electric and electronic equipment, and its rapid development has revolutionized the electronics industry. PCBs are integral part in majority of electronic systems and are commonly found in consumer electronics. PCBs constitutes to about 3% of the total electronic scraps by weight. Most recycling approaches practiced can only recover metal contents of PCB scraps to an extent 30% of the total weight. More than 70% of PCB scraps cannot be efficiently recycled and recovered and have to be incinerated or land filled [1].

The basic structure of the PCBs is the Cu-clad laminate consisting of glass-reinforced epoxy resin and a number of metallic materials including precious metals. The concentration of precious metals especially Au, Ag, Pd and Pt is much higher than their respective primary resources, making waste PCBs an economically attractive **urban ore/secondary resource** for recycling. Additionally, PCBs also contain different hazardous elements including heavy metals (Cr, Hg, Cd etc.), rare earth element (Ta, Ga etc.) and flame-retardants (Br) that pose grave danger to the eco-system during conventional waste treatment of land filling and incineration [2].

Many research works have revealed that the composition of metals, ceramic and plastics in PCBs could reach 40%, 30% and 30%, respectively [3], [4]. Meanwhile, the concentrations of precious metals such as Au and Pd in waste PCBs are richer than in natural ores, which makes their recycling important from both economic and environmental perspectives. Waste PCBs have been paid much more attention from researchers and enterprises, not only due to their rich resource content, but also due to their potential risk for environment and human health with informal recycling. Therefore, factors affecting the extraction of metals are economic feasibility, recovery efficiency and environmental impact. PCB recycling process with the aim of highest recovery of metallic fraction usually includes three stages:

- 1) **Pretreatment** (i.e. optional composition analysis and manual/automatic/semiautomatic disassembly of the reusable and toxic electronic parts) [5],
- 2) **Separation / concentration** (shredding, crushing, pulverizing (100-300 μm), screening, separation etc.) [6], [7] and [8]-[13] and

- 3) **Mechanical / chemical (pyro / hydro / electro / biometallurgical processes) refining/ purification** [14]-[17].

A. Characterization of Waste PCBs

Due to the diverse and complex nature of waste PCBs, characterization in terms of types, structure, components and composition is important to establish the route and process for recycling. Thin films of Sn or Ag are used in the PCBs to protect against oxidation [6]. The base metals mainly found in PCBs are used because of their conductive properties. There are two types of PCBs (FR-4 and FR-2) normally used in personal computers and mobile phones. The FR-4 type is composed of a multilayer of epoxy resin, fiberglass coated with a Cu layer. The FR-2 type is a single layer of fiberglass or cellulose paper and phenolic coated with the Cu layer [18], [19]. The FR-4 type is used in small devices such as mobile phones and FR-2 type is used in televisions and household appliances such as PCs [20].

B. PCB Structure

All PCBs essentially consist of three basic parts:

- 1) A non-conducting substrate or laminate,
- 2) Conducting Cu substrate printed on or inside the laminate and
- 3) The components attached to the substrate (chips (Ga, In, Ti, Si, Ge, As, Sb, Se and Te), connectors (Au, Ag), capacitors (Ta, Al), etc.).

Depending on the structure and alignment, PCBs can be classified as single-sided, double-sided or multilayered. Single and double-sided PCBs have the conducting layer on one or both sides of the laminates and with or without plated through-holes to interconnect the sides. The material present in PCBs can be categorized in three groups: organic materials, metals, and ceramics. Fig. 1 shows materials and their properties in PCBs from EoL e-waste. Organic materials in PCB are mainly composed of plastics with contents of flame-retardants and paper. The type of plastics is predominantly C-H-O and halogenated polymers. Metals in PCBs consist of a large amount of **base metals**; such as Cu, Fe, Al and Sn; **rare metals** like Ta, Ga and other rare platinum groups metals (PGMs); **noble metals** such as Au, Ag, and Pt. **Hazardous metals** such as Cr, Pb, Be, Hg, Cd, Zn, Ni are also present. Ceramics present in the PCB are primarily silica and alumina. Other ceramic materials include alkaline earth oxides, mica and barium titanate. WEEE plastics contain Brominated Flame Retardants (**BFRs**), including polybrominatedbiphenyls (**PBB**) and polybrominateddiphenyl ethers (**PBDEs**), and the combustion of these produces the formation of highly toxic gases. Thermoset resins cannot be refunded or reshaped because of their net structure; thus, they are regarded as nonrecyclable [22]. PC scrap primarily contains ABS, PS and PVC plastics with the density range of +1.0-1.5 g/cm³, whereas PCB scrap mainly contains glass fiber reinforced epoxy resins plastics with the density range of +1.5-2.0 g/cm³ [22].

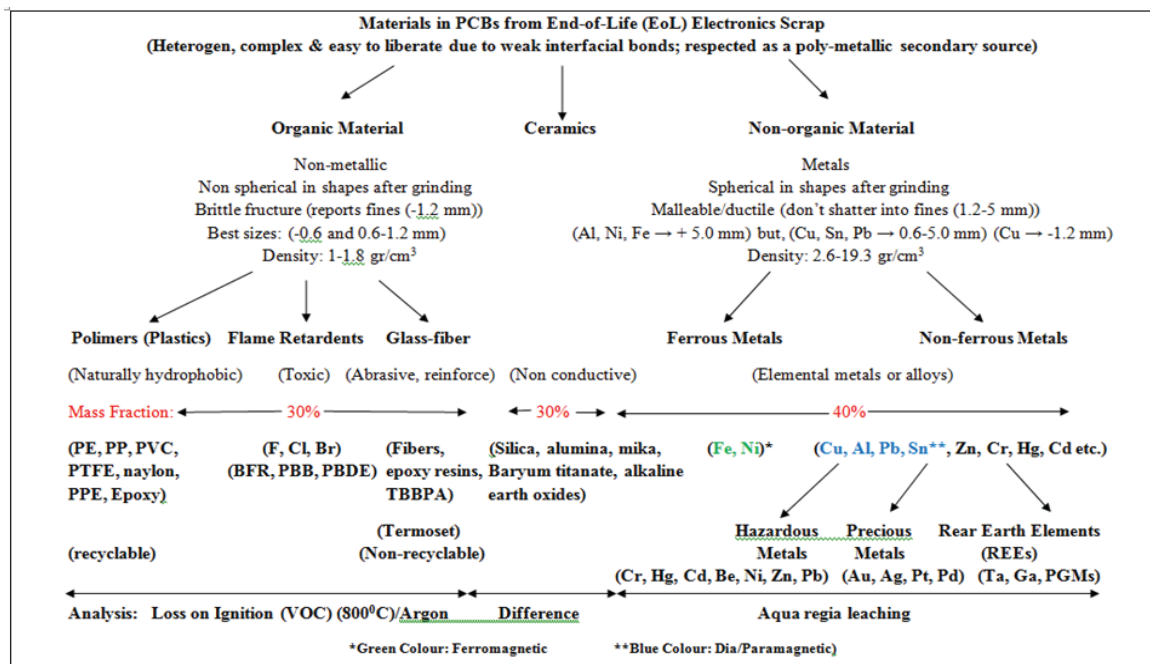


Fig. 1 Materials and their properties in PCBs from EoL scrap

C.Methods of Joining Components in PCBs

Electronic components are mounted on PCBs using various types of connections. These connections are typical of following type: socket pedestal (Press-fit), through-hole device (THD) (Wave type solder), surface mounted device (SMD) (Solder by reflux), screw joint, and rivet. There are several methods by which these connections can be broken. For example, components with socket pedestal connection can be disassembled directly by nondestructively force, but the method used to disassemble components with SMD or THD connections are always destructive, involving removal of solder or pins [2].

Welding is a process through which chemically and mechanically two metals are joined at a low melting point. Welding occurs at a temperature of 40°C above the melting point of the solder alloy, and is valid for any type of solder, including electronic welding. It has a relatively low melting point (183°C), good wettability, good mechanical and electrical properties (high conductivity); the cost of the alloy is low [23]. The oldest and most common Pb-based solders are 63Sn-37Pb. Legislation promotes new technologies such as lead-free welding, a new technology, free of lead, which is used because of the need to ban lead, as it causes damage to both humans and the environment. The eventual elimination of lead-based solder has major implications for the processing, assembly, reliability, and electronic packaging cost aspects due to the solder melting temperature, processing temperature, wettability, mechanical and thermo-mechanical fatigue, and so on [24]. Special liquor, methylphenenyl silicon oil can be used as the medium to transmit heat to melt solder from the PCBs [25].

III. PHYSICAL/MECHANICAL RECYCLING TECHNIQUES

The drive to recover the valuable metals in particular Au, Ag, Pd and Cu has received tremendous attention in recent years using extraction processes such as mechanical, **chemical and hydro / pyrometallurgical leaching separation techniques**. Methodology generally includes PCBs characterization and a combined route of physical and hydrometallurgical processing. The outcome of a recycling process can be evaluated from two aspects: the material recovering efficiency and the environmental impact of the processing. Physical separation processes benefit from low capital and operating costs and suffers from high valuable metal loss (10-35%) due to insufficient metal liberation.

A.Dismantling (Manual, Automated, Semi Automated)

Attachment regimes of materials encountered in electronic scrap are fastening, inserting, welding, binding, wrapping, coating and plating. Basically, it is not energy intensive to unlock the associated materials such as ceramics, glasses and metals with different mechanical properties, depending on the locking regimes of materials involved. In general, materials locked through fastening, by screws, clinks and rivets etc., inserting, wrapping and packaging can readily be detached. Materials locked by means of coating, binding, welding and encapsulating are relatively difficult to be unlocked and materials locked by alloying and filling cannot be liberated by mechanical means [22]. On the basis of assembly of PCBs, two methods can be used for automatic disassembly: **selective disassembly and simultaneous disassembly**.

- In selective disassembly some specific components are located and removed as per the disassembly objectives. The connection type and coordinates of connection are

determined and components are disassembled individually. This principle is called “look and pick”.

- Under simultaneous disassembly, the whole flat board is heated to desolder components from the board and all components are “wiped off” simultaneously. These components are then identified and sorted by geometrical and physical criterions. This principle is also called “evacuate and sort.” Simultaneous disassembly method has high efficiency, but also a higher risk of damaging the components. This method also requires an additional sorting process that increases the processing time and cost. In the “evacuate and sort” system, the components are identified and sorted on the basis of geometry, density, or using magnetic effect. This recognition process is different from the one in selective disassembly.

Selective dismantling is an indispensable process since: the reuse of components has first priority, dismantling the hazardous components is essential, and it is also common to dismantle highly valuable components and highly graded

materials such as battery in order to simplify the subsequent recovery of materials.

B.Comminution for Liberation of Metallic and Non-Metallic Fractions (Shredding/ Crushing)

An effective liberation of various materials like metals and plastics is a crucial step towards mechanical separation. In addition, classification of electronic scrap is also important to be able to provide an appropriate feed material for the subsequent separation process [26]. The purpose of shredding / crushing is to strip metals from the base plates of waste PCBs. Crushing technology is intimately related to not only energy consumption of crushing equipment, but also further selective efficiency. Waste PCBs are comprised of reinforced resin and metal parts such as wires and joints. They have a high hardness and tenacity. Comminution of waste PCBs and high effective liberation of the metal composition from non-metals is the prerequisite of the following sequence separation for better recovery of waste PCBs. Potential process flowsheet for metals recovery from e-waste with two step crushing is given in Fig. 2.

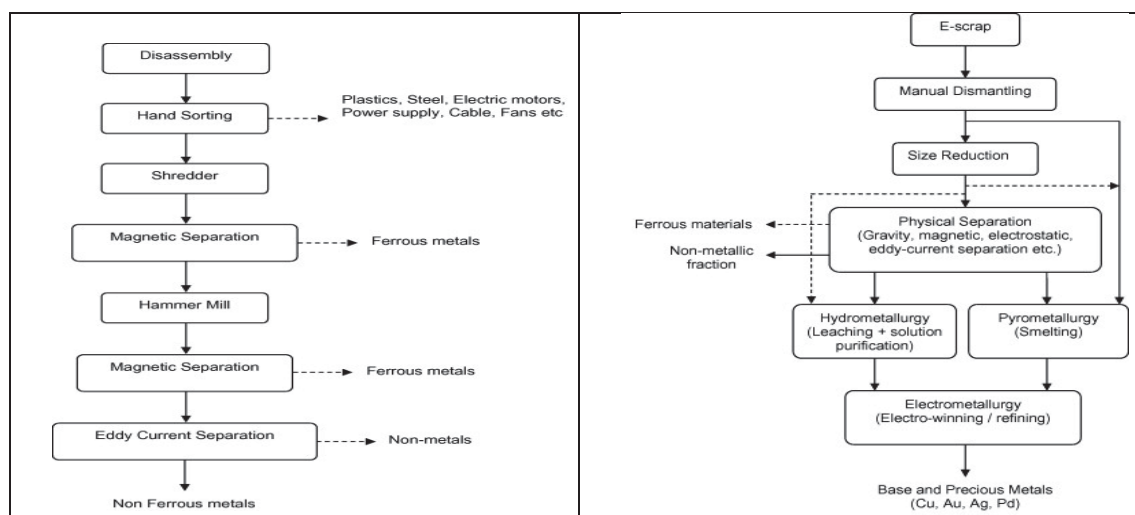


Fig. 2 Two-step PCB comminution and physical/metallurgical separation flowsheet [13]

After removal of the hazardous components (i.e. capacitors, liquid crystal displays (LCD) and batteries), different mineral processing unit operations such as shredding, crushing and grinding can be used to liberate metals from cladding materials such as resin, fiberglass and plastics. Various types of hammer crushers, rotary crushers, disc crushers, shredders, cutters equipped with a bottom sieve, are used for liberation. Ball milling and disc milling are also reported for pulverizing the PCBs after cutting into small sizes [2]. Low speed high torque shear shredders (-10 mm) are basically ideal for the primary crushing, while a number of mills have been reported for the finer comminution [27], [22] and [28], with the swing hammer types appearing to have become the industry standard [29]-[31]. Reference [31] gave a good review of the different modifications of the swing hammer mills; the comminution mechanism is essentially the same. It breaks mostly by impact,

with shear, compression and abrasion; a combination of stress modes appropriate for the diverse material types, from brittle to ductile, present on printed circuit boards. The product discharges through a screen – basically, a closed circuit grinding. Below 500 μm is necessary for liberation. If we use froth flotation for separation, then -74 μm is enough for total liberation [32].

The PCBs were first cut with a bench guillotine (employing a shearing action as in shear shredders) into roughly 4-6 cm fragments appropriate for the choke of the swing hammer mill (Eriez magnetics MACSA Pedestal Type Model 300) used for the fine crushing and grinding. -75+38 μm is enough for liberation. Very few composite particles remain. Pb would be inseparable from neither Zn nor Sn in a solder particle. A realistic pursuit will be to recover as much as possible of the metallic values in bulk into a product fraction [32].

Beneficiation operation therefore cannot attempt to separate such alloy particles into constituent elements; realistic schemes can aim only at achieving some bulk collection of metallic values into a concentrate.

Copper is found between layers of resin. Ferromagnetics and Cu liberate at -2 mm and Al at +7 mm [26]. The PCB scraps having small size particles can be separated by various separation methods like: size, density, magnetic, electrostatic, eddy current and gravity separation. Reference [26] studied the liberation characteristics of PCBs and the effect of shape and size on liberation. It was concluded that below 6 mm size, ferromagnetic and Cu are completely liberated and at the same time, Al is found to be liberated in much coarser fraction. Reference [33] reported that glass fiber-reinforced epoxy resin undergoes brittle fracturing more readily than metallic materials and concentrates in the finer fraction during impact milling of PCB scraps. Reference [34] demonstrated the use of stamp mill for the liberation of various metallic components. Reference [35] also reported that after milling to below 150 μ m size, no interlocking of metallic and non-metallic particles is observed.

C.Sieving for Classification

In size separation, a sieve is used to classify the different sized particles. The size of sieve apertures can be varied as per the particulate size. Screening has not only been utilized to prepare a uniformly sized feed to certain mechanical process, but also to upgrade metals contents. Screening is necessary because the particle size and shape properties of metals are different from that of plastics and ceramics. The primary method of screening in metals recovery uses the rotating screen, or trammel, a unit which is widely used in both automobile scrap and municipal solid waste processing.

D.Chemical Composition Determination

Chemical composition and liberation are critical attributes in characterizing EoL PCB, which is recognized as a valuable secondary resource stock, for beneficiation investigations. No procedural standard exists for the determination of its chemical composition, nor for the 75 μ m fines generated during its comminution. [32]. Reviews and investigations on EoL PCBs have mentioned techniques such as AAS, ICP-OES, ICP-MS, fire assay, XRF and XRD as applicable [22]. Generally, spectroscopic techniques – X-rays, flame, plasma, infra-red – can give good qualitative information, but for quantitative analysis, every source of error (sampling, digestion, dilution, calibration, interference, etc.) can be of very detrimental effect with such highly heterogeneous sample [32].

The elemental composition of PCBs varies depending on the type of PCBs and its applications. In general PCBs contain ~28% metals, ~23% plastics and the remaining percentage as ceramics and glass materials [36]. The substrate is mainly made of epoxies or cyanate resins (for multilayered) or phenolic resins (for single layered PCBs). Along with the resin, different types of hardener are required for cross-linking to form thermoset plastics. The most commonly used

hardeners are dicyanodiamide, 4,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl methane [2]. The loss-on-ignition can be used to determine the polymeric fraction (volatile organic materials) and the aqua regia leaching can be used to determine the metal fraction. The ceramic fraction can be calculated by the mass difference [37].

The principal reinforcing material for PCB substrate is cloth, made of glass fibers or silica. Other inorganic materials such as alumina, alkaline and alkaline earth-oxides and small amounts of other mixed oxides such as barium titanate, are also present. Ceramic materials such as BeO, glasses can also be found in the bridges and slots of PCBs. Around 10-20% of the PCB is made up with Cu, which forms the conducting layer for electrical connection between different components. Precious metals especially Au and Pd are used as contact materials in joints. Typical Pb/Sn solders, which are used for joining different components in PCBs, account for 4-6% of the total PCB weight. Components that are mounted on PCBs also contain different metallic values such as Ga, In, Ti, Si, Ge, As, Sb, Se, Te, Ta, etc. The PGMs are present in relays, switches or in sensors [38].

E.Gravity Separation

Gravity separation is based on the fact that every material particle has a specific density. Gravity concentration methods separate materials of different specific gravity by their relative movement in response to gravity. Nonetheless, this separation is not only dependent on the density of the components, but also on their size. Besides gravity one or more of the other forces like, force exerted by the viscous liquid (such as water or air), can serve as the separation medium. By using different heavy liquids, the metals can be separated from the plastics. Different metal particles can be further separated. For this purpose, the PCB material is processed on concentrating tables. The tables exploit the difference in the specific gravity and particle size to achieve desired separation. The principle of the air classification technique is based on the suspension of the particles in a flowing air stream and the separation of the particles based on their density difference. Density separation techniques which are well-known in the mineral processing industry have found their way into electronic scrap recycling based on the fact that electronic scrap consists essentially of plastics, with a density less than 2.0 g/cm³; light metal, primarily Al and glass, with a density of 2.7 g/cm³; and heavy metals, predominantly Cu and ferromagnetics, with a density more than 7 g/cm³. In sink-float separation, both PC and PCB scrap ~50% (weight) of floats which is primarily plastics can be separated out at the specific density of 2.0 g/cm³ [22].

F.Magnetic Separation

Magnetic separation can be used to separate magnetic particles from non-magnetic particles. Magnetic separators, in particular low-intensity drum separators are widely used for the recovery of ferromagnetic metals from non-ferrous metals and other non-magnetic wastes. Over the past decade, there have been many advances in the design and operation of high-intensity magnetic separators, mainly as a result of the

introduction of rare earth alloy permanent magnets capable of providing very high field strengths and gradients. There are some problems associated with this method. One of the major issues is the agglomeration of the particles which results in the attraction of some non-ferrous fraction (such as NMF) attached to the ferrous fraction. This will lead to the low efficiency of this method. Through the process of magnetic separation, it is possible to obtain two fractions: magnetic fraction, which concentrated Fe; and non-magnetic fraction, which concentrated Cu [37].

Two magnetic separations at 700 and 3000 Gauss were performed to separate the magnetic and non-magnetic substances from the milled PCBs. The milled PCBs of particle size > 5.0 mm and the heavy fraction separated from the < 5.0 mm PCBs particles by gravity separation [39].

G. Electrostatic Separation

Electric conductivity-based separation separates materials of different electric conductivity (or resistivity). There are three typical electric conductivity-based separation techniques: (1) eddy current separation, (2) corona electrostatic separation and (3) triboelectric separation. In the corona electrostatic separation, electrode system, rotor speed, moisture content and particle size have the greatest effect in determining the separation results. The corona-electrostatic method is perhaps the most effective separation technology for the metallic and non-metallic fractions at present. The method has the advantage that it is environmentally friendly, producing no wastewater and no gaseous emissions.

The separating capability depends on the difference in polarity and the amount of charge acquired by particles to be separated. Induction or corona charging can successfully separate the mixed particles that have large difference in conductivities. Tribo electricity or contact charging is useful for charging and separating materials that have similar conductivities. The principle of eddy current separation is that in separation zone gravitational, centrifugal, frictional, and magnetic deflection forces influence the falling particles, but only magnetic force deflects the ferrous particles to a higher degree. To separate ferrous particles, the magnetic deflection force acting on the ferrous particles has to be greater than all competing forces [40].

It has been found that particle sizes of 0.6–1.2 mm are the most suitable size for separation in industrial applications. Therefore, a two-step crushing process has been proposed to achieve this particle size (Fig. 2). Reference [41] found that as the angle of the static electrode reduced and the corona electrode angle was increased, the separation efficiency was enhanced. It was reported that applied voltage of 20–30 kV, center distance of 21 cm, static electrode radius of 1.9 cm, corona wire radius of 11.4 cm, static electrode angle of 20° and corona electrode angle of 60° were the optimum operating parameters influencing the separation efficiency. Considerable work is continuing in this area with particular focus on the electrostatic behavior of the system and the field intensity [42]. Corona electrostatic methods are now capable of producing two streams from PCB waste comprising a metallic

and a non-metallic portion with little cross-contamination; the method is dry at room temperature and as such is almost zero polluting depending on the quality of the dust extraction system. Eddy current separation technology is used to recover aluminum, which consists of approximately 2.8% by weight of a typical PCB scrap [40].

H. Froth Flotation

Exploiting natural hydrophobicity, as well as reverse flotation is quite common in coal and Fe ore flotation, respectively, while some application of flotation has also been reported in waste processing [43]–[47]. A major challenge to the physical processing alternative is the poor recovery of the base and precious metal values deported to the $74\ \mu\text{m}$ fine fraction generated during the comminution operation. Assessing this as an applied minerals processing problem, froth flotation has been advanced as a promising beneficiation technique for this fine fraction [48].

IV. CHEMICAL RECYCLING TECHNIQUES

Many recycling processes of waste PCBs have been tested in a laboratory scale. For instance, the pyrolysis process was employed to obtain high pure metals. Uncertainty and potential pollution have declined the process to expand into a field scale [49]. In this type of recycling, the PCBs are depolymerized into smaller useful molecules by several techniques, such as pyrolysis, gasification or application of supercritical fluids. The obtained products (fuels, gases and tar) are refined by conventional approaches and the metallurgical approaches are employed for the treatment of the metallic fraction. A major shortcoming is the presence of the significant amount of dioxin precursors in pyrolysis oils, which can possibly be reduced by adding CaCO_3 , Fe_2O_3 during pyrolysis. In recent years, supercritical fluids have been an effective medium for the destruction of epoxy adhesive layer.

V. PYROMETALLURGICAL PROCESSES (SMELTING)

Pyrometallurgy, energy intensive and high-cost process, is the traditional approach for metal recovery from the waste PCBs but selective recovery of individual metals can hardly be done by this route. Pyrometallurgical techniques include incineration, smelting in plasma arc furnace, blast furnace or copper smelter, high temperature roasting in presence of selective gases to recover mainly non-ferrous metals. Currently, more than 70% of waste PCBs is treated in smelters rather than through mechanical processing [12]. The main advantage of pyrometallurgical treatment is its ability to accept any forms of scrap. Hence, electronic scrap can be used as a part of raw materials in the smelters for recovery of copper along with Au and Ag [38]. A recycling method, developed by Technical University Berlin in 1997, turned waste PCBs into a Cu-Ni-Si alloy, a mixed oxide (mainly Pb and Zn) and environmentally agreeable slag by a top blown reactor [50], [1]. At Boliden Ltd. Ronnskar smelter, Sweden, waste PCBs are directly fed into Cu converter to recover Cu, Ag, Au, Pd, Ni, Se and Zn while the dust containing Pb, Sb, In

and Cd is processed separately for metal recovery [51]. At Umicore's integrated metal smelter and refinery, electronic scraps are first treated in IsaSmelt furnace to recover precious metals along with Cu the form of Cu-bullion. Cu is first recovered from this bullion through Cu leaching and electrowinning followed by precious metals recovery from Cu-leached residue in precious metal refinery [52]. Fig. 3 shows a flowsheet for Cu recovery as Cu cathode from waste electronic equipment by a pyrometallurgical route combined with electrolysis [53], [54]. A popular method to recover the Cu and precious metals is primary smelting. Waste PCBs can be used to produce a Cu-Ni-Si alloy, a mixed oxide (mainly Pb and Zn) and slag by a top blown reactor. Vacuum metallurgy separation (VMS) is suitable for Bi, Sb, Pb and other heavy metals with high vapor pressure.

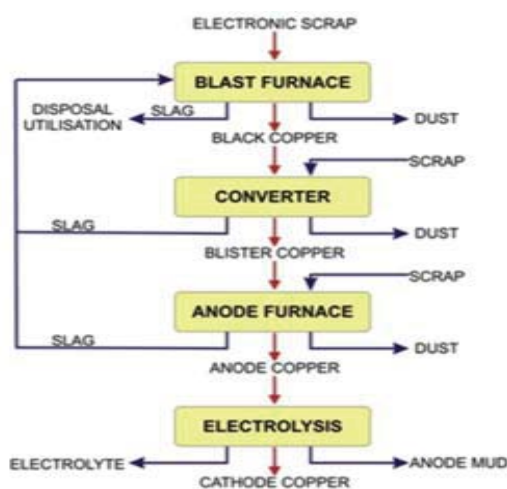


Fig. 3 Recycling process of e-waste containing Cu [53]

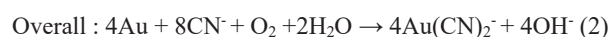
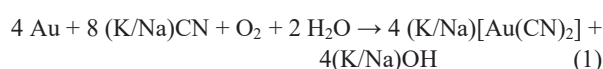
VI. HYDROMETALLURGICAL PROCESSES (LEACHING)

Hydrometallurgical route is more selective towards metal recovery from waste PCBs or pretreated PCBs, easier to control over reaction and creates less environmental hazards than pyrometallurgical approach. The base metals recovery has a substantial impact on the economics of the process due to larger available amount in waste PCBs. Moreover, recovery of base metals also ensures the enrichment of precious metals in the solid residue, making it easier to leach out subsequently [2]. Low capital cost hydrometallurgical processes are mainly used for recycling of the metallic-ferrous fraction where the extraction of the metal is profitable. Depending on the substrate material (ceramic, glass, or polymer) there are different hydrometallurgical processes used [40].

A. Precious and Base Metal Recovery by Acid Leaching

Currently, around 300 tons of Au are used in electronic industries along with other precious and strategic metals like Ag, Pd, Pt, Nb, Ta, etc. [55]. Most of the precious metals are present in elemental form and in proximity of other metals, which makes very difficult to separate the individual ones [2].

To improve the selectivity of the precious metals and minimize the impurities, leaching is preferably carried out after the removal or recovery of base metals. Reference [56] in sequential steps first dissolved the base metals in nitric acid, followed by leaching of the first step leach residue in aqua regia to extract Au and finally precipitation of Au with ferrous sulfate. Nevertheless, the construction of the leaching reactor suitable for highly corrosive nitric acid and aqua regia, limits its industrial feasibility. Currently, the active research has been shifted towards the development of less corrosive reagents such as cyanide, halide, thiourea, potassium persulfate and thiosulfate for precious metals leaching from waste PCBs [2]. Fig. 4 summarizes precious metal leaching reagents, reactions, results, conditions, advantages and disadvantages along with references. Au leaching by cyanide follows the following reactions:



In recent years, the recovery of gold by thiourea has gained worldwide attention due to its less environment impact. Unlike cyanide, thiourea forms a cationic complex with gold in acidic medium and can dissolve up to 99% gold as per the following reaction:



Previous studies [55]–[67] achieved 86–99.5% Au, 93% Ag and 93–99% Pd recoveries. Fig. 5 summarizes base metal leaching reagents, reactions, results, conditions, advantages and disadvantages along with references. Previous studies obtained 12–100% Cu, 5.7–62% Fe, 51–83% Zn and >90% Ni recoveries.

B. Bio-Hydrometallurgical Leaching Processes

Although predominantly targeting the valuable metal fraction recovery from waste PCB, bioleaching could benefit the materials recovery from e-waste in two ways. The use of microorganisms to extract metals by generating weaker organic acids will save on the manufacture of the currently used strong inorganic acids for metal leaching and also save the environment significantly in terms of treating and disposing of strong inorganic acid waste compared to the weaker and more readily treatable organic acids generated by the microorganism cultures. Bioleaching has considerable potential to offer by selectively extracting the metals at low temperatures by microorganism generated organic acids, thus significantly reducing the pollution from strong acid leaching and also leaving an unpolluted non-metallic residue for further processing. Bio-hydrometallurgical processing is well established as an alternative route for recovering metals especially Cu and Au from very low-grade ores and concentrates. The investigations have also been extended to other metals due to low investment cost, less environmental

impact, less energy consumption and better control than the [12].
conventional pyrometallurgy or hydrometallurgy routes [69],

Lixiviant Reagent	Cyanide	Thiourea	Thiosulfate	Potassium persulfate	Halide
	CN ⁻ , O ₂ (air) KCN •65.12 g/mol •1.52 g/cm ³ •71.6 g/100 mL (25°C) NaCN •49.10 g/mol •1.596 g/cm ³ •63.7 g/100 mL (25°C)	SC(NH ₂) ₂ , Fe ³⁺ CH ₄ N ₂ S •76.12 g/mol •1.405 g/mL •14.2 g/100mL (25°C)	S ₂ O ₃ ²⁻ , NH ₃ , Cu ²⁺ (NH ₄) ₂ S ₂ O ₃ Na ₂ (S ₂ O ₃) ₅ •5H ₂ O hypo •158.11 g/mol (anhydrous) •248.18 g/mol (pentahydrate) •1.667 g/cm ³ •70.1 g/100 mL (20 °C)	2[SO ₄] ⁻ K ₂ S ₂ O ₈ •270.322 g/mol •2.477 g/cm ³ •4.49 g/100 ml (20 °C)	Chlorine/chloride Cl ⁻ /Cl ₂ NaCl, hypochlorite, HCl, HClO ₄ , NaClO Iodide I ⁻ /I ₂ KI Bromide Br ⁻ /Br ₂
Reactions	4Au+8CN ⁻ +O ₂ +2H ₂ O → 4Au(CN) ₂ ⁻ +4OH ⁻	2Au+4CS(NH ₂) ₂ +2Fe ³⁺ ↔ 2Au(CS(NH ₂) ₂) ₂ ⁺ +2Fe ²⁺	4Au+8S ₂ O ₃ ²⁻ +O ₂ +2H ₂ O → 4Au(S ₂ O ₃) ₂ ³⁻ +4OH ⁻	Dissolve all base metals retaining only gold in solid residue	2Au+11HCl+3HNO ₃ ↔ 2HAuCl ₄ +3NOCl+6H ₂ O
Species and Their Stability	Au(CN) ₂ ⁻ (log K: 38.3) Ag(CN) ₂ ⁻ (log K:20.3)	Au(CS(NH ₂) ₂) ₂ ⁺ (log K: 22) Ag(CS(NH ₂) ₂) ₂ ⁺ (log K: 13)	Au(S ₂ O ₃) ₂ ³⁻ (log K:28.7) Ag(S ₂ O ₃) ₂ ³⁻ (log K:13)		AuCl ₄ (log K: 29.6)
Conditions	E ⁰ :-0.67 V, pH>10, 25°C	E ⁰ :0.38 V, pH: 1-2, 25°C	E ⁰ :0.274-0.038V, pH>8-11, 25°C		E ⁰ :1.0 V, pH<4, 25°C
References	[55] Column leaching of crushed PCBs: 46.4% Au, 51.3% Ag, 47.2% Nb, 62.3% Cu	[58], [59] Crushed PCBs, 10 g/L H ₂ SO ₄ and CS(NH ₂) ₂ 5 g/L ferric sulfate, 2h 90% Ay, 68% Cu, 45%Fe, 43%Pb and 28% Zn	[61] Crushed PCBs, 0.2 M (NH ₄) ₂ S ₂ O ₃ 0.02M CuSO ₄ 0.4M NH ₄ OH 400C, 48 h 95% Au, 100% Ag	[63] 99.5% Au with melting	[57] Oxidative leaching using HNO ₃ or H ₂ O ₂ in chloride medium (HCl and NaCl), 75°C 93-95% Pd
References	[57] Bench scale, PCBs 1.Oxidative H ₂ SO ₄ leach to dissolve Cu and Ag. 2.Oxidative chloride leaching to dissolve Pd and Cu. 3.Cyanide leaching Au, Ag and Pd. 95%Au, 93% Ag and 99% Pd	[60] 20 g/L CS(NH ₂) ₂ 6 g/L 5 g/L ferric sulfate 10 g/L H ₂ SO ₄ S/L: 1/10 (g/mL) Ambient temp., 3h 85.76% Au, 71.36% Ag	[62] 0.12 M (NH ₄) ₂ S ₂ O ₃ 20 mM CuSO ₄ 0.2 M NH ₄ OH 2h 98% Au PCB 10 h 90% Au mobile phone		[64] Iodide leaching 1-1.2% iodide conc. 1-2% H ₂ O ₂ S/L: 1/10 pH: 7 Ambient temp., 4h 95% Au
Commands Ads/Pros	Toxic and have serious environmental issues	Non-toxic, non-corrosive, less environmental impact. Cost and consumption important factors.	Oxygen carrying catalyst Cu(NH ₃) ₄ ²⁺ is required. Non toxic and non-corrosive	Non-toxic, strong oxidizing agent	Non-toxic, non-corrosive, very selective. Consumption, reagent cost, chlorine gas, special reactor requirement

Fig. 4 Precious metal leaching reagents, reactions, conditions, advantages and disadvantage

Lixiviant Reagent	H ₂ SO ₄ (H ₂ SO ₄ + H ₂ O ₂)	H ₂ SO ₄ + H ₂ O ₂	H ₂ SO ₄ + H ₂ O ₂	H ₂ SO ₄ + H ₂ O ₂	HNO ₃
	First Stage •H ₂ SO ₄ 1M 1/10 w/v Second Stage •H ₂ SO ₄ 1M 1/10 w/v + •240 mL H ₂ O ₂	•2M 100mL H ₂ SO ₄ + 20 mL 30% H ₂ O ₂	•2M 100mL H ₂ SO ₄ + 20 mL 30% H ₂ O ₂	•2M H ₂ SO ₄	•6M HNO ₃
Reactions	H ₂ O ₂ + 2H ⁺ + 2e ⁻ → 2H ₂ O Cu + H ₂ SO ₄ + H ₂ O ₂ → CuSO ₄ + 2H ₂ O Zn + H ₂ SO ₄ + H ₂ O ₂ → ZnSO ₄ + 2H ₂ O Sn + H ₂ SO ₄ + H ₂ O ₂ → SnSO ₄ + 2H ₂ O Fe + H ₂ SO ₄ + H ₂ O ₂ → FeSO ₄ + 2H ₂ O Ni + H ₂ SO ₄ + H ₂ O ₂ → NiSO ₄ + 2H ₂ O	H ₂ O ₂ + 2H ⁺ + 2e ⁻ → 2H ₂ O Cu + H ₂ SO ₄ + H ₂ O ₂ → CuSO ₄ + 2H ₂ O Zn + H ₂ SO ₄ + H ₂ O ₂ → ZnSO ₄ + 2H ₂ O Sn + H ₂ SO ₄ + H ₂ O ₂ → SnSO ₄ + 2H ₂ O Fe + H ₂ SO ₄ + H ₂ O ₂ → FeSO ₄ + 2H ₂ O Ni + H ₂ SO ₄ + H ₂ O ₂ → NiSO ₄ + 2H ₂ O	H ₂ O ₂ + 2H ⁺ + 2e ⁻ → 2H ₂ O Cu + H ₂ SO ₄ + H ₂ O ₂ → CuSO ₄ + 2H ₂ O Zn + H ₂ SO ₄ + H ₂ O ₂ → ZnSO ₄ + 2H ₂ O Sn + H ₂ SO ₄ + H ₂ O ₂ → SnSO ₄ + 2H ₂ O Fe + H ₂ SO ₄ + H ₂ O ₂ → FeSO ₄ + 2H ₂ O Ni + H ₂ SO ₄ + H ₂ O ₂ → NiSO ₄ + 2H ₂ O	H ₂ O ₂ + 2H ⁺ + 2e ⁻ → 2H ₂ O Cu + H ₂ SO ₄ + H ₂ O ₂ → CuSO ₄ + 2H ₂ O Zn + H ₂ SO ₄ + H ₂ O ₂ → ZnSO ₄ + 2H ₂ O Sn + H ₂ SO ₄ + H ₂ O ₂ → SnSO ₄ + 2H ₂ O Fe + H ₂ SO ₄ + H ₂ O ₂ → FeSO ₄ + 2H ₂ O Ni + H ₂ SO ₄ + H ₂ O ₂ → NiSO ₄ + 2H ₂ O	H ₂ O ₂ + 2H ⁺ + 2e ⁻ → 2H ₂ O Cu + H ₂ SO ₄ + H ₂ O ₂ → CuSO ₄ + 2H ₂ O Zn + H ₂ SO ₄ + H ₂ O ₂ → ZnSO ₄ + 2H ₂ O Sn + H ₂ SO ₄ + H ₂ O ₂ → SnSO ₄ + 2H ₂ O Fe + H ₂ SO ₄ + H ₂ O ₂ → FeSO ₄ + 2H ₂ O Ni + H ₂ SO ₄ + H ₂ O ₂ → NiSO ₄ + 2H ₂ O
Species and Their Stability	ΔG = - 77.941 kcal/mol (Cu) ΔG = - 127.965 kcal/mol (Zn) ΔG = - 136.895 kcal/mol (Sn) ΔG = - 115.847 kcal/mol (Fe) ΔG = - 101.244 kcal/mol (Ni)	ΔG = - 77.941 kcal/mol (Cu) ΔG = - 127.965 kcal/mol (Zn) ΔG = - 136.895 kcal/mol (Sn) ΔG = - 115.847 kcal/mol (Fe) ΔG = - 101.244 kcal/mol (Ni)	ΔG = - 77.941 kcal/mol (Cu) ΔG = - 127.965 kcal/mol (Zn) ΔG = - 136.895 kcal/mol (Sn) ΔG = - 115.847 kcal/mol (Fe) ΔG = - 101.244 kcal/mol (Ni)	ΔG = - 77.941 kcal/mol (Cu) ΔG = - 127.965 kcal/mol (Zn) ΔG = - 136.895 kcal/mol (Sn) ΔG = - 115.847 kcal/mol (Fe) ΔG = - 101.244 kcal/mol (Ni)	
Conditions	•75°C, 4h	•50°C, 3h, pH: 1.48 •PCBs (-3 mm) •	•50°C, 3h, pH: 1.52 •WPCBs (-3 mm)	•85°C, 12 h •PCBs (-1.0 mm)	•80°C, 6h •PCBs (-2.5 mm)
References	[74]	[65] 46.3% Cu, 5.7% Fe, 21.1% Sn, 51.1% Zn	[65] 11.5% Cu, 62.2% Fe, 26.4% Sn, 31.8% Zn	[61] 100% Cu and Zn, 95% Fe, Ni and Al	[66] Cu and Pb > 95%
Commands Ads/Pros	H ₂ O ₂ environmentally friendly and oxidant				

Lixiviant Reagent	HNO ₃	<i>Sulfobacillus thermosulfidooxidans</i>		
	• 6M HNO ₃	• Scrap Conc: 10 g/L		
Conditions	• 80°C, 24h • PWBs (10*20*2 mm)	• 45°C, 18d, pH: 2.0, 180 rpm • PCBs (50-150 μm)		
References	[67] Cu and Ni > 90%	[68] 81% Ni, 89% Cu, 79% Al, 83% Zn		

Fig. 5 Base metal leaching reagents, reactions, conditions, advantages and disadvantages

In recent years, biohydrometallurgy has also been applied for metal recovery from waste PCBs. The extraction of metals such as Cu, Ni, Zn, Cr and precious metals from PCB scrap is technically feasible by the use of bacteria-assisted reaction [70]-[72]. Reference [70] indicated that it is possible to mobilize metal from e-waste by the use of the microorganisms such as bacteria (*Thiobacilli*) and fungi (*A. niger*, *P.*

simplicissimum). Reference [71] used different cryogenic bacterial strains (*Chromobacterium violaceum*, *Pseudomonas fluorescens*, *Bacillus megaterium*) to recover Au from waste PCBs and found maximum 14.9% Au dissolution as dicyanaoaurate [Au(CN)₂]. An investigation on the extraction of Cu from waste PCBs using bacterial consortium enriched from natural acid mine drainage establishes that extraction of

Cu is mainly accomplished indirectly through oxidation by Fe^{3+} ions generated from Fe^{2+} oxidation by bacteria [73]. The Cu recovery rate primarily depends upon the initial pH, Fe^{2+} concentration and bio-oxidation rate of Fe^{2+} . The sequential reactions are $4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O}$ and $\text{Cu} + 2\text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + 2\text{Fe}^{2+}$ [10]. Toxic influence of ingredients on the growth of microorganisms and slow reaction rate are some of the major drawbacks projected by various researchers during bioleaching of PCB scrap [70], [12], [73], [2].

VII. PURIFICATION

Metals from PCBs were solubilized on leaching process and can be recovered by purification techniques such as: liquid/liquid extraction (extraction by solvent), precipitation/cementation and electrolyte refinement (electrowinning/electro-recovery) [17], [74]. Direct solvent extraction (DSX) or synergistic solvent extraction (SSX) can be carried out using Cyanex 301, 302 or 272 lixiviates along with kerosene and TBP for $\text{Ni} > \text{Co} > \text{Ca} > \text{Mg}$ extraction. Versatic 10, which is neodecionic acid, TBP and ShellSol 2046 can be used in Cu/Ni separation or Ni extraction. Extraction, scrubbing and stripping steps are performed for a compound or metal production. Electrochemical metal extraction route, on the other hand, is considered as more environment friendly than chemical leaching because it involves on the electron transfer process aided by the supplied electrode potential with minimum chemical reagents requirement. Aqueous processing route mostly generates multi-metal containing solutions and recovery of individual metal either in metal form or as salt is a challenging task. Cementation of Au/Ag using Cu/Zn powders or Cu solvent extraction followed by Cu electrowinning processes are no doubt established, but issues regarding other metals recovery from the PCB leach liquor are still unresolved. Fig. 6 shows Hoboken integrated smelter and refinery plant flowsheet of Umicore. This plant includes Cu-smelter, lead blast furnace, Cu, Pb (Sn, Bi and Sb), Ni (As), precious (Au, Ag, Pt, Pd, Rh, Ru and Ir) and special metals (In, Te, Se) refineries along with sulphuric acid plant.

Biosorption, another facet of biohydrometallurgy, is a procedure to recover metals from the leach liquor. The procedure is based on the different physicochemical interactions (such as ion exchange, complexation, coordination and chelation) between metal ions and the charged surface groups of microorganisms [2].

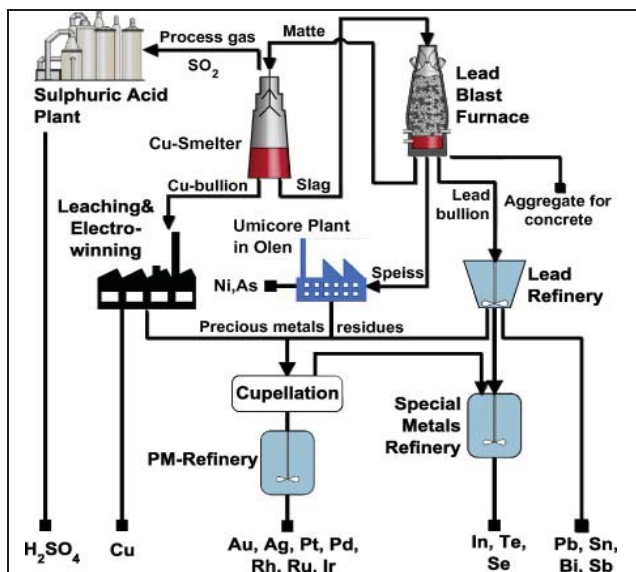


Fig. 6 Flowsheet of Umicore-Hoboken integrated smelter and refinery plant [13]

VIII. ALTERNATIVE USES OF NON-METALLIC FRACTION

The milled PCB particles of < 5.0 mm were separated into a light fraction of mostly non-metallic components and a heavy fraction of metallic components by gravity separation using a zigzag classifier (Model 1-40 MZM, Hosokawa Alpine Ag.) [34]. In terms of the research into the utilization of the 70% (w/w) non-metallic fraction of PCB waste, the potential opportunities to generate and recycle value added products has not made the same progress and is limited to: - Incorporating the non-metallic fraction into plastic molds has a higher value than when it is used as a filler in cement and asphalt industries; - The application in the production of adsorbent/resins for water treatment applications would represent a major break-through if scale-up succeeds; - Research into the production of silicon or the recovery of silica would also be attractive opportunities for new research on non-metallic e-waste and provide sustainable recycling into the micro electronics industry if successful.

Currently most of the non-metallic fractions are subjected to land filling, incineration and open dumping causing potential threat to the environment as well as loss of resources [21], [2]. In summary, physical recycling process for recovery of non-metallic is much more advantageous than chemical recycling as the former is relatively convenient and environment friendly, equipment and environment control measures are less and the potential applications of products are diverse [2].

IX. CONCLUDING REMARKS

Waste PCBs account for about 3% of nearly 50 Mt/year global E-waste generations. A significant amount of Cu and Au in it attracts crude recyclers in some parts of Asia and Africa leading to substantial environmental and health problems. Due to the heterogeneous composition and hazardous material contents, proper recycling methodology is

a still a challenging task. PCBs assay far above many base and precious metals natural deposits and is therefore recognized as a respectable poly-metallic secondary resource. The primary objective of recycling PCB scrap is to minimize the harmful environmental impact caused by hazardous material and ensure maximum material recovery. To achieve these goals, detailed information of the PCB boards and electronic parts are required for selecting the right recycling method and facility [40]. The rapid proliferation of electronic devices in the last few decades has compelled the researchers to find a remedy for one of the most toxic and hazardous waste materials. Numerous articles have been published demonstrating the process routes for recycling of this toxic but otherwise useful waste due to nearly 30% metal content.

Selective disassembly of hazardous components from the PCBs minimizes the toxic elements ending up in the mainstream of the recycling process. Following the dismantling, good liberation of non-metals from metals is required for effective separation. In general, milling to size below 150 μm ensures no interlocking of metallic and non-metallic particles. For physical separation of metals and non-metals, the density-based separators are quite popular. The latest developments include Corona Electrostatic Separator, which is based on the difference in density and electrical conductivity between plastics, metals and ceramics. Potential applications of recovered non-metallic fractions are diverse e.g. as filler material or as composites having similar properties of traditional filler materials. Recovered glass fibers perform better than commercial sound absorbing materials and have great potential as insulation materials.

Hydrometallurgical route mostly focused on Cu recovery. Although sulfuric acid is the most preferable reagent for Cu leaching but downstream processing becomes complicated due to poor leaching selectivity in inorganic acids. Ammonia leaching, on the other hand, has more selectivity towards Cu. Recycling of PCBs can only be profitable with substantial Au recovery. Thiosulfate and thiourea seem to be promising one alternative to cyanide for Au leaching. An interesting approach for Au recovery is the persulfate based leaching where all base metals including Ag dissolve keeping Au in the solid residue, which can be later purified by melting. In the previous studies, 12-100% Cu, 6-62% Fe, 51-83% Zn, >90% Ni, 86-99.5% Au, 93% Ag and 99% Pd recoveries were achieved. Bioleaching using microorganisms such as bacteria and fungi is technically feasible for the extraction of base metals and precious metals from PCB scrap. Apart from low reaction rate, metal precipitations as well as bacterial toxicity are some of the major issues projected by various researchers.

For metal extraction, pyrometallurgy route has the main advantage of its ability to accept any forms of scrap but suffers from the limitation of selective refining. Waste PCBs can be used to produce a Cu-Ni-Si alloy, a mixed oxide (mainly Pb and Zn) and slag by a top blown reactor. Vacuum metallurgy separation (VMS) is suitable for Bi, Sb, Pb and other heavy metals with high vapor pressure.

In contrast to physical separation, chemical separation generally involves decomposition of plastics through pyrolysis

producing oils, gases, tar, etc. Purification and recovery of metals various methods and options are available for the purification and selective recovery of the target metals from the pregnant leach liquor. These methods include solvent extraction, cementation, ion exchange, precipitation, adsorption, etc. The route to recover the metal(s) depends upon the economy of the process and how much efficient it is for a specific metal. However, very limited numbers of articles are available on purification and separation of individual metals from PCBs leach liquor [2].

For long-term sustainability, an integrated waste management system primarily consisting of three key factors - **reduce, reuse and recycle or better known as 3R policy** [75], is the preferable approach. Considering the 3R policy, the highest emphasis should always be given on the **recycle and reuse** of the waste electronics to reduce the quantity of waste PCBs ending up in the disposal [2]. Recycling in an environmentally sound way, reduces the consumption of natural resources, lowers the carbon footprint and lessens the environmental hazards.

The author hopes that the coverage of items in the paper will assist the scientific community, policy makers and other stakeholders to find the gap areas in achieving a cleaner and economical recycling process. Evidently, more studies are needed in the area of metal separation and recovery from PCB leach liquor. Author feel hydrometallurgical route will be a key player in the metal recovery.

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