Chapter Number

Recycling of Printed Circuit Boards

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1. Introduction

Printed circuit boards (PCBs) can be found in any piece of electrical or electronic equipment: nearly all electronic items, including calculators and remote control units, contain large circuit boards; an increasing number of white goods, as washing machines contains circuit boards for example in electronic timers. PCBs contain metals, polymers, ceramics and are manufactured by sophisticated technologies.
Wastes from electric and electronic equipments (WEEE) show an increasing upward tendency: a recent annual estimation for WEEE was almost 6.5 million tonnes, and it has been predicted that by 2015 the figure could be as high as 12 million tonnes (Barba-Gutiérrez et al., 2008). A significant proportion of WEEE is constituted by PCBs which represent about 8% by weight of WEEE collected from small appliances (Waste & Resources Action Programme Project, WRAP 2009) and 3% of the mass of global WEEE (Dalrymple et al., 2007).
However there is an increasing interest in the end-of-life management of polymers present in WEEE mainly due to high quotas of recycling and recovery set by legislation which can only be fulfilled by including the plastic fraction in recycling and recovery approaches. Furthermore, disposal of PCB in landfill is no longer accepted in developed countries because of environmental impact and loss of resources. So far recycling of waste PCBs is an important subject in terms of potential recovering of valuable products but several difficulties still exist due to environmental problems involved in end-of-life WEEE management. Due to its complex composition, PCBs recycling requires a multidisciplinary approach intended to valorise fibres, metals and plastic fractions and reduce environmental pollution, which are here reviewed in an attempt to offer a an overview of the latest results on recycling waste PCBs.

2. PCB composition

PCBs are platforms on which integrated circuits and other electronic devices and connections are installed. Typically PCBs contain 40% of metals, 30% of organics and 30% ceramics. Bare PCB platforms represent about 23% of the weight of whole PCBs (Duan et al., 2011). However there is a great variance in composition of PCB wastes coming from different appliances, from different manufacturers and of different age. As an example, after removing hazardous batteries and capacitors which, according to current legislation, must follow a separate recycling, the organic fraction resulted about 70% in PCBs from computers and TV set and 20% in those from mobile phones (William & Williams, 2007).

PCBs contain large amount of copper, solder and nickel along with iron and precious metals: approximately 90% of the intrinsic value of most scrap boards is in the gold and palladium content. However the board laminate mainly consists of a glass fibre reinforced thermosetting matrix which actual legislation imposes to be also conveniently recycled or recovered.

2.1 Polymer matrix and reinforcement

Platforms are usually thermoset composites, mainly epoxies, containing high amount of glass reinforcement; in multilayer boards multifunctional epoxies or cyanate resins are used; in TV and home electronics PCBs are often made with paper laminated phenolic resins. Biobased composites have been recently proposed as possible substitute of traditional resins used in PCBs (Zhan. & Wool, 2010).

Due to the risk of ignition during soldering of the components on the platform or impact with electric current, the matrix is often a bromine-containing, fire retarded matrix likely to contain 15% of Br. Fire retardance can be attained either using additive or reactive fire retardants. The two primary families of brominated flame retardants are the polybrominated diphenyl ethers (PBDPE) and fire retardants based on tetrabromo-bisphenol A (TBBA). Despite PBDPE have now been restricted in electrical and electronic equipment they have been found above detection limits in some PCB wastes collected in 2006 in UK; as these results relate to equipment manufactured at least 15 years ago, these levels can be considered to be likely maximum levels. Future waste PCBs are expected to contain significantly lower amount (Department for Environment, Food and Rural Affairs [DEFRA], 2006).

One of the main reasons for the current concerns regarding the use of BFR is that nearly all of them generate polybrominated dibenzo-dioxins (PBBD) and polybrominated dibenzo-furans (PBDF) during the end of life processes involving even a moderate heating. Environmental impact of BFR has been considered (Heart, 2008; Schlummeret al., 2007) and several ecofriendly strategies of fire retardancy have been investigated particularly in Europe, United States and Japan, including incorporation of metal oxides, phosphorous (Pecht &. Deng 2006) and phosphorous-nitrogen compounds (El Gouri et al., 2009). However, these approaches still suffer for drawbacks and the market has not selected a standard replacement for bromine-based flame retardants yet. On the other hand in 2008, European Commission's Scientific Committee on Health and Environmental Risks concluded no risk for TBBA when used as a reactive fire retardant and does not foresee restrictions onTBBA marketing and use. (Kemmlein et al., 2009)

The majority of reinforcements in PCBs are woven glass fibres embedded in the thermoset matrix. However because of the crushing stage preliminary to most recycling technologies, they can be recovered as shorter fibres still possessing high length/density ratio, high elastic modulus and low elongation for being used in thermoplastic polymers.

2.2 Metals

Precious metals in electronic appliances serve as contact materials due to their high chemical stability and their good conducting properties. Platinum group metals are used among other things in switching contacts or as sensors. The typical Pb/Sn solder content in PCB scraps ranges between 4-6% of the weight of the original board. Copper-beryllium alloys are used in electronic connectors where a capability for repeated connection and disconnection is desired and such connectors are often gold plated. A second use of

beryllium in the electronics industry is as beryllium oxide which transmits heat very efficiently and is used in heat sinks.
Typically PCBs contain about 5%weight of Fe, 27% of Cu, 2% of Al and 0.5% of Ni, 2000 ppm of Ag 80 ppm of Au; however there is no average scrap composition and the values given as typical averages actually only represent scraps of a certain age and manufacturer. Additionally, non-ferrous metals and precious metals contents have gradually decreased in concentration in scraps due to the falling power consumption of modern switching circuits: in the '80s the contact layer was 1–2.5 μm thick, in modern appliances it is between 300 and 600 nm (Cui & Zhang, 2008).

3. WEEE legislation

Concern about environment prompts many governments to issue specific legislation on WEEE recycling: however with the notable exception of Europe, many countries seem to be slow in initiating and adopting WEEE regulations. In Europe the WEEE Directive (European Union 2003b) and its amendments as a first priority aims to prevent the generation of WEEE. Additionally, it aims to promote reuse, recycling and other forms of recovery of WEEE so as to reduce the disposal of wastes. In both developed and developing nations, the landfilling of WEEE is still a concern and accumulation of unwanted electrical and electronic products is still common. Handling of WEEE in developing countries show high rate of repair and reuse within a largely informal recycling sector (Ongondo et al., 2011).
The WEEE Directive requires the removal of PCB of mobile phones generally, and of other devices if the surface of the PCBd is greater than 10 cm^2: To be properly recovered and handled waste PCBs have to be removed from the waste stream and separately recycled. Batteries and condensers also have to be removed from WEEE waste stream.
The RoHS Directive (European Union 2003a) names six substances of immediate concern: lead, mercury, cadmium, hexavalent chromium, polybrominated diphenyl ethers (Penta-BDE and Octa-BDE) and polybrominated biphenyls. The maximum concentration values for RoHS substances were established in an amendment to the Directive on 18 August 2005. The maximum tolerated value in homogenous materials for lead, mercury, hexavalent chromium, polybrominated diphenyl ethers and polybrominated biphenyls is 0.1% w/w weight and for cadmium 0.01% w/w.

4. Disassembling WEEE and PCBs

Nearly all of the current recycling technologies available for WEEE recycling include a sorting/disassembly stage. The reuse of components has first priority, dismantling the hazardous components is essential as well as it is also common to dismantle highly valuable components, PCBs, cables and engineering plastics plastics in order to simplify the subsequent recovery of materials. Moreover cell batteries and capacitors should be manually removed and separately disposed in an appropriate way. The PCBs can then be sent to a facility for further dismantling for reuse or reclamation of electric components.
Most of the recycle plants utilize manual dismantling. The most attractive research on disassembly process is the use of an image-processing and database to recognize reusable parts or toxic components. The automated disassembly of electronic equipment is well advanced but unfortunately its application in recycling of electronic equipment still face lot of frustration. In treatment facilities components containing hazardous substances are only

partly removed particularly in small WEEE. This implies that substantial quantities of hazardous substances are forwarded to subsequent mechanical crushing processes, causing significant dispersion of pollutants and possibly reduction of quantities of valuable recyclable materials (Salhofer & Tesar 2011).
Electronic components have to be dismantled from PCB assembly as the most important step in their recycling chain, to help conservation of resources, reuse of components and elimination of hazardous materials from the environment. In semi-automatic approaches, electronic components are removed by a combination of heating and application of impact, shearing, vibration forces to open-soldered connections and heating temperature of 40-50 °C higher than the melting point of the solder is necessary for effective dismantling; pyrolysis probably occurs during the dismantling, which means there is a potential for dioxin formation when this scrap is heating (Duan et al., 2011).

5. Physical recycling

Thermosetting resins, glass fibres or cellulose paper, ceramics and residual metals can serve as good filler for different resin matrix composites. Physical recycling always involves a preliminary step were size reduction of the waste is performed followed by a step in which metallic and non-metallic fractions are separated and collected for further management.

5.1 Size reduction and separation

A crushing stage is necessary for an easier further easier management of PCB waste. The PCB are cut into pieces of approximately 1 -2 cm^2 usually with shredders or granulators giving the starting batch easily manageable for supplementary treatments (PCB scraps). Further particle size reduction to 5-10 mm can be carried out by means of cutting mills, centrifugal mills or rotating sample dividers equipped with a bottom sieve. The local temperature of PCB rapidly increases due to impacting and reaches over 250°C during Crushing, so a pyrolytic cleavage of chemical bonds in the matrix produces brominated and not brominated phenol and aromatic/aliphatic ethers (Li et at., 2010)
Effective separation of these materials based on the differences on their physical characteristics is the key for developing a mechanical recycling system; size and shape of particles play crucial roles in mechanical recycling processes because the metal distribution is a function of size range: aluminum is mainly distributed in the coarse fractions (> 6.7 mm), but other metals are mainly distributed in the fine fractions (< 5 mm).
Almost all the mechanical recycling processes have a certain effective size range and mechanical separation processes is performed in a variety of technique. Shape separation by tilted plate and sieves is the most basic method that has been used in recycling industry. Magnetic separators, low-intensity drum separators are widely used for the recovery of ferromagnetic metals from non-ferrous metals and other non-magnetic wastes. The use of high-intensity separators makes it possible to separate copper alloys from the waste matrix. Electric conductivity-based separation such as Eddy current separation, corona electrostatic separation and triboelectric separation separates materials of different electric conductivity such non ferrous metals from inert materials. (Veit at al., 2005; Cui & Forssberg, 2003). Density-base separation of particles such as sink-float separation, jigging, upstream separation are also used to separate metal from non metal fractions in PCB scraps.

5.2 Applications in composites

Physical recycling for non metallic fraction sorting from separation stage has been recently reviewed by Guo (Guo et al. 2009). The thermal stability of the non metallic fraction of PCBs is very important for physical recycling methods which must be suitable for moulding processes.

The thermosetting matrix more suitable for making composites with PCB scraps are phenolic resins, unsaturated polyester resins and epoxy resins. To ensure the surface smoothness, the size of non metallic fractions used was less than 0.15mm. The non metallic items so produced are used for trays, sewer grates, kitchen utensils, electronic switches. etc. with properties comparable to that of composites with traditional filler. The 300-700 °C pyrolysis residues (75–80%) can be easily liberated for metal's recovery, and the glass-fibres can be re-compounded into new SMC and BMC structures as a filler replacement (Jie et al., 2008).

Nonmetals reclaimed from waste PCBs are used to replace wood flour in the production of wood plastic (polyethylene) composites (Guo et al., 2010). In analogy, addition of PCB non-metallic fraction as reinforcing fillers in polypropylene (PP) has proven to be an effective way to enhance strength and rigidity: particles 0.178-0.104 mm, modified by a silane coupling agent, could be successfully added in PP composites as a substitute of traditional fillers. Larger particles (> 0.178mm) are fibre-particulate bundles showing weakly bonded interface which make easier crazes initiation and particle detach from the polymer matrix. (Zheng et al., 2009a).

As one of the plastic wastes to a certain extent, the non-metallic fraction of PCB can also be used with some effectiveness as a partial replacement of inorganic aggregates in concrete applications to decrease the dead weight of structures. Lightweight concrete is extensively used for the construction of interior and exterior walls of buildings for the case where the walls are not designed for lateral loads (Niu & Li, 2007). The glass fibres and resins powder contained in the non-metallic fraction can also be used to strengthen the asphalt.

6. Chemical recycling

Chemical recycling refers to decomposition of the waste polymers into their monomers or some useful chemicals by means of chemical reactions. In this view, chemical recycling consists of pyrolysis process, depolymerization process by using supercritical fluids, hydrogenolytic degradation and gasification process. The refining of the products (gases and oils) is included in the chemical recycling process, and can be done with conventional refining methods in chemical plants. Metal fraction can be treated by pyrometallurgical and hydrometallurgical approaches, biotechnological processes being still in their infancy.

6.1 Pyrolysis

Pyrolysis of polymers leads to the formation of gases, oils, and chars which can be used as chemical feedstocks or fuels. Pyrolysis degrades the organic part of the PBC wastes, making the process of separating the organic, metallic and glass fibre fractions of PCBs much easier and recycling of each fraction more viable. Additionally, if the temperature is high enough, the pyrolysis process will melt the solder used to attach the electrical components to the PCBs. The combination of the removal and recovery of the organic fraction of PCBs and the removal of the solder aid the separation of the metal components.

The thermal behaviour of epoxy resins, the most common polymer matrix in PCB, has been widely investigated as a basis for pyrolytic recycling. In thermogravimetry brominated

epoxy resins are less thermally stable that the corresponding unbrominated ones. They exhibit a steep weight loss stage at 300-380°C depending on the hardener, those hardened by aromatic amines and anhydrides decomposing at higher temperature (Fig. 1).
Mostly brominated and unbrominated phenols and bisphenols are found in the pyrolysis oil however the balance phenols/bisphenols and brominated/unbrominated species depends on the temperature and residence time in the reactor: higher temperatures and longer times making debromination more extensive (Luda et al., 2007, 2010). The size of the PCB particles effects as well on the decomposition temperature: degradation is postponed when particles are larger than 1 cm^2 due to heat transfer limitation (Quan et al., 2009).

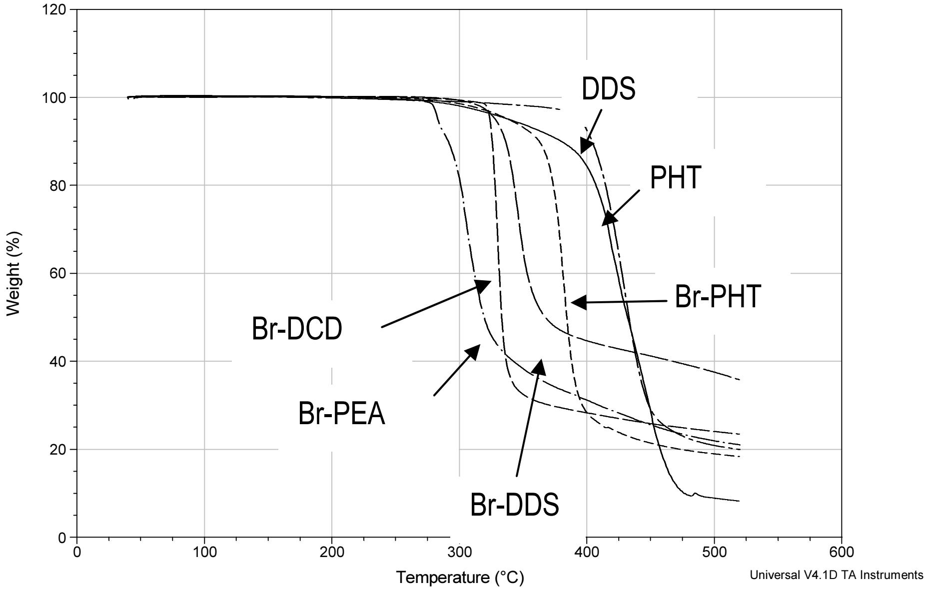

Fig. 1. TGA of epoxy-system based on Diglycidyl ether of bisphenol A or Diglycidyl ether of tetrabromobisphenol A (Br) crosslinked using different hardeners; DSS: Diaminodiphenylsulphone; DCD: Dicyandiamide; PEA: Polyethylene-polyamine, PHT: Phthalic anhydride. (20°C/min, Nitrogen)

When PCBs (4 cm^2) were pyrolyzed in a tubular type oven in the range 300 - 700 °C, no significant influence of temperature was observed over 500 °C both in gases and oil yields (9 and 78% respectively) as well as in the gross calorific value (30kJ/kg). However the oil resulted contaminated by polluting element and must be purged for further utilization. (Guan et al., 2008). The boards pyrolysed in a fixed bed reactor at 850°C were very friable and the different fractions could be easily separated (Hall & Williams, 2007) .

6.1.1 Vacuum pyrolysis

Recently studies on application of vacuum pyrolysis to PCBs appear in the literature. They were mostly aimed to recover solder and facilitate separation of metals and glass fibres from PCB scraps. Vacuum pyrolysis shorts organic vapour residence time in the reactor and lowers decomposition temperature, reducing the occurrence and intensity of secondary reactions.

The residue of vacuum pyrolysis at 550 °C of bare PCB scraps (25 cm^2) was crushed and size classified; about 99% of original copper was confined in particles > 0.4 mm, fibres remained in the smaller particles were recovered after calcinations. Pyrolysis oil and gases were collected from pyrolysis reactor for further refining (Long et al., 2010).

Two different arrangement for recycling disassembled PCBs (10-15 cm^2) were proposed: in the first centrifugal separation of solder (240°C) was followed by vacuum pyrolysis of the residue (600 °C); in the second vacuum pyrolysis (600 °C) was followed by centrifugal separation of the residue at 400°C in order to collect solder ready for reuse (Zhou & Quj, 2010; Zhou et al., 2010)

6.1.2 Dehalogenation

Contamination of oil by harmful compounds remains a severe issue with a strong impact on material and thermal recycling: bromine-containing phenols are potentially hazardous compounds emitted during heating of polymers flame retarded with TBBA based fire retardants. In effect brominates phenols likely form PBDD/PBDF through Ullmann condensation, contaminating pyrolysis products. So that reduction of the amount of brominated phenols in the pyrolysis oil in favour of less toxics substances is a way to add value to the whole PCB recycling process. Dehalogenation attempts have been carried out on model compounds, directly in the pyrolysis of PCB scraps or on refining the pyrolysis oil. Successful approach to debrominate PCB scraps was carried out by pyrolysis in the presence of NaOH or sodium-containing silicates resulting in an enhanced bromomethane evolution and depression of brominated phenol formation (Blazso et al., 2002). Various combination of cracking catalysts and absorbers for halogenated compounds ($CaCO_3$ and red mull) decreased as well the amount of all heteroatoms in pyrolysis oils of PCBs: after pyrolysis at the 300-540 °C the oils were passed into a secondary catalytic reactor (Vasile et al., 2008).

PBDD/PBDF formed during pyrolysis at 850 to 1200 °C of PCBs were destroyed under controlled combustion conditions (1200 °C): the total content decreased by approximately 50% increasing the pyrolysis temperature from 850 to 1200 °C. If CaO is added in the feeding, inhibition of 90% PBDD/PBDF occurs with prevention of evolution of HCl and HBr that corrode the equipment (Lai et al., 2007).

Liquid products obtained from pyrolysis of general WEEE, PCBs and their mixtures were upgraded by thermal and catalytic hydrogenation. The effect of thermal hydrogenation was improved by using catalysts such as commercial hydrogenation DHC-8 and metal loaded activated carbon. The upgraded degradation products were separated in residue, liquids and gases; liquids with high amount of aromatics were obtained but most of hazardous toxic compounds were eliminated after hydrogenation by converting them into gaseous HBr (Vasile et al., 2007).

Hydrodehalogenation with hydrogen-donating media is a promising option for the destruction of halogen-containing aromatics in the pyrolysis oil, converting them into non-halogenated aromatics and valuable hydrogen halide. It was found that PP was an effective and selective hydrodehalogenatig agent because only HBr was recovered at 290–350 °C from a mixture of chlorinated and brominated phenols PP was effective as well in upgrading pyrolysis oil (Hornung et al. 2003, Balabanovich et al., 2005). Recently other polymers have been tested for dehalogenation of a model brominated phenol. From pyrolysis of equimolecular mixture of various polymers with 2,4- dibromophenol (DBP) bromine was recovered as valuable HBr in gases, as toxic brominated compounds in oil or confined in the charred residue.

Pyrolysis conditions		% of total Br in the pyrolysis fractions			
components	T (°C)	gases	oil	Residue	H_2O sol.
DBP	330	5	88	7	0
DBP+HDPE	330	77	0	23	0
DBP+LDPE	330	85	0	15	0
DBP+PBD	330	73	1	26	0
DBP + PS	330	49	51	0	0
DBP+PA-6	350	45	20	0	35
DBP+PA-6,6	350	59	4	12	26
DBP+PAN	330	35	23	15	27

Table 1. Percentage of the bromine resulting in the various fractions from pyrolysis of 2,4-dibromophenol (DBP) with low density polyethylenes (LDPE), High density polyethylene (HDPE), polystyrene (PS), polybutadiene (PBD) Polyamides (PA-6, PA-6,6), polyacrylonitrile (PAN).

LDPE was found nearly as effective as PP; PBD and HDPE were slightly less effective while activity of PS, polyamides and PAN was poor. Br was partially recovered in the water soluble fraction when polymers contained nitrogen (Tab. 1) (Luda & Balabanovich, 2011). Because these polymers are present in significant amount in the organic fraction of WEEE, or even in other solid wastes, their action can be considered as a viable and convenient route of recycling of PCBs.

6.1.3 Depolimerization in supercritical fluids

Supercritical methanol and water have been tested for depolymerization of thermoset resins in PCBs for recycling purposes: the lower critical temperature and pressure of methanol (Tc :240 °C, Pc : 8.09 MPa) on comparison to those of water (Tc : 374 °C, Pc: 22.1 MPa) allow milder conditions.

At 350°C the oils of comminuted PCB (<1mm) treated with supercritical methanol included phenol with 58% purity, much higher than that produced by other conventional pyrolysis processes. The oils did not contained brominated compounds due to the complete decomposition and debromination during the process. Large amount of HBr existed in the gaseous products, which could be recovered effectively by simple distillation. Metallic elements in waste PCBs were concentrated effectively up to 62% in the solid residue. Longer reaction time and lower temperature was favorable for obtaining a higher oil yield (Xiu & Zhang, 2010).

6.2 Gasification and co-combustion

Gasification converts organic materials into carbon monoxide and hydrogen (syngas) by reacting the raw material at high temperatures with a controlled amount of oxygen and/or steam: syngas is itself a fuel or can be used as intermediates for producing chemicals or even combusted in gas turbines for electric power production. Staged-gasification of WEEE and PCB comprises pyrolysis (550°C) and high temperature gasification (>1230°C). Combustion or co-combustion competes with gasification producing electric power as well. A certain

amount of bromine contained in the waste turns into ashes (co-combustion) or char (gasification), while most turns into combustion gases or into syngas where: bromine can be recovered using suitable wet scrubbing systems.
A comparative environmental analysis of these two competing scenarios, intended for bromine recovery and electric power production, was carried out on recycling of the same mixed feeding PCB/green waste. While both processes resulted eco-efficient, staged-gasification was more efficient from an energy point of view, had a potentially smaller environmental impact than co-combustion and allowed a more efficient collection of bromine (Bientinesi & Petarca, 2009).

6.3 PCB recycling of the Metal Fraction

Despite the fluctuant average scrap composition amongst the various WEEE, cell phones, calculators and PCB scraps reveal that more than 70% of their value depends on their high content in metals. Metallurgical recovery of metals from WEEE is therefore a matter of relevance and has been recently reviewed by Cui (Cui & Zhang, 2008) underlining three possible approaches: pyrometallurgy, hydrometallurgy and biotechnology.

6.3.1 Pyrometallurgy

Some techniques used in mineral processing could provide alternatives for recovery of metals from electronic waste. Traditional, pyrometallurgical technology has been used for recovery of precious metals from WEEE to upgrade mechanical separation which cannot efficiently recover precious metals. In the processing the crushed scraps are burned in a furnace or in a molten bath to remove plastics, and the refractory oxides form a slag phase together with some metal oxides. Further, recovered materials are retreated or purified by using chemical processing. Energy cost is reduced by combustion of plastics and other flammable materials in the feeding. It should be stated, however, that applying results from the field of mineral processing to the treatment of electronic waste has limitations because the size of particles involved and material contents are quite different in the two systems.
Despite differences in the plants, general electronic scraps are treated together with other metal scraps by pyrometallurgical processes in the Noranda process at Quebec, Canada, at the Boliden Ltd. Rönnskår Smelter, Sweden (Association of Plastics Manufacturers in Europe [APME], 2000), at Umicore at Hoboken, Belgium (Hageluken, 2006). The used electronics recycled in the smelters represent 10-14% of total throughput, the balance being mostly mined copper concentrates at Noranda, lead concentrates at Boliden, various industrial wastes and by-products from other non-ferrous industries at Umicore.
Recently a modified pyrometallurgy to recover metals from PCBs has been proposed (Zhou et al., 2010) showing that addition of 12 wt.% NaOH as slag-formation material promotes the effective separation of metals from slag; the remaining slag in the blowing step was found to favour the separation of Cu from other metals and allow noble metals to enter the metal phase to the greatest extent. Additionally, the resulting slag was shown to be very effective in cleaning the pyrolysis gas. Eventually 68.4% Cu, 92.6% Ag and 85.5% Au recovery could be achieved in this process, confirming preliminarily the feasibility of modified pyrometallurgy in recovering metals from PCB.
However, pyrometallurgical processing of electronic waste suffers from some limits in particular the recover as metals of aluminum and iron transferred into the slag is difficult , the presence of brominated flame retardants in the smelter feed can lead to the formation of dioxins unless special installations and measures are present and precious metals are

obtained at the very end of the process. Furthermore pyrometallurgy results in a limited upgrading of the metal value and hydrometallurgical techniques and/or electrochemical processing are subsequently necessary to make refining.

6.3.2 Hydrometallurgy

Leaching is the process of extracting a soluble constituent from a solid by means of a solvent: for electronic wastes leaching involve acid and/or halide treatment due to the fact that acid leaching is a feasible approach for removing of base metals so as to free the surface of precious metals. The solutions are then subjected to separation and purification procedures such as precipitation of impurities, solvent extraction, adsorption and ion-exchange to isolate and concentrate the metals of interest. Consequently, the solutions are treated by electrorefining process, chemical reduction, or crystallization for metal recover.

A bench-scale extraction study was carried out on the applicability of hydrometallurgical processing routes to recover precious metals from PCBs in mobile phones (Quinet et al, 2005). An oxidative sulfuric acid leach dissolves copper and part of the silver; an oxidative chloride leach dissolves palladium and copper; and cyanidation recovers the gold, silver, palladium and a small amount of the copper. To recover the metals from each leaching solution, precipitation with NaCl was preferred to recuperate silver from the sulfate medium; palladium was extracted from the chloride solution by cementation on aluminum; and gold, silver and palladium were recovered from the cyanide solution by adsorption on activated carbon. The optimized flowsheet permitted the recovery of 93% of the silver, 95% of the gold and 99% of the palladium.

Recovery of Cu, Pb and Sn from PCB scraps equipment has been performed by a mechanical processing which concentrate metals. At the second stage, the concentrated fraction was dissolved with acids and treated in an electrochemical process in order to recover the metals separately (Veit et al. , 2006).

Recently a general approach for recycling of scrapped PBC by hydrometallurgy was proposed. First the crushed PCB scraps were leached in the NH_3/NH_5CO_3 solution to dissolve copper. After the solution was distilled and the copper carbonate residue was converted to copper oxide by heating. The remaining solid residue after copper removal was then leached with hydrochloric acid to remove tin and lead. The last residue was used as a filler in PVC plastics which were found to have the same tensile strength as unfilled plastics, but had higher elastic modulus, higher abrasion resistance and were cheaper (Liu et al., 2009)

6.3.3 Biometallurgy

Biotechnology is one of the most promising technologies in metallurgical processing. Microbes have the ability to bind metal ions present in the external environment at the cell surface or to transport them into the cell for various intracellular functions. This interaction could promotes selective or non-selective in recovery of metals. Bioleaching and biosorption are the two main areas of biometallurgy for recovery of metals.

Bioleaching has been successfully applied for recovery of precious metals and copper from ores for many years. Despite, limited researches were carried out on the bioleaching of metals from electronic wastes but it has been demonstrated that using *C. violaceum*, gold can be microbially solubilized from PCB (Faramarzi et al., 2004) and using bacterial consortium enriched from natural acid mine drainage, copper could be efficiently solubilised from waste PCBs in about 5 days (Xiang et al., 2010). The extraction of copper was mainly accomplished indirectly through oxidation by ferric ions generated from ferrous ion oxidation bacteria; a two-step process was necessary for bacterial growth and for obtaining an appropriate oxidation rate of ferrous ion.

Biosorption process is a passive physico-chemical interaction between the charged surface groups of micro-organisms and ions in solution. Biosorbents are prepared from the naturally abundant and/or waste biomass of algae, fungi or bacteria. Physico-chemical mechanisms such as ion-exchange, complexation, coordination and chelation between metal ions and ligands, depend on the specific properties of the biomass (alive, or dead, or as a derived product). Compared with the conventional methods, biosorption-based process offers a number of advantages including low operating costs, minimization of the volume of chemical/biological sludges to be handled and high efficiency in detoxifying. However further efforts are required because the adsorption capacities of precious metals on different types of biomass is greatly variable and much more work should be done to select a perfect biomass from the billions of microorganisms and their derivatives. Most of the researches on biosorption mainly focused on gold, more attentions should be taken into biosorption of silver from solutions and on recovery of precious metals from multi-elemental solutions.

7. Conclusion

A successful recycling approach of PCB should take into consideration the valorisation of the recycled items to compensate for recycling costs. Recycling of WEEE, and of PCB in particular, is still a challenging task due to complexity of these materials and possible evolution of toxic substances. Traditionally, recovering of valuable metals by waste PCBs was carried out on a large scale for a positive economic revenue. Legislation pushes now toward a more comprehensive processes which includes recovering and recycling of the ceramic and organic fractions in substitution to not-ecoefficient disposal in landfill.

A disassembly stage is always required to remove dangerous components such as batteries and condensers. Manual dismantling is still in operation despite the attempts to proceed by automatic procedures which however need more progress to be really effective. Crushing and separation are then key points for improving successful further treatments.

Physical recycling is a promising recycling method without environmental pollution and with reasonable equipment invests, low energy cost and diversified potential applications of products. However separation between the metallic and non metallic fraction from waste PCBs has to be enhanced.

Pyrolytic approach is attractive because it allows recovering of valuable products in gases, oils and residue. Evolution of toxics PBBD/PBDF can be controlled by appropriate treatments such as addition of suitable scavengers or dehydrohalogenation, which are still under development. New technologies are proposed such as vacuum pyrolysis or depolymerisation in supercritical methanol.

Metal recovery can be performed by traditional pyrometallurgical approaches on metal-concentrated PCB scraps fractions. Comparing with the pyrometallurgical processing, hydrometallurgical method is more exact, more predictable, and more easily controlled. New promising biological processes are now under development.

It should be kept in mind however that the chemical composition of e-waste changes with the development of new technologies and pressure from environmental organisations to find alternatives to environmentally damaging materials. A sound methodology must take in account the emerging technologies and new technical developments in electronics.

Miniaturisation of electronic equipment in principle would reduces waste volume of PCBs but make collection more difficult and repair more costly, so that a large amount of PCBs Is still expected in the e- waste in the future.

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