Chapter 1

INTRODUCTION

1. Introduction

1.1. E-waste

The rapid global rise in technology, tied in with consumer pressures for upgrades in functionality and design, has generated advanced electrical and electronic equipment (EEE). Global consumption of EEE increases annually by 2.5 x 10^6 metric tons (Mt) [1]. Technological advances have led to the reduction in lifespan of EEE and resulted in the generation of vast quantities of the waste stream, and which is referred to as waste electrical and electronic equipment (WEEE) or electronic waste (e-waste) [2].

E-waste is broadly classified into six categories. They are

1. Temperature exchange equipment (Refrigerators, air conditioners, heat pumps etc.)
2. Screens and monitors (Televisions, monitors, laptops, tablets etc.)
3. Lamps (Fluorescent lamps, high-intensity discharge lamps, LED bulbs etc.)
4. Large equipment (Washing machines, electric stoves, printing machines etc.)
5. Small equipment (calculators, radio sets, video cameras, electrical and electronic toys, small electrical and electronic tools, small monitoring and control instruments etc.)
6. Small IT and telecommunication equipment (mobile phones, routers, personal computers, printers, telephones etc.)

Among them, mobile phones are considered a valuable secondary resource of metals due to their enormous production volume, short lifespan, and rich metal content that includes base, precious, and critical elements [3].

1.1.1. Global e-waste generation statistics

The annual global production of e-waste has reached 53.6 x 10^6 Mt in 2019 and is expected to reach 74.7 x 10^6 Mt by 2030 [1]. It is increasing drastically with an average growth of 3-5% per annum, three times more than other municipal waste streams [4]. Asia has generated the highest quantity of e-waste (24.9 x 10^6 Mt) in 2019, followed by the Americas (13.1 x 10^6 Mt), Europe (12 x 10^6 Mt), Africa (2.9 x 10^6 Mt) and Oceania (0.7 x 10^6 Mt). However, in the case of per-capita generation, Europe and Oceania ranked first with 16 kg per capita, followed by the Americas (13.3 kg), Asia (5.6 kg) and Africa (2.5 kg) [1].

1.1.2. Indian scenario

India is the third-largest e-waste generator in the world after China and USA. The Associated Chambers of Commerce and Industry of India (ASSOCHAM) reported in 2020 that the annual growth of e-waste reached 3.23 x 10^6 Mt and increased 43% during 2018-2020. The report highlighted that two lakh tons of e-waste were generated annually from Delhi, Mumbai and Bangalore only [5]. The availability of e-waste generation data in India is a primary constraint due to the following reasons [6].

i) Informal sector participation in e-waste management.
ii) Grey market domination.
iii) Waste collection and processing is not under mercantile transactions.

1.1.3. Recycling statistics

It is estimated that more than 70% of globally produced WEEE enter China, Africa and India for reprocessing, much of it illegally, and often using crude, hazardous and inefficient processes [7], [8]. Balde et al., (2017) reported that only 20% of the generated e-waste is being recycled every year and from the remaining, 4% is being thrown into the residual waste by the wealthiest countries, and 76% is not known [9] (**Figure 1.1**).

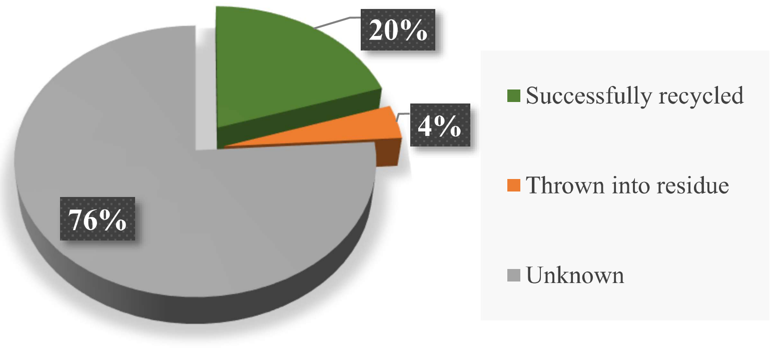


Figure 1.1- World e-waste recycling statistics

1.1.4. Consequences of e-waste generation

Dumping or landfilling e-waste creates a severe impact on human life and the environment, as they contain toxic affluence [10]–[12]. Their incineration (for example, by smelting) releases pollutants such as dioxins, furans, polyhalogenated organics, and polycyclic aromatic hydrocarbons [11], [13]–[15], resulting in associated health impacts, particularly for children [16]. Hence the day by day generation of e-waste pollutes our eco-system, and this problem has to be fixed by successful recycling techniques [17]. The presence of valuables in e-waste also makes them attractive secondary resources [18]. An effective recycling process can replace the existing promising technologies for energy saving and valuables recovery enhancement. It is estimated that recycling one ton of mobile phones could produce on average 130 kg of copper, 3.5 kg of silver, 0.34 kg of gold and 0.14 kg of Pd [19]. On this basis, the global e-waste management market is projected to produce annual revenue of USD 96 billion by the end of 2028 [20]. With an estimated 97% of the world population owning a mobile phone [21], it can be viewed as a plentiful feedstock for a recycling process. As such, the treatment of e-waste not only helps minimise the environmental impact of our technology-driven society by reducing pollution and energy demands compared to conventional mining practice [22], it also presents economic drivers for wealth creation and circular economies [23]–[28].

1.2. Printed circuit boards

The printed circuit board (PCB) is a valuable part of any electronic device and is an attractive secondary resource due to its inherently high concentration of base, precious, and critical metals compared with primary mining deposits [2], [18], [29]–[32]. It may contain up to 60 different chemical elements [33], and have a metal content as high as 40% by weight [34]. Within WPCBs, copper and nickel are the most abundant metals to be found, with the concentration of the former ca. 13-26 times higher compared to natural resources [35]. The extensive use of these elements in many consumer products, including stainless steel, electromagnets, motors, generators, coinage and special alloys [36], combined with the depletion of primary ores, makes a compelling case for the repurposing of secondary resources such as electronic waste to return metals to active use [37]. The most valuable metal in WPCBs is gold due to both its intrinsic value and higher concentration (ca. 100x) compared with its natural ore [24], [38]. Gold estimates its consumption to fuel our technology-driven society at 263.3 Mt/year [39].

1.3. Opportunities for metal recovery from PCBs

A typical PCB comprises 40% metals, 30% plastics and 30% ceramics [7], [34], with the metal fraction comprising 10-27% Cu, 2-8% Al, 1-4% Pb, 1-8% Fe, 1-6% Sn, 0.2-3.6% Ni, 0.1-1.5% Zn and < 0.1% precious [8], [21], [30], [40]–[60]. These data were typically obtained by milling the waste PCBs and then leaching the powder with aqua regia (a 1:3 molar mixture of nitric and hydrochloric acid), or alternatively hydrochloric acid followed by aqua regia. The levels of precious metals in electronic waste vary considerably, from 10-1600 ppm of Au, 200-20,000 ppm of Ag, and 5-970 ppm of Pd, but in most cases exceed those expected in conventionally mined ores. A rich gold-containing ore is typically 2-4 g/ton of gold [61] and a typical silver-bearing ore contains 0.085% of silver [62]. It is also apparent that the concentration of precious metals found in electronic waste is dependent on the age of the device. The thickness of gold contacts halved from ca. 1.0 μm in devices manufactured in the 1980s to 0.6-0.3 μm for those made in the 2000s [63]. Recycling waste PCBs for metal recovery is generally carried out by a physical pre-processing disassembly step, followed by pyro-, hydro- or bio-hydrometallurgical processes [44], [64], [65].

1.4. Pre-separation treatment

Pre-processing of e-waste typically begins with a manually intensive dismantling phase, during which circuit-board components and the lithium battery are removed for recycling elsewhere (**Figure 1.2**). The PCBs are subsequently graded according to their metal to plastic ratio and shredded, typically into 1x1 cm^2 pieces. The shredded PCBs need to be separated into metallic (ferrous and non-ferrous) and non-metallic (polymer and ceramic) components and a broad range of methods have been identified for this purpose, including mechanical crushing, followed by separation using gravity, electrical conductivity and magnetism, as well as delamination using organic solvents.

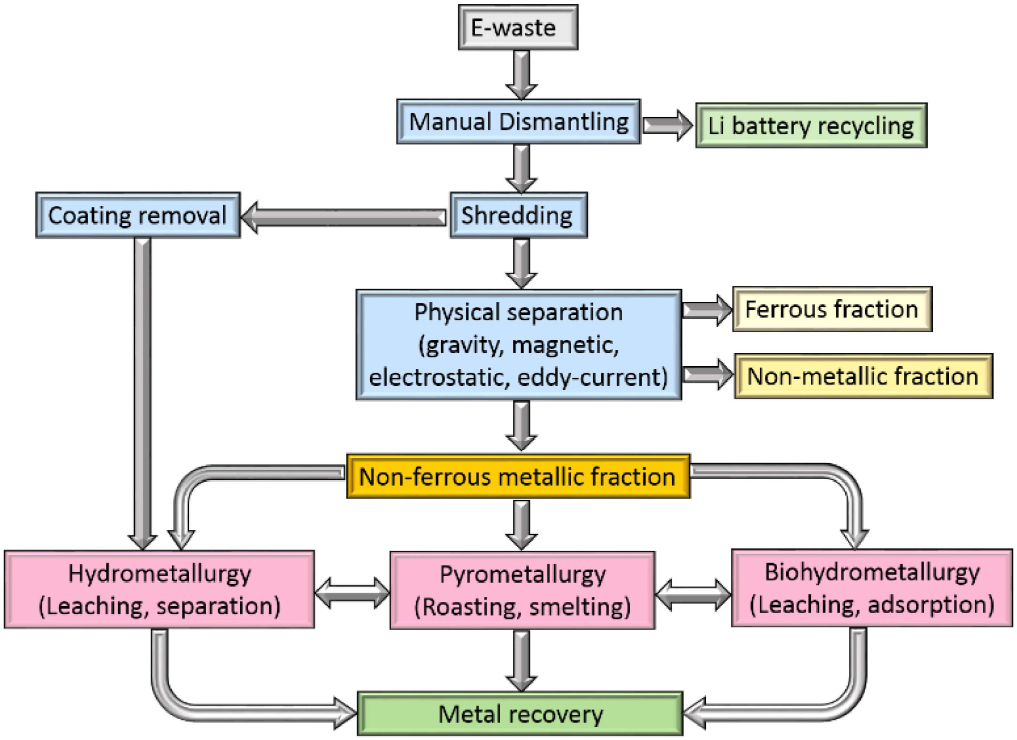


Figure 1.2- Overview of stages involved in metal recycling from electronic waste [29]

Multistep crushing provides high shear forces that detach the metals from PCBs, with copper wires and joints particularly prone to disintegration. Whilst this is a reasonable energy-efficient process [4], crushing alone cannot typically yield the fine particles that are required to improve metal recovery rates [66]. Consequently, the output from a crusher is typically subjected to a further mechanical separation step. One option uses gravity separation in which waste PCBs are milled to a particle size to below 5 mm, allowing the lighter (non-metallic) fraction to be separated from the heavier (metallic) fraction [67]. Alternatively, electrostatic methods separate metallic and non-metallic components based on their electrical conductivity or resistivity. However, practical difficulties exist, such as the treatment of the so-called middling product (a granular intermediate product of conducting and non-conducting materials) and the removal of non-conducting materials. Nevertheless, both of these issues have been mainly addressed by the development of a two-roller type corona-electrostatic separator of a high productivity rate and good energy efficiency [68]. Moreover, the process does not evolve wastewater or dust during the process, which is an advantage over other separation methods [66]. Alternatively, the Eddy current separator is widely used [34], which exploits rare-earth permanent magnets to separate non-ferrous metals from the waste once all ferrous metals have been removed [69].

As a chemical technique, delamination of the interwoven metallic and non-metallic layers in a PCB, which are bonded together with halogenated epoxy resin, can be undertaken. The resin can be dissolved using organic solvents such as dimethyl sulfoxide [70], N,N-dimethyl pyrrolidone [71], dimethylformamide, or dimethylacetamide. Amide-based solvents have been found to give superior results primarily due to their lower evaporation rates [72], [73]. The used amide can be recycled and reused with a small loss of 3-5% after each cycle and the dissolved resin recovered as a residue [73]. Ionic liquids, such as 1-butyl-3-methylimidazolium chloride have also been shown to dissolve up to 90% of the bonding resin [74].

1.5. Chemical techniques for metal recovery

1.5.1. Pyrometallurgy

Pyrometallurgical processes include roasting, in which compounds are converted at temperatures just below their melting points, and smelting, which involves higher temperatures to completely melt the material which is then separated into two liquid layers, one of which contains the metals for further refining [7], [75]. Oxygen-enriched air and fuel may be injected into the molten bath through a lance to oxidise and remove any volatile components present, while passage of an electric current in electrometallurgy processes acts to dissociate any metallic compounds present in the electrolyte and deposits the metal at the cathode. Pyrometallurgy offers the advantage that a pre-treatment step beyond unit dismantling and shredding of the components is rarely required [76], [77]. The output from the smelter for electronic waste is best described as a copper bullion, due to the high copper content found in PCBs. The copper can be separated by leaching and recovered by electrowinning, leaving a residue of precious metals for further refining (see later).

The smelting process is energy-intensive, but the overall reliance on fossil fuels (*e.g.* coke) can be partially offset by exploiting the plastic content of PCBs as both a fuel and a reducing agent in the smelter [78]. However, as PCBs contain halogenated flame retardants this leads to the formation of furans and dioxins, which, along with the creation of volatile metals and dust gives rise to environmental challenges [30]. While pyrometallurgical recycling processes are a cost-effective solution for electronic-waste recycling due to economy of scale and ability to deal with a broad range of scrap materials with minimal pre-processing, they carry a large environmental burden. This type of recycling also displays poor selectivity for individual metals, meaning that multiple stages are required to recover metals in their pure elemental form [7].

Recently, an optimized process for the recycling of complex metallic materials such as waste PCBs was developed, based on a top-blown rotary converter smelter, with an oxygen-propane lance and a 360° rotating chamber that tilts to different angles to allow poring of slag and casting fractions [79]. Pyrolysis is introduced as a pre-processing method for enhanced separation of the non-condensable gas and liquid fractions and solid residue, with the resulting solid material making the separation of metals, glass fibre and organic fractions easier and consequently the recycling of each portion more viable. Umicore's Hoboken plant in Belgium has developed an advanced process which includes the recovery of copper and precious metals, along with a waste gas and water utilization system [30]. Furthermore, a new process has been introduced for the simultaneous extraction of precious metals from waste mobile phone PCBs and honeycomb-type autocatalysts by smelting with industrial-waste copper slag. This process is simpler than conventional pyrometallurgical process as the addition of any external collectors are not required [80].

1.5.2. Hydrometallurgy

Pyrometallurgical processes require elevated temperatures and have several drawbacks including the loss of noble metals to slag, the generation of high amounts of gaseous effluents, and low recovery of other metals [54]. In biometallurgical processes, microorganisms solubilise the metals which, while environmentally benign, is very slow and the complete recovery of metals is usually not possible [81]. In contrast, hydrometallurgical processes have the potential to reduce environmental impact, are suitable for small scale applications, and have low capital cost [82]. These processes mainly comprise pre-processing of the WPCBs, followed by leaching, separation, and purification stages [29]. From a sustainable chemistry perspective also, hydrometallurgy is often favoured as it can lead to excellent material and energy balances, as reagents can be recycled through multi-step processes, and the emission of toxic substances is limited [32], [50], [82]. However, challenges arise from the complexity of the feed stream, the need for strong acids in leaching processes, the need to minimise the organic solvents and chemical reagents in the separation processes.

In the hydrometallurgical recovery of a metal from electronic waste, the PCBs are leached by a suitable lixiviant, usually after pre-treatment as presented in **Figure 1.3** [14]. The resultant pregnant leach liquor then undergoes a separation step to obtain single metal streams from which pure metals are obtained, for example by electrowinning.

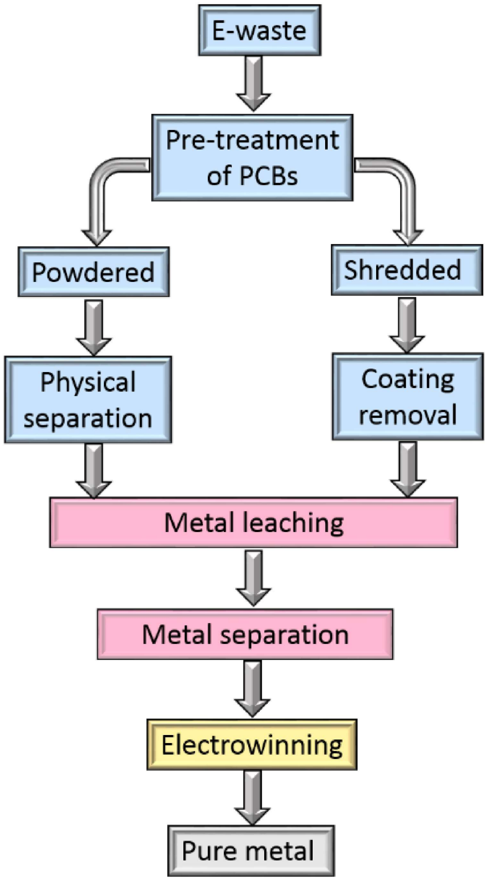


Figure 1.3- Main stages in hydrometallurgical process to recover metals from e-waste [29]

1.5.2.1. Leaching

The selection or development of a leaching process plays a pivotal role in hydrometallurgy, as it must provide efficient dissolution of metals from PCBs and deliver them in a suitable form for the separation step. Importantly, metals such as gold are in their elemental form in electronic waste, so they will need to be oxidised during dissolution, e.g. to Au(I) or Au(III). This contrasts with conventional mining from ores in which metal cations are already present as oxides or sulfides.

i) Base-metal leaching

As the concentration of precious metals present in e-waste is very low compared to the base metals, presents challenges with their recovery [83]. As such, the first step undertaken in recovering metals from WPCBs is often the selective dissolution of the base metals in order to concentrate the precious metals in a solid residue for subsequent recovery. While aqueous acids such as sulfuric or hydrochloric acid are used widely for the leaching of base metals, they must be employed in tandem with an oxidant as the metals are present as their elemental forms in WPCBs. Suitable oxidants are H_2O_2, Cl_2, O_2, or bacteria [82]. On the other hand, nitric acid has a peculiarity of strong oxidising behaviour as well as more effective in leaching base metals [31]. Several researchers have studied the leaching of metallic components from WPCBs. Oh and co-workers reported the leaching behaviour of copper from shredded metallic parts by dilute sulfuric acid (2 M) with H_2O_2 (0.2 M) as an oxidant, which resulted in more than 95% leaching of copper after heating at 85 °C for 12 h. Co-dissolution of iron, zinc, nickel and aluminium was also observed [84]. Similar results were reported by Birloaga and Yang, who investigated the effects of changing the H_2O_2 concentration, leach time, temperature, and solid-to-liquid ratio [85], [86]. Kumar and co-workers highlighted the improved leaching performance offered by nitric acid over sulfuric acid/hydrogen peroxide mixtures [31]. Long Le and co-workers studied the recovery of copper from personnel computer PCBs using 3.5 M nitric acid which dissolved 99% copper at 323 K in 1 h [87], while Bas and co-workers showed that nitric acid concentrations of $\geq$ 2-3 M were required for copper dissolution at 70 °C [2].

As an oxidising acid, HNO_3 has been shown to act as a two-stage leachant, selectively dissolving copper, nickel and gold [88]. Initially, a dilute HNO_3 (0.1 M) leach step results in suppression of copper leaching but enhanced nickel leaching due to its higher chemical reactivity. Increasing the concentration of HNO_3 (to 1.0 M) results in high recovery of copper (97%) and separation of gold as solid flakes. A solvent extraction step (using a commercial oxime-based reagent) separated this latter mixed-metal stream.

The oxidation of waste PCBs using supercritical water ($T > 647$ K, $P > 218$ atm) and sodium hydroxide as a first step for the removal of harmful organic species originating from the degradation of toxic matter (*e.g.* brominated flame retardants) from waste PCBs has been reported [89]. This process was later modified to enhance the leaching of copper along with precious metals gold, silver and palladium [90]. In this latter case, HCl was used as the leachant for the initial recovery of copper, followed by iodine-iodide (oxidant and complexing agent, respectively) for subsequent dissolution of the precious metals.

ii) <u>Gold leaching</u>

Cyanide is a cheap but highly toxic reagent that is very effective in leaching gold from low-grade minerals as the water-soluble cyanoaurate $[Au(CN)_2]^-$ as shown Eq. 1.1).

$$4Au_{(s)} + 8CN^-_{(aq)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow [Au(CN)_2]^-_{(aq)} + 4\ OH^-_{(aq)} \quad (1.1)$$

The well-documented toxicity and environmental concerns around the use of cyanide in the gold mining industry [19] has led to the adoption of the International Cyanide Management Code, a voluntary program intended to reduce the potential exposure of workers and local communities to the harmful effects of cyanide. It is estimated that cyanide leaching is used in around 90% of gold production from primary ores [91], and a similar story emerges for e-waste recycling, with cyanide reported as the principal gold leaching agent currently in use in China [92]. Although cyanide leaching from minerals is very effective, it was reported that just 60% of the gold could be recovered from pulverised waste PCBs using a commercial cyanide leachant [19].

Much work has been undertaken to develop alternatives to cyanide leaching [75], [93]–[95]. Thiocyanate has been found to leach gold as $[Au(SCN)_2]^-$ or $[Au(SCN)_4]^-$ in the presence of an Fe(II)/Fe(III) catalyst. It can act as a lixiviant over a wide pH range and is reported to be partly recyclable, but its use is restricted to higher temperatures [95], [96]. Similarly, thiosulphate leaching (Eq. 1.2.) has been exploited in gold leaching and, although relatively cheap and less toxic than cyanide, it is also less efficient and significant problems exist due to complex reaction kinetics. Even with the addition of oxidisers such as H_2O_2, the level of gold recovery by thiosulfate can be lower than 15% [19], [97], [98].

$$4Au_{(s)} + 8S_2O_3{}^{2-}{}_{(aq)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow 4[Au(S_2O_3)_2]^{3-}{}_{(aq)} + 4OH^-{}_{(aq)} \quad (1.2)$$

Thiourea has also been investigated as a leachant, which, in the presence of iron sulfate, creates the water-soluble cationic gold(I) complex $Au\{SC(NH_2)_2\}_2{}^+$ (Eq. 1.3.) [99]. A potential drawback in thiourea leaching is that the high abundance of copper in PCBs increases the rate of thiourea decomposition to elemental sulphur, which passivates the gold surface [100]. Even so, it was reported that thiourea could extract up to 90% of the gold from mobile phone PCBs [101].

$$Au_{(s)} + 2SC(NH_2)_{2(aq)} + Fe^{3+}{}_{(aq)} \rightarrow Au\{SC(NH_2)_2\}_2{}^+{}_{(aq)} + Fe^{2+}{}_{(aq)} \quad (1.3)$$

Other alternatives to cyanide include halide leaching, whereby the strong oxidants Cl_2 or Br_2 are generated *in-situ*, either electrochemically or by reaction between sulfuric acid and hydrochloric or hydrobromic acid or a halide salt, with the latter reported as effective in copper leaching [80], [102], [103]. Other oxidants such as O_2, Cu(II), Fe(III) or nitric acid are also used in addition to halides [93], and the non-toxic ammonium persulphate is reported to have greater lixiviant properties than potassium or sodium persulphate [104]. More recently, synergistic mixtures of N-bromosuccinamide (NBS, a strong oxidant) with pyridine (py, an effective complexing ligand) have been found to offer a cheap and low-toxic route to selective gold leaching as represented in **Figure 1.4** [105]. Initial oxidation of gold by NBS from the surface of CPU pins occurs to form low concentrations of bromoaurate $[AuBr_4]^-$, which is stabilised by the formation of the neutral complex $AuBr_3(py)$ by reaction with pyridine; about 90% of the gold is leached using this mixture compared with ca. 40% recovery of other metals found in waste PCBs.

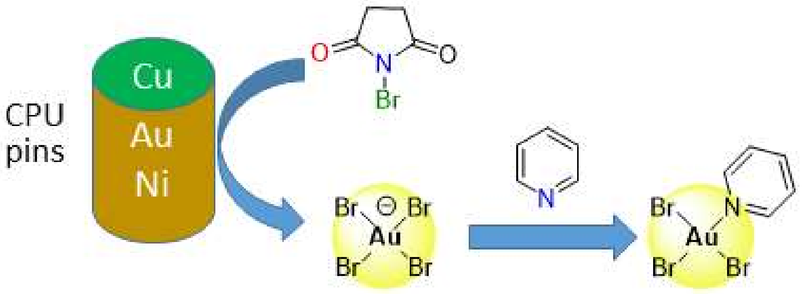


Figure 1.4- Leaching of gold from e-waste using N-bromosuccinimide/pyridine mixtures [29]

Dissolution of elemental gold was also accomplished using dimethylformamide solutions of pyridine-4-thiol as a reactive ligand and hydrogen peroxide as an oxidant [106]. In this case, the thiol isomerises to the thione (PS) which interacts with Au(0) at the surface. Oxidation to Au(I) by H_2O_2, with complementary oxidation of the ligand, ultimately to sulfuric acid, results in $[Au(PS)_2]_2[SO_4]$ as the final gold product in solution.

Aqua regia has received attention in recent years in the leaching of gold due to its complete dissolution and fast rates [107], [108]. While its strongly oxidising and corrosive nature render it unsuitable for full-scale operations [101], it is a suitable leachant for use in fundamental research. The nitric acid acts as a powerful oxidising agent to form Au^{3+} ions, while the hydrochloric acid provides a large excess of Cl^- ions to form $H[AuCl_4]$ as given in Eq. 1.4 and Eq. 1.5.

$$Au_{(s)} + 3HNO_{3(aq)} + 4HCl_{(aq)} \rightleftharpoons H[AuCl_4]_{(aq)} + 3NO_{2(g)} + 2H_2O_{(l)} \quad (1.4)$$

$$Au_{(s)} + HNO_{3(aq)} + 4HCl_{(aq)} \rightleftharpoons H[AuCl_4]_{(aq)} + NO_{(g)} + H_2O_{(l)} \quad (1.5)$$

1.5.2.2. Purification of leach solution

The selective recovery of a particular metal from mixed-metal leach solutions can be achieved by a number of routes including adsorption, cementation, solvent extraction (SX), electrolysis, ion exchange and polymer inclusion membranes [12], [109]–[112].

i) Cementation and Adsorption

In cementation, a highly reactive metal or metal with higher oxidation potential replace less reactive metals by allowing them into precipitation. However, the disadvantages are re-dissolution of sacrificial metal, time-consuming and more critical at low pH. For example, purification of zinc electrolyte is done by the addition of zinc powder. While zinc is more electropositive (-0.76 V) than most of the common metals, it can replace them easily, and those impurities are precipitated as residue according to cementation, as shown in Eq. 1.6.

$$Zn + M^{2+} = M + Zn^{2+} \quad (1.6)$$

where M = Cu, Cd and Pb etc.

Adsorption and cementation are also prominent techniques for the recovery of gold from low concentration cyanide solutions derived from commercial mining [110]. Adsorption methods are cheap and simple to operate and typically involve adsorbing the cyanoaurate $[Au(CN)_2]^-$ on activated carbon particles, which due to their large size can be readily separated from the leach liquor by filtration. The gold is then subsequently released from the loaded carbon by heat (*e.g.* using a smelter) or pH control (*e.g.* on contact with sodium sulfide) [113]. These methods are referred to as Carbon-in-Pulp (CIP) methods, with Carbon-in-Leach (CIL) and Carbon-in-Column (CIC) as other variants on this theme [114]. Cementation methods involve passing the gold leachate solution through a bed of metal shavings or powder. The Merrill-Crowe process uses zinc cementation in which the filtered cyanide solution is passed through deaerating columns to remove the oxygen before adding zinc dust to reduce and precipitate the gold (Eq. 1.7) [113]. The precipitated gold is then recovered by filtration, mixed with fluxes (borax, silica, or sodium carbonate) to bind with impurities, and smelted to form bars which are then sent for the further refining processes.

$$Zn_{(s)} + 2Au(CN)_2^{-}{}_{(aq)} \rightarrow 2Au_{(s)} + Zn(CN)_4^{2-}{}_{(aq)} \qquad (1.7)$$

The selective recovery of gold (as $K[AuBr_4]$) has been demonstrated through its co-precipitation with α-cyclodextrin as shown in **Figure 1.5** [115], [116]. In this case, the insoluble 1D supramolecular polymer $\{[K(OH_2)_6][AuBr_4](\alpha\text{-cyclodextrin})_2\}_n$ is formed in which precise molecular recognition between $[AuBr_4]^-$ and α-CD occurs. The axial orientation of the anion within the α-CD cavity favours specific second-sphere electrostatic and hydrogen bonding interactions between the anion and $K(OH_2)_6^+$ cation. Life-cycle analysis indicated that application of this technology could significantly reduce the current environmental impact of gold nanoparticle synthesis [117].

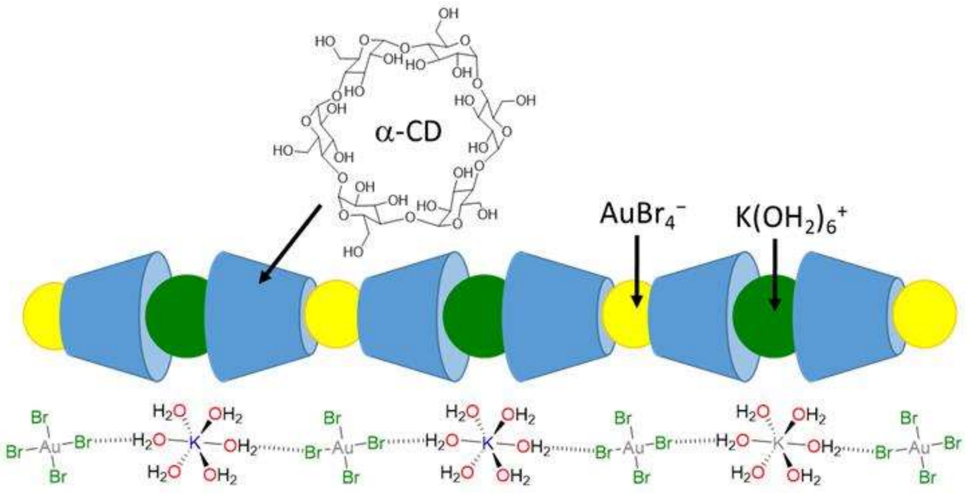


Figure 1.5- Selective precipitation of gold as a $KAuBr_4$/α-cyclodextrin assembly [29]

Metal organic framework (MOF) materials also appear promising for gold recovery as displayed in **Figure 1.6**. The large pores in the framework Fe-BTC (where BTC= 1,3,5-benzenetricarboxylate), have been lined with short redox-active poly(*meta*-aminophenol) chains that bind and reduce gold complexes formed in a solution similar to that expected from an N-bromosuccinimide/pyridine leached solution from waste PCBs (see **Figure 1.4.)** [118].

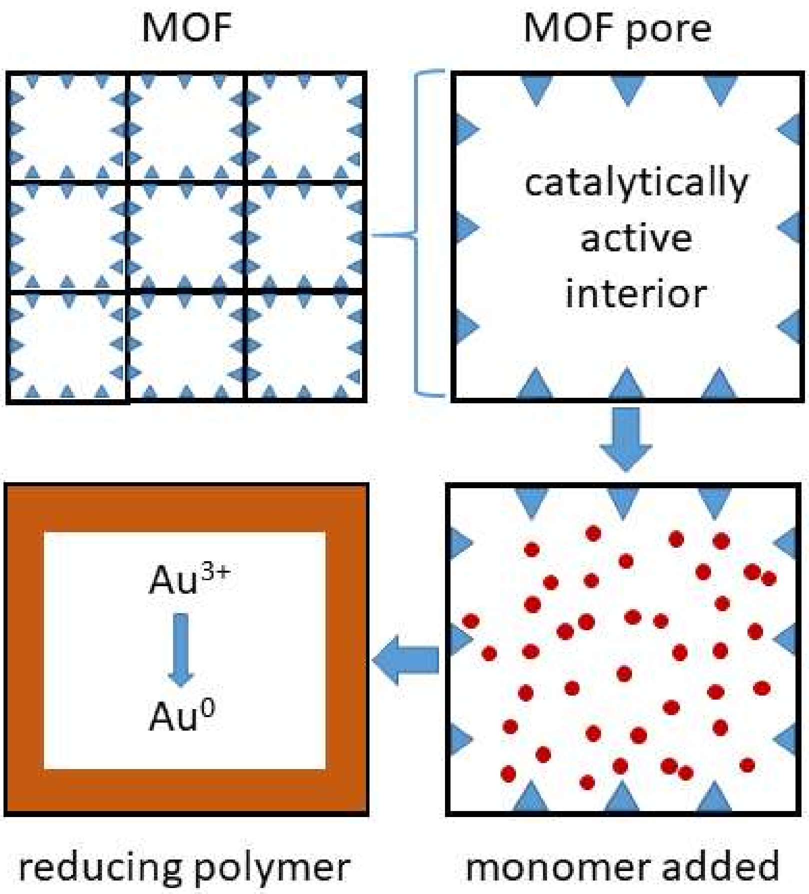


Figure 1.6- Metal organic frameworks, with catalytically active metal sites that bind and polymerise monomers within the pores, forming short redox-active polymer chains that bind and reduce gold [29]

MOFs that arrange sulphur-donor atoms within their porous cavities have been prepared and exploited for the adsorption of gold from water solutions (**Figure 1.7**) [119]. These MOFs were constructed from copper complexes of chiral bis(L-methionine)oxalamide ligands that, on addition of Ca(II) ions, formed porous solids with hexagonal channels of ca. 0.3 nm diameter. Soaking these materials in water solutions of $AuCl_3$ or AuCl resulted in the formation of the thioether complexes of gold (RS)AuCl and (RS)$AuCl_3$ within the porous channels, with aurophilic interactions evident between the Au(I) centres. Gold recovery of 90% from acidic leach solutions from waste PCBs was achieved using polyaniline films to reduce the gold to its elemental state [120]. The polymer could subsequently be regenerated, offering potential for efficient gold recovery without the use of extractant reagents or external energy input. Similarly, a simple and efficient water-soluble fluorescent conjugated polymer (poly(2,5-bis(polyethylene glycol oxybutyrate)-1,4-phenylethynylene-*alt*-1,4-phenyleneethynylene; PPE–OB–PEG)) was prepared from commercially available 1,4-diethynylbenzene and PEG-2000, for selective detection and extraction of Au(III) cations in e-waste [121]. An 80% extraction efficiency was reported through the selective formation of alkynyl-Au bonding interactions.

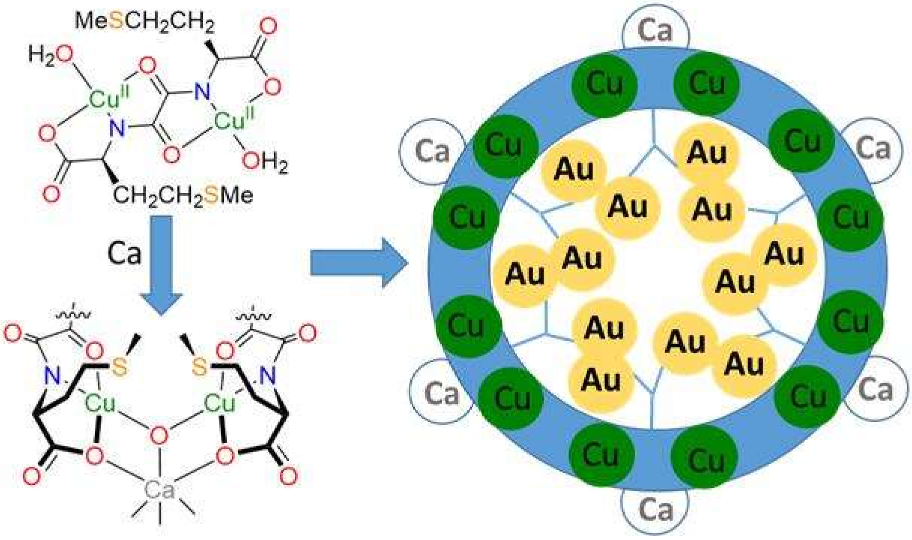


Figure 1.7- Metal-templated formation of MOFs with thioether-decorated pores for gold adsorption [29]

ii) Ion exchange process

Ion-exchange process involving the adsorption of metal from a leach solution using an ion-exchange polymer resin have been utilised for metal recovery from e-waste [111]. The basic process for the recovery gold is similar to CIC except that the elution (metal stripping) stage from the loaded resins does not require high temperatures. Interestingly, 3D printed meshes and columns of nylon-12 in which amide-group scavengers (see later) are intrinsically present have shown to selectively adsorb 78% of $[AuCl_4]^-$ from PCBs leached by aqua-regia. Multiple wash steps using dilute nitric acid resulted in 99% gold recovery [122]. An advanced technology for the selective recovery of gold from waste electronics using electro-generated chlorine gas as an oxidant in an HCl leach stream has been proposed [38]. In common with other studies, the copper was separated first using 2 M HCl, leaving a residue from which gold was recovered (99.99%) by ion-exchange chromatography.

iii) Solvent extraction

Solvent extraction is a particularly versatile option among purification processes due to its amenity of scale, and it finds application for the recovery of both trace and macro amounts of metal ions [37], [123]–[125]. In SX, a mixed-metal aqueous solution is contacted with an extractant or ligand to form a neutral complex that transports the desired metal into a water-immiscible phase. Following phase separation, the aqueous solution (the raffinate) is recycled back into the leaching phase, while the water-immiscible phase is contacted with an aqueous stripping solution to release the metal ions for reduction to generate pure metal [123]. The whole process is depicted in **Figure 1.8**. A critical aspect of this process is choosing a highly selective extractant that will transport only the desired metal from the mixed-metal solution. Selectivity is achieved through coordination and supramolecular chemistry principles, by designing extractants that can differentiate between the various metal ions based on size, charge and shape [126], [127]. This technique is particularly important for the recycling of waste electronics, where the concentrations of base metals far outweigh the concentrations of precious metals. The success of the solvent extraction process resides with the efficiency and selectivity of the metal extractant and ensuring that good separation is achieved between the two phases.

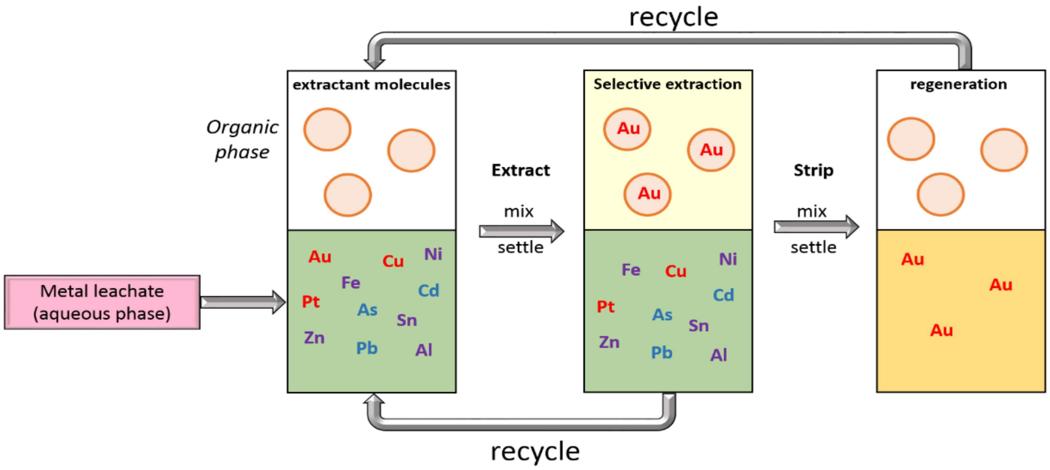


Figure 1.8- Stages of solvent extraction for the selective recovery of gold

Optimisation of metal recovery is achieved through control of various parameters, including the concentration of the extractant, pH of the aqueous phase, the organic to aqueous phase ratio, the stirring speed, equilibrium time and temperature [125], [128]. A commonly applied class of industrial extractant, which is widely used for the recovery of a broad range of metals including copper from primary ores, are hydroxy-oximes derived from aldehydes and ketones [82] and are marketed under the brand names LIX and ACORGA [129]. In comparison, ACORGA's load capacity, net copper migration, adaption to acidity and temperature are better than LIX [130]. ACORGA M5640 contains the extractant 5-nonylsalicylaldoxime (**Figure 1.9**) and the diester 2,2,4-trimethyl-1,3-pentanediol diisobutyrate as a stripping modifier [131].

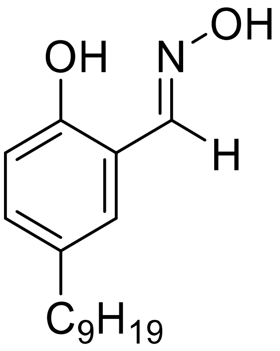


Figure 1.9- Structure of the extractant (5-nonylsalicylaldoxime) in ACORGA M5640 [132]

The solvent extraction of halometalates such as $[AuCl_4]^-$ from halide leach solutions derived from gold ores is carried out commercially using simple solvents such as methyl isobutyl ketone (MIBK), dibutyl carbitol (DBC), or 2-ethyl hexanol (2-EH). However, selectivity, safety, and mass balance issues are evident in separations using these solvents and the chemical modes of actions remain poorly understood [133]. Organic amides have been long studied as reagents for selective gold recovery by solvent extraction (**Figure 1.10**). Tertiary amides such as DOAA and DOLA show good selectivity for gold over other precious metals such as Pd, Pt, and Rh and base metals such as Fe, Cu, Ni, and Zn [134]. However, third phases are often formed and the strip stage of the solvent extraction process can require the use of thiourea, thus affecting mass balance. The use of unsymmetrical substituents in MBHA enhance extraction efficiency, and slope analysis (log D vs log L, where D = distribution coefficient and L = ligand) suggested the formation of complexes of the stoichiometry $HAuCl_4(amide)_2$ in the organic phase (**Figure 1.10**) [135].

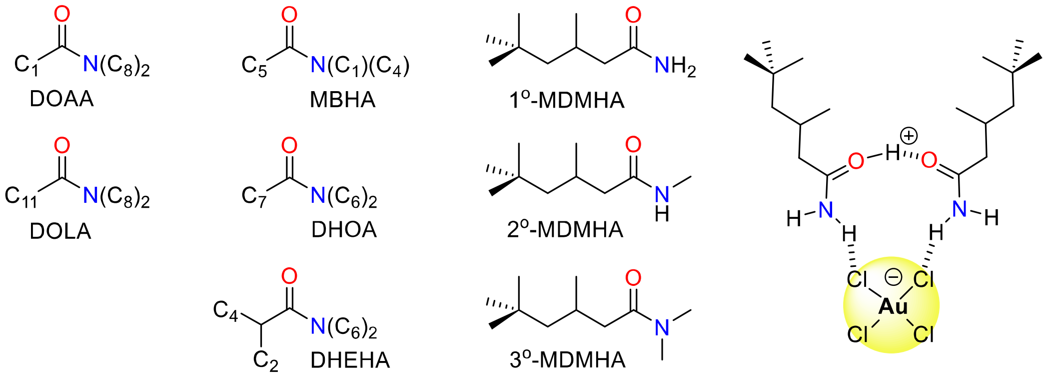


Figure 1.10- Amide reagents exploited for the recovery of gold by solvent extraction [29]

More recently, the simple primary amide 1°-MDMHA was shown to achieve the selective separation of gold as $[AuCl_4]^-$ from an aqueous mixed-metal solution of composition similar to that obtained from HCl leaching of waste PCBs [136]. Protonation of MDMHA plays a crucial role in the selective extraction of gold, as combination of the protonated and neutral amide with $[AuCl_4]^-$ through hydrogen bonding and electrostatic interactions creates a neutral assembly which is transported into the organic phase (**Figure 1.10**). Maximum extraction of gold (*ca.* 80%) was observed at 2.0 M HCl, a point at which the extraction of the other metal ions (*e.g.* Fe, Cu, and Zn) typically found in a PCB was very low. The concentration of extractant needed was low (0.1 M) which, along with the observation that the back transfer of $[AuCl_4]^-$ into a clean aqueous solution can be achieved using just water, is in stark contrast with commercial gold extractants such as MIBK and DBC.

Subsequent studies on secondary (2°-MDMHA) and tertiary amide (3°-MDMHA) analogues of 1°-MDMHA have shown that the 2° and 3° amides are stronger extractants for gold from single-metal solutions, yet show poor extraction efficiency from a mixed-metal solution representative of e-waste [137]. In these cases, the presence of high concentrations of other metals such as copper, iron and tin cause the formation of viscous third phases (insoluble in both aqueous and organic phases). The use of a more polar organic phase circumvents third-phase formation, but with a loss in selectivity for gold. The identities of the species formed in the organic phase was probed using spectroscopic, diffraction, and computational methods, and further highlighted that transport of the proton into the organic phase by the amide as $H(L)_2^+$ (where L = amide) is important, and that little or no water is involved in the organic-phase assembly process.

iv) Polymer Inclusion Membrane

A Polymer Inclusion Membrane (PIM) utilization is another technique for the separation and recovery of low-concentration of metal ions from leach solution. The benefits of PIM are including selective separations, simultaneous extraction and back extraction of metal ions, and environmentally friendly. PIM is also having long-term stability with negligible carrier loss and high efficiency. PIMs can be synthesized at laboratory scale by dissolving the components such as polymer, plasticizer and extracting agent in an appropriate solvent like Chloroform (or) Tetra hydro furan (THF). The mechanical strength has been provided to the membrane with the base polymer. In contrast, a carrier or extractant is used to transport metal ions and a plasticizer provides elasticity to the membrane [12]. The solvent evaporates slowly, and the leftover residue is the desired membrane for metal extraction.

The transport mechanism of metal ions through PIMs is generally involved in two-compartment cells where simultaneous extraction and back extraction processes occur. Leached liquor of WPCBs is used as the feed phase and another inorganic acid is used as a stripping phase as shown in **Figure 1.11.**

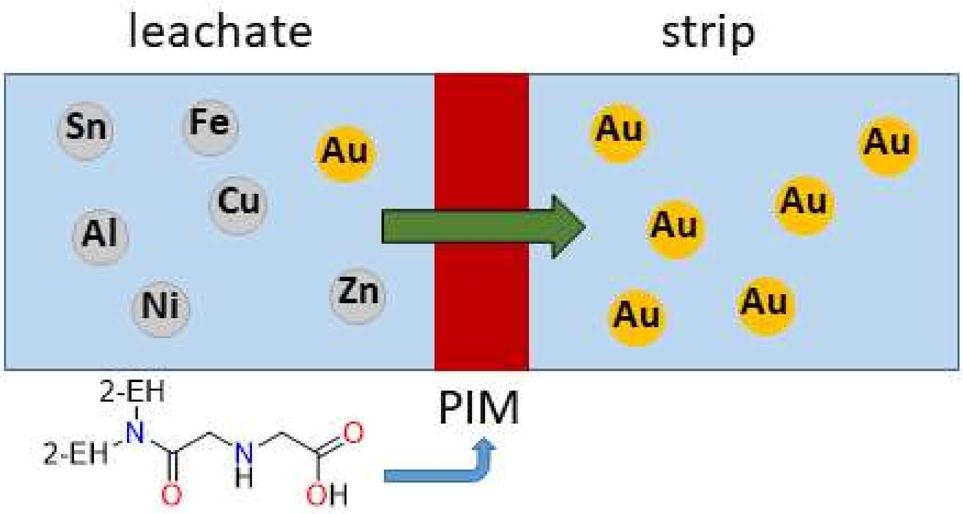


Figure 1.11- Transport of Au from an aqueous leach solution into and aqueous strip solution with selectivity provided by the extractant-embedded polymer inclusion membrane (PIM) [29]

The metal ions exchange via the membrane phase takes place during the transport process across PIMs and the removal of metal ions is not restricted by the equilibrium conditions [138]. For the separation of copper cations, initially, the extractant is dissolved in the membrane phase as a dimer form in a non-polar solvent [139], which reacts at the interface of the feed phase membrane with metal ions by ion exchange of protons. The formed copper complex diffuses across the membrane and reacts with the protons at the stripping interface of the membrane. The excess number of protons in the stripping phase provides the driving force for the mass transfer. After the stripping process, the carrier is re-generated and re-used at the feed interface to repeat the process. Several researchers have studied the recovery of metal ions through PIM techniques with the help of various carriers. Kavitha et al., 2012 studied the recovery of copper using D2EHPA as an extractant [138]. The mechanism of complexation in forward direction and stripping in backward can be written as

$Cu^{2+}{}_{(aq)} + 2\,(HL)_2{}_{(org)} \rightleftharpoons CuL_2(HL)_2{}_{(org)} + 2\,H^{+}{}_{(aq)}$ HL is D2EHPA

They observed that using PIM in the study effectively transports copper from the feed phase to the strip phase. It was also determined that the transportation of copper ions increased with the concentration of carrier and stripping reagent (sulphuric acid). The effective transportation of copper was observed with 4.8x10-2 mol/L D2EHPA in the membrane phase, 1 mol/L sulphuric acid in the strip phase. Parhi et al., 2008 studied the sequential separation of copper, zinc, cobalt and nickel ions with a supported liquid membrane technique using LIX 84I, TOPS-99 and Cyanex 272 from a leach solution [140]. Chakraborty et al., 2007 studied the extraction of copper and nickel ions with an emulsion liquid membrane having D2EHPA as a carrier from a dilute sulphate solution [141]. Hydrochloric acid is used as a stripping reagent. They have observed that the recovery of copper (II) and nickel (II) is 90% and 46% at a pH of 3.5 feed phase. Zajac et al., 2020 studied the effect of temperature on the flux of silver transportation through a membrane containing KC (calixpyrrole). They found that silver ions' transport increases with the temperature in the range of 25-60 °C [142]. In addition, pressure plays a significant role in membrane filtration techniques for waste streams containing heavy metals and recovering them. The driving force for the separation is the differential pressure on feed size and the permeate [143].

1.5.3. Electrochemistry

Removing the dominant copper metal from the PCB as a first step can allow the precious metals to be processed in a more efficient manner. The use of an acidic ferric chloride solution, along with simultaneous electrowinning, results in a higher weight percentage of gold in the remaining solid residue [83]. In this instance copper recovery was high (99%), and electrochemical recovery of gold was more efficient as the residues were 25 times more concentrated in gold compared to the original PCB samples. Similarly, gold was leached from the solid residue with HCl/H_2O_2, followed by electrowinning, to generate a high purity (99.99%) gold deposit [144]. A complete process has been developed for the processing of waste PCBs which also favours stripping out the dominant metals as a first step [49]. Iron and aluminium were removed first using magnetic and Eddy current separation, followed by dissolution of the copper (by ammonium sulfate leaching, solvent extraction and electrowinning) to leave a solid residue (*ca.* 2 wt% of the original material) which was leached using aqua regia and the gold extracted using tetraoctylammonium bromide in toluene. The recovered gold was then converted into nanoparticles (97 wt%) in the presence of dodecanethiol and sodium borohydride to increase the value of the final product.

Several electrochemical separations have also been developed, including a process to recover gold from a cyanide leachate solution using a highly porous glassy carbon cathode [145]; 99% of gold was recovered in 1 h due to the electrode's large porous surface area, high void volume, rigid structure and low resistance to fluid flow (**Figure 1.12**). This process was improved by purging the electrochemical cell with nitrogen gas to remove any dissolved oxygen which was known to inhibit the deposition of gold [22], allowing gold recovery from solutions of low concentration (*ca.* 100 mg/L). Cyclic voltammetry experiments applied to aqua regia leach solutions from PCBs have demonstrated that pure gold can be electro-deposited directly from solution without interference from the other metal ions present [146]. Gold extraction levels of 99.9% were achieved using gold electro-deposition from cyanide leach solutions with a zinc powder cathode system [110].

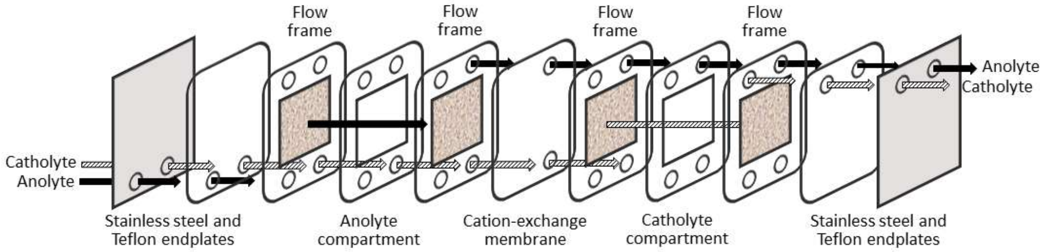


Figure 1.12- Schematic diagram of a flow-through electrogenerative reactor (modified from ref. [145])

1.5.4. Biohydrometallurgy

Until relatively recently biohydrometallurgy was largely confined to just two industrial applications: the processing of low-grade copper ores [147], and the recovery of ultrafine gold particles from refractory ores that are resistant to cyanation [148]–[150]. The BIOX®[151] and Bacox™ processes[152] are examples of this and are estimated to generate around 5% of global gold production [153]. Two general types of organisms are used (i) chemolithotropes that use Fe sulfides as an energy source, producing sulfuric acid that leaches metals and (ii) cyanobactieria and fungi that produce cyanide that leaches gold as $[Au(CN)_2]^-$ for which recovery follows conventional methods.

Recent reports on the treatment of waste PCBs focus on the combined bioleaching of copper and gold. A two-step process with Cu and Au recovery efficiencies of 98% and 44%, respectively was reported in which copper leaching is accomplished with the chemolithotropes *Acidithiobacillus ferrovorans* and *Acidithiobacillus thiooxidans* followed by gold leaching using the cyanide-producing *Pseudomonas putida* under very mild operating conditions (pH 7.3-8.6 at 30°C in 2 days) [154]. Successful gold leaching (of around 15%) from electronic waste using the cyanogenic bacterium *Chromobacterium violaceum* has also been reported [155], and similar findings were seen in the successful copper and gold recovery (both around 10%) from waste PCBs [156]. As with conventional chemical leaching processes, gold recovery rates were improved if the copper was separated first. This last finding was echoed in the use of the cyanogenic bacterium *Bacillus megaterium* for gold leaching [3]. The use of microorganisms to recover metals opens up avenues of investigation using synthetic biology. Genetically engineered strains of *Chromobacterium violaceum* with enhanced cyanide production have been created and have been shown to boost the level of gold recovery from 11% to 30% [157].

A recent biomass adsorption process was developed for the recovery of gold and silver along with base metals, from waste PCBs using a thiourea/sulfuric acid leachant, followed by selective adsorption on a low-cost and environmentally benign biomass gel prepared from leaf tannin [109]. This gel was found to be more efficient at recovering gold and silver from the leached PCBs than the traditional cementation processes, and the adsorbed metals, which were reduced to their metallic form, were easily recovered by incinerating the metal-loaded gel. A high adsorption capacity bioadsorbant powder has been prepared from *Lagerstroemia speciosa* leaf tannins and polyethyleneimine, which successfully recovered gold from electronic waste and demonstrated four recyclable cycles using acidic thiourea as the eluting agent for gold recovery [158]. Finally, the biosorption of gold from a thiourea leached liquor obtained from discarded PCBs using chitin, a fibrous polysaccharide which is chemically similar to cellulose, has been studied [159]. In this case, N-acetyl and hydroxyl groups act as metal binding sites, and gold recovery rates of around 80% were observed at room temperature over a time scale of just four hours.

1.6. Importance of Eh-pH diagrams in metal recovery

The chemistry of the aqueous or organic system during separation of metallic fraction can be obtained by Eh-pH diagram based on available thermodynamic data. The diagram represents various stable phases of a compound in the co-ordinates pH and the oxidation potential (Eh) in relation to the normal conditions (Temperatures: 25 °C, pressure: 0.1 Mpa) or at high temperatures [160]. This has been initially introduced by pourbaix and valensi then studied by many other researchers. Various useful relations such as Nernst equation using Gibbs free energy and equilibrium constant for the formation of aqueous or solid compounds. The pourbaix diagram of copper water system is shown in the **Figure 1.13** (re-drawn from [161]). It represents the stability of various phases such as Cu, Cu_2O, Cu^{+2} and $Cu(OH)_2$ in the mentioned co-ordinates.

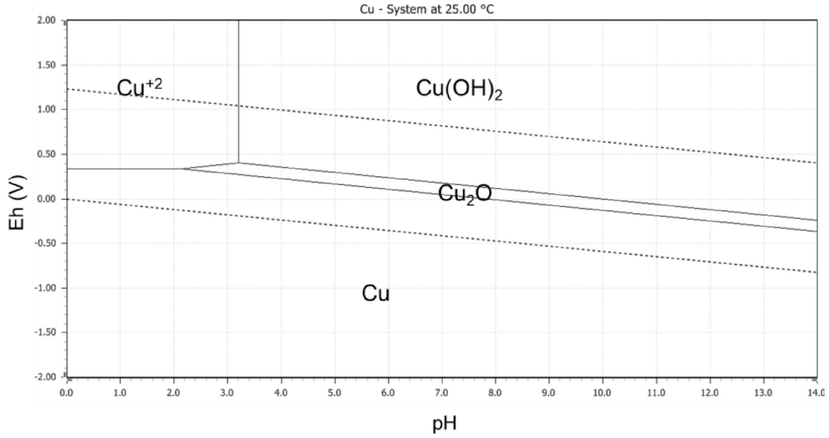


Figure 1. 13- Pourbaix diagram for copper-water system (re-drawn from [161])

The feasibility of gold in halide solutions is studied by Harjanto et al. 2019 and Cui et al., 2020 with an Eh-pH diagram [162][163]. But the chlorination leaching method has disadvantages, including difficulty in controlling chlorine gas released and corrosion problems. Similarly, in the case of iodine, high reagent consumption is also observed. Generally, the formation of stable complex ions can be observed during gold leaching. In the formation of chemical compounds. Gold had the number of oxides such as aurous (+1) and auric (+3). Based on the Eh-pH of the gold diagram in the chloride-based solution, the formation of stable complex ions occurred at a low pH and high potential

[162]. The Eh-pH diagram for the Au-Br-H2O system is studied by *Encinas et al., 2015* as shown in **Figure 1.14 [**re-drawn [164]**]** . It indicates that in the region of pH 2 to 4, the thermodynamically stable species are $AuBr_2^-$ and $AuBr_4^-$. The potential range for $AuBr_2^-$ turns out to be smaller (0.68-0.81V) compared to that of $AuBr_4^-$, (0.81-1.34 V) as shown in figure [164].

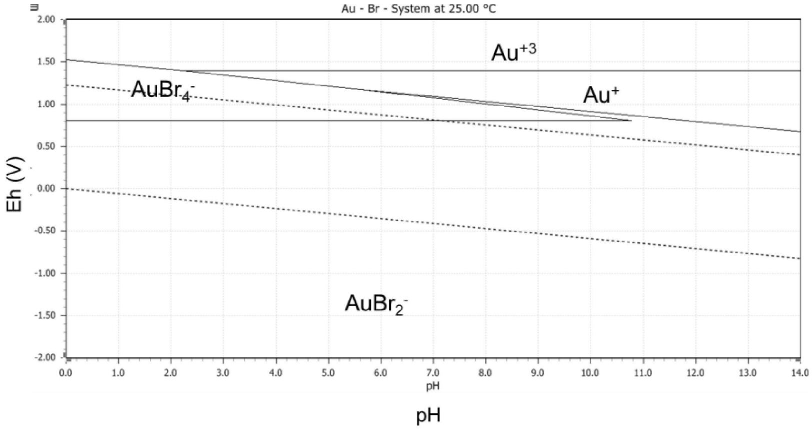


Figure 1. 14-Pourbaix diagram for Gold-Bromine system in aqueous solution (re-drawn from [164])

Meshram et al., 2020 studied for the copper citrate system at 1M copper activity and 0.667 M citrate activity. They examined the occurrence of copper citrate complex at various pH and redox potential thermodynamically with a ligand L. The formation of stable phases such as Cu, CuO, CuL^- and $Cu(OH)L^{2-}$ were observed in the mentioned coordinated as represented in **Figure 1.15** [redrawn from [161]].

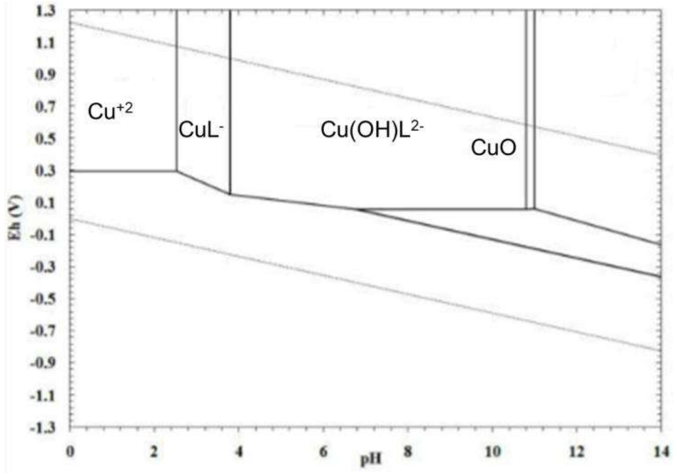


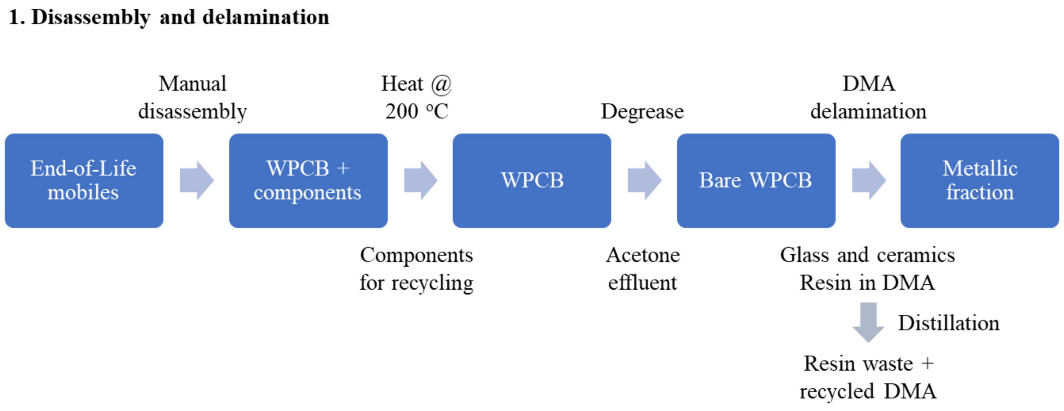
Figure 1. 15-Pourbaix diagram for copper-citrate system (re-drawn from [161])

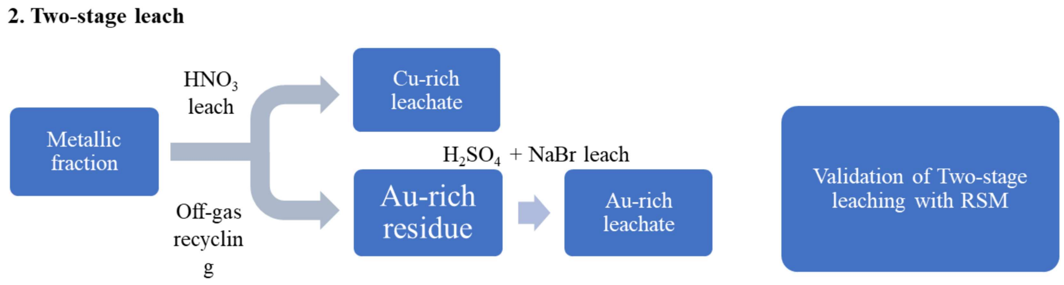
1.7. Aim and scope of the present work

It is clear from most of the previous research that the leaching of metals from a separated metallic fraction from WPCBs, *i.e.* where the WPCB is first delaminated using organic solvents such as dimethylacetamide (DMA) to separate the non-metallic and metallic components, has not been considered yet. Moreover, reports on the sequential recovery of base and precious metals are limited. Therefore, the present study was undertaken initially to optimize the parameters for the effective leaching of the predominant metals in WPCBs, *i.e.,* copper and nickel, such that the resulting gold and silver-rich residues are more easily treated. Our goal was to optimize the leaching conditions that would facilitate a two-stage metal separation process, with the predominant base metals separated first and precious metals second. In contrast to previous reports, we have focused on the extraction of metals from delaminated WPCBs to avoid complications arising from the presence of glasses, ceramics, and resins.

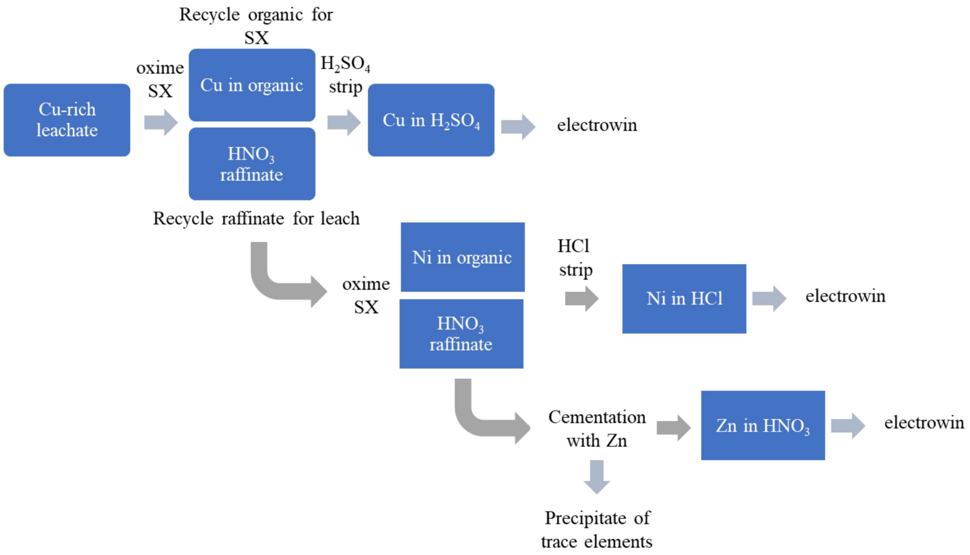
The use of an industrial extractant ACORGA M5640 to achieve substantial recovery for copper and nickel from PCBs, where the range of metals present and their concentration profile is substantially different from the primary ores that the industrial ligands were designed to operate under, has also not yet been reported and forms the aim of this work. Optimization of various parameters, such as the concentration of the extractant, the pH, organic to aqueous phase ratio, and the equilibrium time for the selective extraction of copper and nickel from the stage-1 leach solution is also included in this work, along with the effect of various stripping reagents for the efficient back extraction. The separation of trace elements from the raffinate of nickel SX stage is also studied with the cementation process by adding zinc powder, based on the difference in their reduction potential, which facilitate the electrochemical reaction. In the solvent extraction of gold from halide leach solutions, commercial reagents such as MIBK (isobutyl methyl ketone), DBC (diethylene glycol butyl ether) or 2-EH (2-ethylhexanol) can be used, although these reagents exhibit safety, selectivity and mass balance issues. More recently, the primary organic amide $R_2NC(O)CH_2C(Me)CH_2CMe_3$ (1°, $R_1 = R_2 = H$, $\mathbf{L^1}$), as well as secondary (2°, $R_1 = Me$, $R_2 = H$, $\mathbf{L^2}$) and tertiary (3°, $R_1 = R_2 = Me$, $\mathbf{L^3}$) variants provide excellent, highly selective separation of gold from metals representative of mobile-phone leachate. Therefore, this work also presents a viable solution using sustainable chemistry principles for the selective recovery gold from stage-2 leach solution of waste PCBs. Finally, various parameters for the leaching of copper, nickel and gold have been validated with the employment of Response Surface Methodology (RSM), a statistical modelling technique to study the effect of parameters.

The proposed work is briefly represented as flow diagrams with the below figures.





3. Cu and Ni solvent extraction & separation of trace elements



4. Au solvent extraction and Ag cementation