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Recovery of Cu, Au, Ag and Other Metals from E Waste PCB By Hydrometallurgical and Electrometallurgical Route

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Abstract

With progress of development mobile phones, computers and digital world , the older electronic products became junk and form E-waste. It creates environment hazards by interacting with water body and air in domestic and industrial sectors. Accumulation of growing E-waste is a real problem in the developed and developing countries. On the other hand, Electronic waste contain valuable metals such as Au, Ag, Cu, Ni, Pb, Zn which if economically extracted will not only create a new job world and boost economy but also minimize the health hazards due to this. In the present investigation , PCB from the mother board of the computer are treated hydrometallurgy and electrometallurgy techniques to get pure metals Au, Ag, Cu, Ni, Pb, Zn separately . The ideal conditions of hydrometallurgical process was found out by constructing combined E-PH diagrams of base metals and precious metals . The deposition potential which is a function of metal ion concentration, pH, overvoltage, standard electrode potential is computed for each metal. Metals were separetly electrodeposited at cathode by varying the applied potential according to the right deposition potential of a particular metal. The recovery of the metals were 80-90%.

Keywords:* *Printed circuit board; Recycle; E-Waste; Hydrometallurgy; Electrometallurgy; E-Ph diagram

Introduction

E waste is the discarded electrical or electronic devices in computer CPU, motherboard mobile phones and other Printed circuit boards (PCB) which can be reused and recycled to produce valuable materials salable in the market. 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. Waste PCBs constitute a heterogeneous mixture of metals, non-metals and some toxic substances. Many research works have revealed that the composition of metals, ceramic and plastics in PCBs could reach 40%, 30% and 30%, respectively. 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%), considerable amount of precious group metal (PGM) like Au and Ag. Additionally, PCBs also contain different hazardous elements including heavy metals (Cr, Hg, Cd etc.), rear 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. The e-waste from mobile phones and personal computers (PC) have

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considerable fractions of the Au, Ag and Pd. 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. 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.

E-waste, in particular waste PCBs, represents a rapidly growing disposal problem worldwide. Considering that the lifetime of a mobile phone is approximately 2-5 year and of a computer 5-8 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. Today's era of automation and computer world generate huge e-waste which may be harmful and environment hazardous. So reuse and recycling of e-waste, not only generate economy but also save a country from environment pollution and human prone to decease. Recycling of e-waste for metal recovery is also important from the perspective of saving energy. One of the major benefits is a significant energy saving using recycled materials compared to virgin materials. Moreover, processing of e-waste will reduce burden on mining ores for primary metals. Therefore, scarce resources especially for PGM could be conserved, e.g., metals that exist at low concentrations in primary ores and consume significant energy during extraction. Factually, e-waste is a rich source of PMs compared to their primary ores. The amount of gold recovered from one ton of e-waste from personal computers is more than that recovered from 17 ton of gold ore. The processes for recovering PMs from electronic scrap, in limited cases are easier than their primary ores . If PMs and SEs are unrecovered, it will be a significant loss of precious resource.

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. This shows a typical composition of PCB. It is seen that Au and Ag contents could be as high as 1000 ppm and Ag 2000 ppm respectively with over 20% Cu, along with other valuable metals.. The composition of metals, ceramic and plastics in PCBs could reach 40%, 30% and 30%, respectively.

Pyrometallury, Hydrometallurgy and Electrometallurgy techniques have been used by researchers for extraction of the valuable metals. Željko Kamberović et al proposed three hydrometallurgical processes for the recovery of copper and other precious metals from Waste Printed Circuit Boards (WPCBs) and also optimized it. The use of selective leachants is required for recovery of high purity metals. The metals extracted by hydrometallrgical process is are purified and deposited at cathode at different deposition potential. Hydrometallurgy and Electrometallurgy can be combined in a single reactor to produce metal with the minimum energy requirement and cost. The structure of the deposited metals can be controlled to bright surface with finer grain by controlling the current density, overvoltage and metal ions concentration during electrodeposition.

In the present investigation the conditions of leaching of the metals from PCB are found out by superimposing the E--PH diagrams of the all the metals of interest and finding out the right conditions of metals recovery. The metal ions in the leached solutions are electrodeposited at cathode one by one by changing the electrodeposition potential.

Methods and Materials

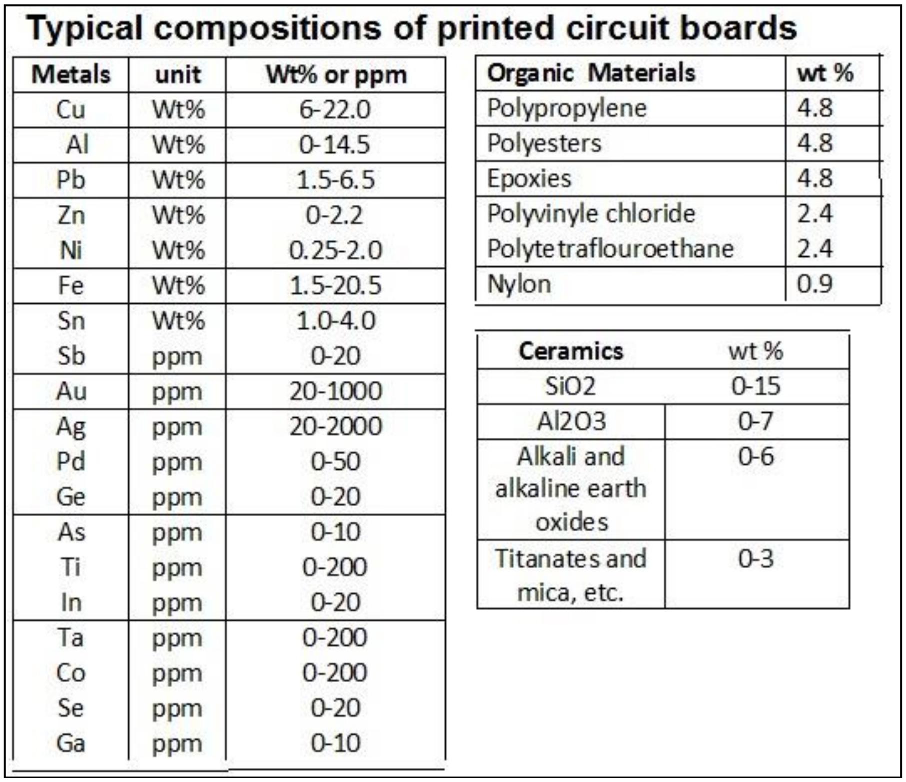
The methods consist of four steps:

- Separation of Metallic and Non-Metallic
- Selecting Leaching of metallic parts
- Enrichment of leached solution of valuable metals
- Production of Pure Metals by Electrometallurgy route

Separation of Metallic and Non-Metallic

This shows that the mother boards of mobile phone and computer were pulverized to obtain the PCB which were heated to 250C to evaporate out all plastics and insulation. The PCBs had chemical coating made of epoxy which neither goes out during heating nor allows the leaching agent to penetrate through it for the recovery of metals. So the plastic removed PCB was soaked in 10M NaOH at 30 C for 100 minutes to make open the metallic parts for leaching . The soaked NaOH solution was analyzed for any valuable metal that might have leached out into it.

Table 1: Typical compositions of printed circuit boards.



Typical compositions of printed circuit boards

Metals	unit	Wt% or ppm
Cu	Wt%	6-22.0
Al	Wt%	0-14.5
Pb	Wt%	1.5-6.5
Zn	Wt%	0-2.2
Ni	Wt%	0.25-2.0
Fe	Wt%	1.5-20.5
Sn	Wt%	1.0-4.0
Sb	ppm	0-20
Au	ppm	20-1000
Ag	ppm	20-2000
Pd	ppm	0-50
Ge	ppm	0-20
As	ppm	0-10
Ti	ppm	0-200
In	ppm	0-20
Ta	ppm	0-200
Co	ppm	0-200
Se	ppm	0-20
Ga	ppm	0-10

Organic Materials	wt %
Polypropylene	4.8
Polyesters	4.8
Epoxies	4.8
Polyvinyle chloride	2.4
Polytetraflouroethane	2.4
Nylon	0.9

Ceramics	wt %
SiO2	0-15
Al2O3	0-7
Alkali and alkaline earth oxides	0-6
Titanates and mica, etc.	0-3

Selecting Leaching of metallic parts

Leaching is a hydrometallurgical process to treat metals in aqueous solution in acidic or alkaline environment under oxidizing or reducing condition to get the metals into the solution as ions. The leaching has to be selective to get the wanted metals into the solution, keeping behind the unwanted metals as residue so that the clear filtered solution is enriched with valuable metals.

Table 2: Selective leaching one needs to examine E-PH diagrams of the metals.

Metals	PH range to dissolve	E (volt) range to dissolve
Al --- Al^{3+}	-2 to 4	Above -1.75
Zn --- Zn^{2+}	-2 to 8.5	Above -1.0
N i--- Ni^{2+}	-2 to 4.8	Above -0.7
Pb --- Pb^{2+}	-2 to 6.0	Above -0.3
Sn --- Sn^{2+}	-2 to 0	Above +0.2
Cu --- Cu^{2+}	-2 to 3.5	Above +0.35
Ag --- Ag^{+}	-2 to 7.7	Above +0.5
Au --- Au^{3+}	-2 to 2	Above +1.5

Enrichment of leached solution of valuable metals

The metals ions in the leached solution need to be enriched by removing the unwanted metallic ions by precipitation and concentrating the solution with metal values by boiling.

Production of Pure Metals by Electrometallurgy route

Metals are produced from the enriched solution By electrolytic decomposition in an electrochemical cell, when a metal is deposited at cathode at preselected cell potential and passing current from the external power source. This shows the circuit diagram of the electrometallurgical metal production.

Table 3: It is seen that all the base metals with good percentage of Cu and Sn have been extracted.

Metals	**E^0_c V**	**Metal**	**Metal**	**volt**	**$E_{cell}= E_c - E_a$**
	vs. HE	**conc.**	**conc.**		**Cell potential**
		%	**mole**		**volt**
Au	1.692	0.0142	$7.21*10^{-6}$	1.706754	0.076754
Ag	0.996	0.0317	$2.93*10^{-4}$	1.054757	0.575243
Cu	0.342	15.2	0.189	0.47326	1.15674
Sn	0.15	3.79	0.0319	0.261248	1.368752
Pb	-0.126	2.81	0.0135	-0.02442	1.654424
Ni	-0.257	0.43	0.0073	-0.16234	1.79234
Zn	-0.762	0.22	0.0034	-0.67593	2.305935
Al	-1.662	1.7	0.063	-1.5431	3.173097

Results and Discussions

Having separated the ceramic and plastic parts from PCB next stage is to selectively leach the valuable metals from the base metals.
Hydrometallurgy
For selectively leaching E-PH diagram is a tool to the right parameters of leaching conditions such potential or degree of oxidizing condition and PH, so that the required metals can be taken in the solution as ions and unwanted residue can be kept aside as residue. The E-PH diagrams of the metals under consideration need to be superimposed along with hydrogen and oxygen lines to find out the conditions of hydrometallurgical extraction of the metals. The diagram has been modified and divided into 2 E-PH diagram one with the base metals and other with the noble metals. This shows a combined E-PH diagram of the metals, Al, Ni, Pb, Sn, Zn and Cu, those are present in PCB. It is seen that extraction of Sn requires high acidic and oxidizing conditions with very narrow range where Sn2+ can be obtained. Cu2+ has a wide region, Al3+, Zn2+, Ni2+, Pb2+, do not require high oxidizing condition for acid leaching.
The E-PH diagram of Au and Ag , along with Cu is shown. It is seen Au can be leached under very high oxidizing condition followed by Ag (Figure 1).

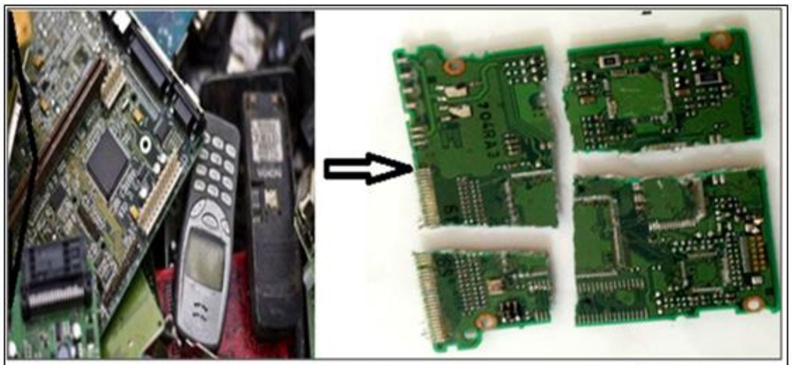


Fig.1 showing electronic waste to Printed circuit board (PCB) used for metal extraction

Figure 1: This showing electronic waste to printed ciucuit board (PCB) used for metal extraction.

The E-PH diagrams guide the selective leaching process so that the valuable metals can be separated from those of less expensive. To get any of metal M into its ionic form M++ , the leaching has to be made in aqueous environment at some fixed pH and under a fixed oxidizing condition(E potential). The hydrogen line and oxygen line are superimposed on the E-PH diagra. The metals which have their lines of M---M2+ below the hydrogen line, can be leached without adding any oxidizing agent or oxygen. It is seen in the that for Al to Al3+, pH needs to be below 4 and the potential anything above -1.7 volt vs. SCE. This illustrates the E-PH conditions for all the metals under considerations. It is understood from the that a PH of less than 2 and potential E between below 0.0 volt potential can leach all the metals except, Sn, Cu, Ag and Au which will remain as residue. For leaching Cu, higher oxidizing condition is required. This can be achieved by oxidizing acid lke HNO3 . For tin Sn, oxidizing condition and very low pH less than 2 is required. Thus the first leaching is carried out in concentrated HNO3 at pH 0, at elevated temperature 70o C for 50 minutes, when the metals Al, Pb, Zn, Ni, Cu and Sn are extracted, leaving behind Au and Ag as residue.This shows the percentage metals extracted. It is seen that all the base metals with good percentage of Cu and Sn have been extracted. The leaching reactions are given below.

Cu(s) + 4HNO3(aq) —> Cu(NO3)2(aq) + 2NO2(g) + 2H2O(l) (1)
ZnO+ 2HNO3 -> Zn(OH)2 + 2NO2 (2)
3Sn + 4 HNO3 = 3SnO2 + 4NO + 2H2O (3)
3Ni + 8HNO3 → 3Ni(NO3)2 + 2NO + 4H2O (4)
2Al(s)+6HNO3(aq)—>2Al(NO3)3 + 3H2 (5)
Pb + 2HNO3 —> Pb(NO3)2 + H2 (6)

The percentage of the metals extracted are well above 80%. It is observed from the fig.4 that Au and Ag need much higher oxidizing condition for leaching to get them into the solutions as ions. The potential of leaching condition for Au and Ag is above 0.5 and 1.5 volt respectively. Such high oxidizing condition can be achieved by cyanide leaching. So the residue is leached by cyanide under high oxidizing condition by purging air through the leached solution. The reactions are given below

4 Au(s) + 8 NaCN(aq) + O2(g) + 2H2O(l)→ 4 Na[Au(CN)2](aq) + 4 NaOH(aq) (7)

4 Ag(s) + 8 NaCN(aq) + O2(g) + 2H2O(l)→ 4 Na[Ag(CN)2](aq) + 4 NaOH(aq) (8)

The percentage metals extracted is shown. It is seen that over 90% of Au and Ag are extracted and the remaining, Cu, Sn, Ni, Pb, Zn are also extracted. The 1st solution containing mostly the base metals (after HNO3 leaching) and the 2nd solution containing mostly Au, Ag will be separately taken for electrodeposition of the metals in the next section (Figure 2).

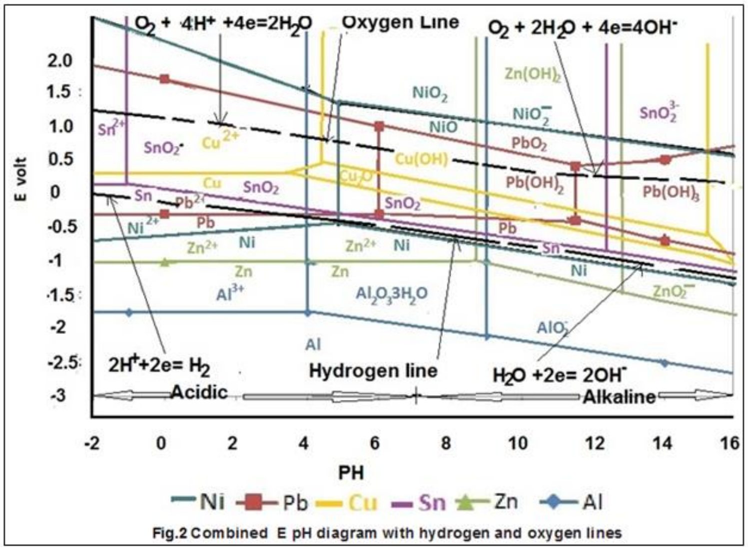


Figure 2: Combined E pH diagram with hydrogen and oxygen lines.

Electrodeposition

The principle is +ve charged metal ions are deposited at the negatively charged cathode, when the predetermined deposition potential is applied across the cathode and anode. The aqueous system electrodeposition process is illustrated by the following equations (Figures 3-6).

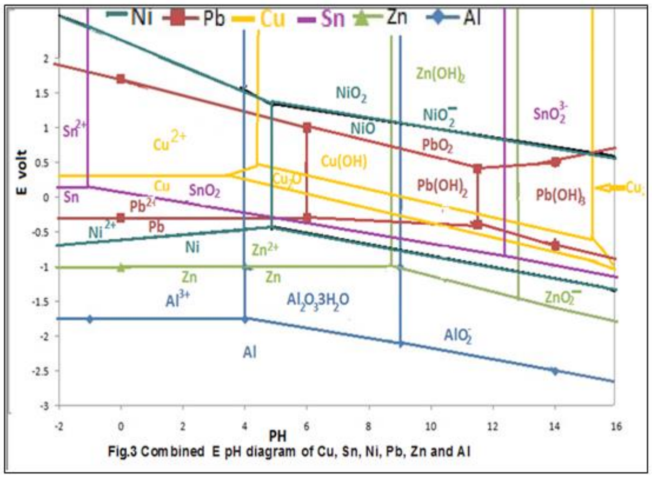


Figure 3: Combined E Ph diagram of Cu, Sn, Ni, Pb, Zn and Al.

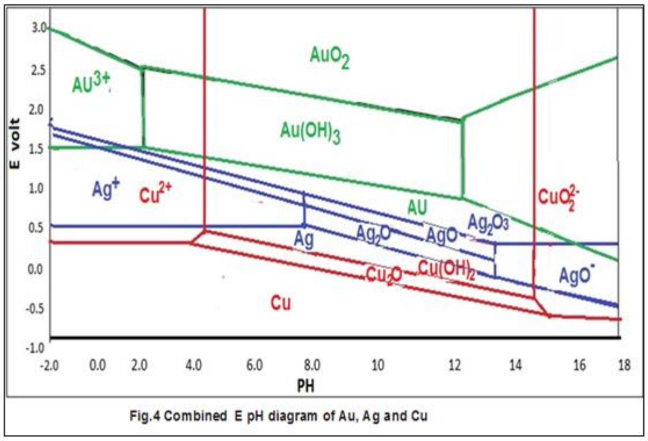


Figure 4: Combined E pH diagram of Au, Ag and Cu.

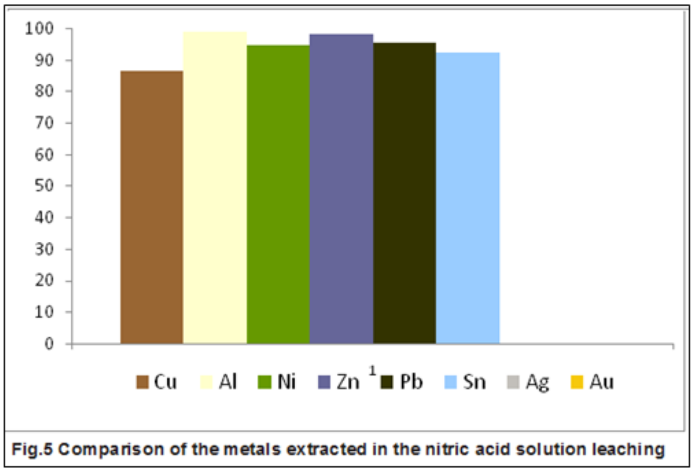


Figure 5: Comparison of the metals extracted in the nitric acid solution leaching.

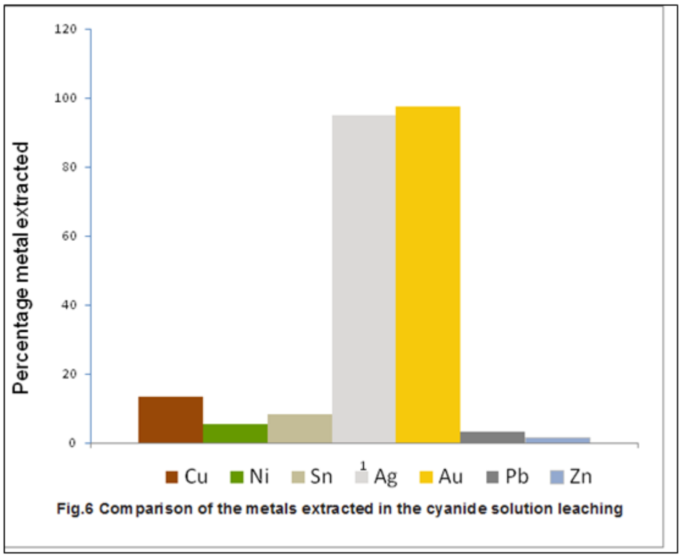


Figure 6: Comparison of the metals extracted in the cyanide solution leaching.

Electrode reactions	Electrode potential	
Cathode $2M^{2+} + 4e = 2M$	E_c	(9)
Anode $2H_2O = 4H^+ + O_2 + 4e$	E_a	(10)

The applied potential for deposition of a particular metal is given by the following equation.

$$E_{applied} = E_c - E_a + \eta_{act} + \eta_{conc} + IR \qquad (11)$$

Where

η_{act}= Activation overvoltage

η_{conc} = Concentration overvoltage

IR= potential drop electrolyte lead wire

$$E^t_c = E^0_c \ + 2.33RT/nF \ \log M^{n+} + \eta_c + IR \qquad (12)$$

$$E^t_a = E^0_a \ - 2.33RT/nF \ \log (H^+)^4 \ p_{O2} + \eta_a \qquad (13)$$

The -log (H+) can be replaced by pH , pO2 =1. E0a = -1.23 volt vs Hydrogen reference electrode (SHE). At room temperature 25 0 C 2.3.3RT/F= 0.059 , n=1,2,3 for mono, bi and tri valent metals respectively. The table –III illustrates the data for electrodeposition of the different metals.

$$Ecell= Etc - Eta + IR \qquad (14)$$

The concentration overvoltage ηconc will be negligible if the rate of electrodeposition is not very high. Using the above equations , the deposition potential to deposit different metals in solution is given. It is seen the deposition potentials of the different metals vary a lot. Au is deposited first with the minimum deposition potential, being the most noble metal, followed by Ag, CU, Sn, Pb, Ni and Zn. Al being very active metal cannot be electrodeposited from the aqueous solution and is not considered (Figures 7 and 8).

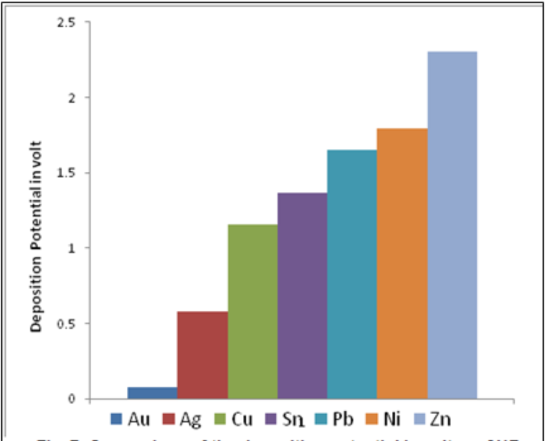


Fig. 7 Comparison of the deposition potential in volt vs. SHE of the different metals at different concentration of their ions in the hydro metallurgically extracted solution of PCB

Figure 7: Comparison of the deposition potential in volt vs. SHE of the different metals at different concentration of their ions in the hydro metallurgically extracted solution of PCB.

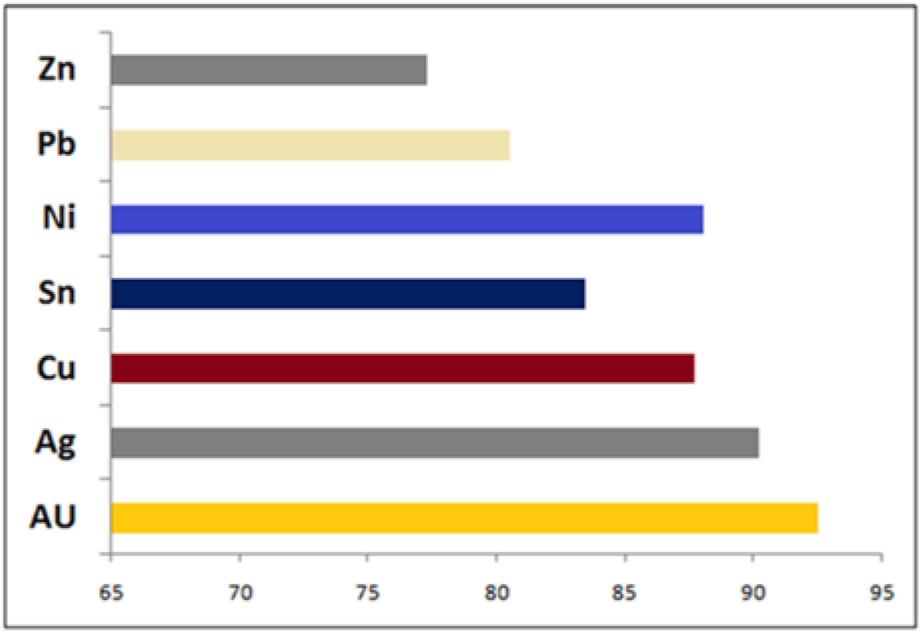


Fig.8 showing the % of metal recovery of the different metals in PCB by hydro and electrometallurgical extraction

The cell potential to be applied , depends on the concentration of the metal ions in the solution , standard electrode potential E0 , over voltage η, and the electrode potential of the anodic reaction and is shown. So Au is deposited first with the least potential, wit increase in potential Ag is deposited and so on for other metals. The cathode material , graphite rod, is changed, each time a metal is electrodeposited so that all the metals produced are separated. Fig.8 shows the percentage of metals from PCB by hydro and electro metallurgical process. It is seen that 80% metallic values from PCB have recovered for all metals (except Zn). The process proves to be efficient and economical of getting metals from E waste. The metals so obtained at cathode were analyzed for purity and has been illustrated in the Table-IV. It is seen that the purity of the most metals are close to 90%.

Conclusion

It can be concluded from the above results and discussions that respective E-PH diagram of the metals is the most important part for hydrometallurgical extraction of metals from PCB. Having obtained metallic ions in aqueous solution, each metal can be separately deposited at cathode at a time by varying the applied potential, since the deposition potentials of different metals widely vary. The recovery of the metals were over 80% with over 90% purity.

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