



DESIGN FOR RECOVERY OF PRECIOUS AND BASE METALS FROM E-WASTE USING ELECTROWINNING PROCESS

Amil H. Memon¹, Reshma L. Patel², DR. JAYESHKUMAR PITRODA³

¹Department of Civil Engineering, Birla Vishwakarma Mahavidhyalaya, Vallabh Vidhyanagar, Anand

²Department of Civil Engineering, Birla Vishwakarma Mahavidhyalaya, Vallabh Vidhyanagar, Anand

³Department of Civil Engineering, Birla Vishwakarma Mahavidhyalaya, Vallabh Vidhyanagar, Anand

Abstract — The quick technological advancement induces era of utilized electric and electronic gear waste which is making a genuine danger the earth. Waste printed circuit boards (WPCBs), as the principle constituent of the waste, are source of base and precious metals particularly copper and gold. Printed circuit boards (PCBs) are as of now being dumped in landfills or burned which is bringing on a genuine ecological harm as toxic gasses or leached hazardous mixes. To recover these metals from waste has dependably been a test. The review here presents the most proficient strategy for recovering the base and precious metals; Electrowinning. Utilizing Electrowinning a setup has been intended for the recuperation of four unique metals. The review demonstrates the recycling of Gold, Silver, Copper and Palladium in proficient and immaculate form..

Keywords-E-waste, Gold recovery, Electrowinning Process, Printed Circuit Boards (PCB), Electronic Waste recycling

I. INTRODUCTION

Old electronic equipment that has outlived their utilitarian life is categorized as e-waste. As per different numbers published by different research agencies, around 20 to 50 million tons of e-waste is generated worldwide every year. E-waste comprises of more than 5% of all solid waste generated and the volume is expected to increase at a rate of 300% per annum in developing countries. On an average, in India, in case of mobile phones the useful life goes up to 2 years. In case of PCs, it might go up to 5 years. The life of this equipment is extended due to reasons, for example, upgrade, repair and reuse, gift to philanthropy etc.

Electrical and Electronic equipment contains metallic and non-metallic elements, combinations and mixes, for example, Copper, Aluminum, Gold, Silver, Palladium, Platinum, Nickel, Tin, Lead, Iron, Sulfur, Phosphorous, Arsenic etc. In the event that discarded in the open, these metals can cause a severe environmental and health hazard.

All over the world, the quantity of electrical and electronic waste generated each year, especially computers and televisions, has assumed alarming proportions. In 2006, it was projected that 3 billion electronic and electrical appliances would become WEEE or e-waste by 2010. That would tantamount to an average e-waste generation rate of 400 million units a year till 2010. Globally, about 20-50 MT (million tonnes) of e-wastes is disposed off each year, which accounts for 5% of all municipal solid waste. According to the UN Under-Secretary General and Executive Director of the United Nations Environment Programme (UNEP), Achim Steiner, China, India, Brazil, Mexico and others would face rising environmental damage and health problems if e-waste recycling is left to the vagaries of the informal sector.

Electronic devices contain up to 60 different elements, huge numbers of which are valuable, for example, precious and special metals, and some of which are unsafe. Precious metals are rare, normally happening metallic elements which generally have a higher melting point, and are more ductile than other metals. They have a high economic value, as demonstrated by the two most well-known precious metals; gold and silver. Special metals include nickel, nickel base alloys, cobalt base alloys, titanium and titanium base alloys. Electronic equipment is an essential consumer of precious and special metals and therefore it is imperative that a roundabout stream is established in order to recover these metals and valuable elements. Investments are being made to treat e-scrap and reclaim the valuable metals, especially as crude materials become more scarce and expensive. Table 1 shows the concentration of metals in like manner electronic items.

Table 1: Concentration of metals in common electronic products.

Sr. No.	Electronic	Copper (% by Weight)	Silver (ppm)	Gold (ppm)	Palladium (ppm)
1.	Television (TV) Board	10%	280	20	10

2.	Personal Computer (PC) Board	20%	1000	250	110
3.	Mobile Phone	13%	3500	340	130
4.	Portable Audio Scrap	21%	150	10	4
5.	DVD Player Scrap	5%	115	15	4

Source: Balakrishnan Ramesh Babu, "Electrical and electronic waste: a global environmental problem", 2007 [1]

II. DESIGN AND METHEDOLOGY

Considering the Electrowinning process for the recovery of metals a design of plant has been done. A single process or the combination of two or three methods where required for the optimum recovery of metals.

Plant is to be developed based on that method which would have three stages:

- Stage 1 includes size reduction to ~1 mm measurement, trailed by the corona electrostatic separator and the hydro-cyclone which isolate metals from non-metals.
- Stage 2 isolates singular target metals from each other by hydrometallurgical preparing. This stage includes the disintegration of metals in sulphuric acid and Aqua Regia, trailed by the utilization of electrowinning technology which brings about metal purities of up to 99.99%.
- Stage 3 incorporates the treatment of by-products as per ecological, wellbeing, and security standards.

2.1. Projected Design: The plant is divided into four phases in which combination of physical, chemical and electrochemical processes are employed. First stage involves the size reduction where the raw material is crushed and reduced to the size less than 1 mm. Generally the waste boards are in large sizes which cannot be directly reduced to such smaller size. A shredder and then a hammer mill (Pulverizer) are employed for the size reduction process. Second stage involves the separation of metal from the non-metals as the non metals like plastic or ceramics are a hindrance in metal recovery process. Firstly the lighter non-metals are separated by settling in water after that a Electrostatic Separator is used to separate denser non-metals and ceramic base materials. After the separation of metals, they contain ferrous and Non-Ferrous which is separated by Magnetic Separator. Third stage involves the treatment and separation of individual metals. Firstly the impurities present are removed by leaching with sulphuric acid and then the remaining part is leached using Aqua Regia. The metal leached Aqua Regia solution is four consequent EMEW (electrowinning) chambers separating copper, gold, silver and palladium. The final stage includes the treatment of by-products such as the waste Aqua Regia stream, sulphuric acid stream; according to environmental, health, and safety standards.

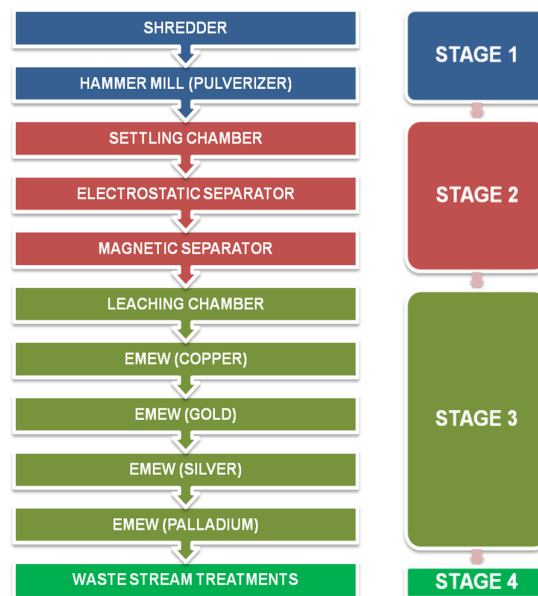


Figure 1: Design

2.2. Stage 1 (Size reduction): The size reduction starts with the board reduced and shredded into smaller segments. The smaller the fragments of the material lesser the load on pulverizer, due to this shredding is necessary. Shredder is a specific arrangement of blades which are rotated counter clock wise using spur gears connected to a pair of gear-box and motor. The literature review shows that Shredding to 5x5 cm plates should be the optimum size for further size reduction.

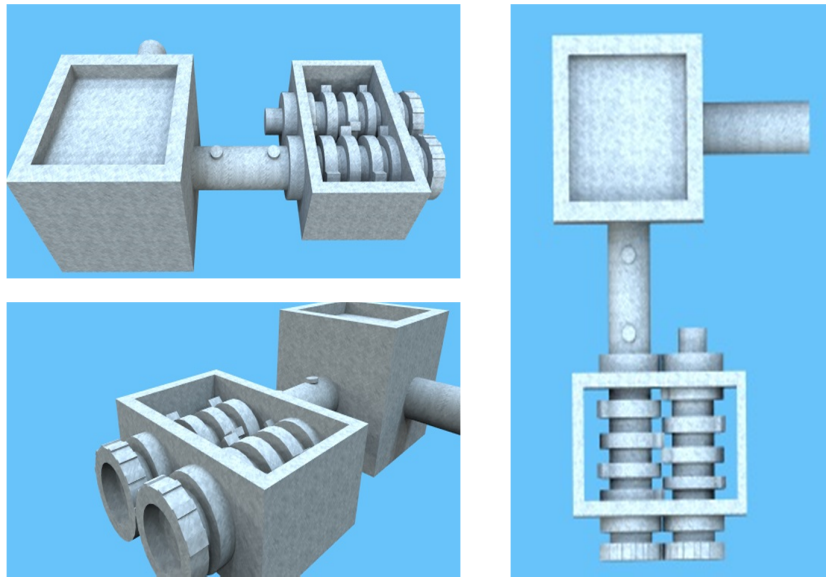


Figure 2: Shredder Design

The reduced fragments from the shredder are sent to the pulverizer for crushing. Here the optimum reduced size is to be decided for which the maximum amount of metal and non-metals are separated from each other. According to a literature the size when reduced to less than 2 mm the separation of metal and plastic is the most. The size when between 0.3 mm to 1.5 mm helps in further separation of metal and non-metal. According to another study when size reduced less than 0.5 mm, hinders the separation and also further equipments such as cyclone separator or dust collector has to be employed, which is not economical. So an average diameter of 1.5 mm was kept which was found to be optimum for further separations.

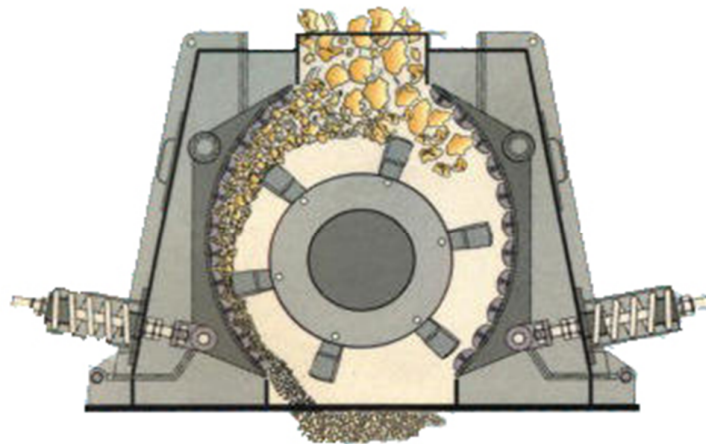


Figure 3: Hammer Mill (Pulverizer) Design

Source: The Hammer Mill manufactures, India

2.3. Stage 2 (Metal and Non-Metal Separation): After the crushing and reducing to the desired size, the separation of Metals and Non-metals can be done. For these, three different processes will be used. Firstly the lighter non-metallic

particles are separated using a simple settling tank in which the crushed powder is agitated in water and kept for settling. The lighter particles float and the metal and denser non-metallic particles settle down. The above layer is removed by decanting; this process can be repeated for better results. This process almost separates 30-40% of non-metals from the crushed lot and also a lot more economical as compared to other separation processes. After the settling process, Electrostatic Separator is to be used to separate the denser non-metals and metals. This technique is profoundly recommended in PCB recycling on account of critical contrasts in conductivity and electrostatic properties of the diverse segments in PCB. Corona electrostatic separation process is known to have an environmental friendly operation and low vitality cost.

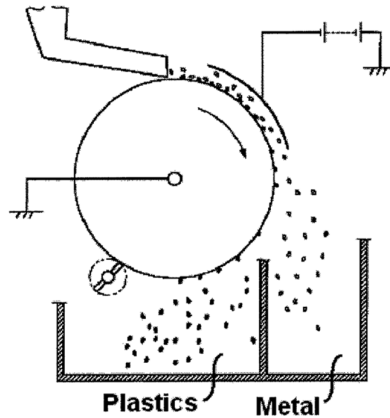


Figure 4: Electrostatic Separator design

Source: Electrostatic separation system for removal of fine metal from plastic, Google Patent, US 7767924 B2

The substances on the roller surface are subjected to an electric charge, ionized from the needle corona electrode and eventually separated due to the differences in conductivity and electrostatic properties. Almost 90% of metals and non-metals are separated, giving a metal stream which can be subjected to Ferrous and Non-ferrous separation. The Ferrous and Non-ferrous separation is done by Magnetic Separator. The ferrous metals hinder the chemical leaching process so they have to be separated.

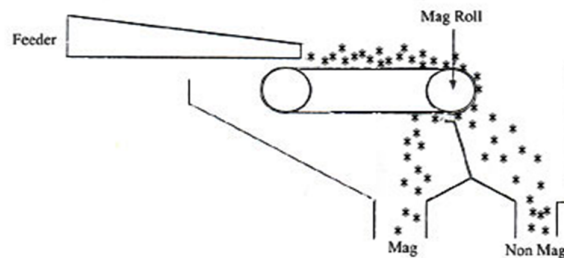


Figure 5: Magnetic Separator Design

Source: Jirang Cui, Lifeng Zhang, "Metallurgical recovery of metals from electronic waste: A review", 2008

2.4. Stage 3 (Leaching & Electrowinning Separation): The final separation has two processes to be carried out; first is the leaching using two different acids and electrowinning separation. The leaching is a chemical process of dissolving the metallic mixture in a reagent commonly an acid. Dissolution of the metallic mixture is vital on the grounds that the ensuing preparing steps are generally subject to the reagents or methods that will be executed for dissolution. The non-ferromagnetic metallic streams are to be broken up and isolated from the non-target metals utilizing sulfuric acid. At that point copper, palladium, silver, and gold are to be broken up all together from the non-ferromagnetic metallic mixture utilizing aqua regia. According to the findings 15-30 ml Acid is required to dissolve 1 g of metal. The optimum value required for the leaching must be decided as, the larger amount of Nitric ions; more it would be difficult to carry out the precipitation. The optimum value according to another research was 20 ml per gram of metal dissolved. So we consider 20 ml to be the optimum dose for both sulphuric acid and Aqua regia. After the dissolution of Non-target metals, the outlet stream contains all the metals of interest and is then sent to treat with Aqua regia. In this, 97%, 98%, 93% and

100% of gold, silver, palladium and copper respectively are found to dissolve with the ratio of 20 ml of acid for every gram of metal. All the metals of interest are dissolved in Aqua regia which can be now treated to separate the individual metal in the pure form using the Electrowinning Process. As discussed before the process would be continuous and in four different chambers separating four different metals.

The major challenges in the Electrowinning were deciding the Electrodes and also the voltage or the potential required to separate the metals from Aqua regia. The electrodes are to be decided based on the galvanic series and the potential can be calculated using the Electrochemistry principles and the Nernst Equation. The electrodes are to be decided based on the reactivity or the galvanic series. The Active metal acts as Anode and the passive or inert metal acts as cathode. The series shows the tendency of different material which are tending to be more active or more inert. The anodic material gives the electron and the metal precipitated from the solution gets deposited on cathode. Thus the reactivity of anode material should be more than the cathodic material.

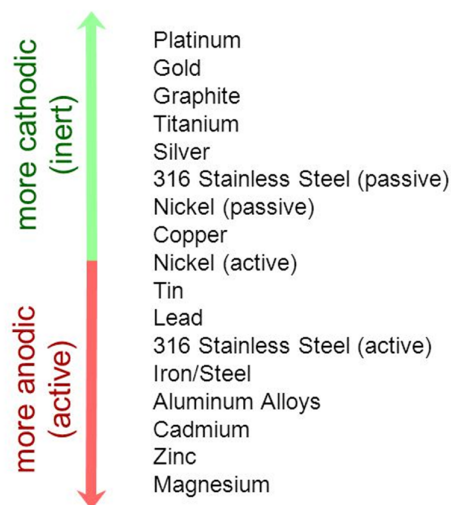


Figure 6: Ranking the reactivity of Metals (Galvanic Series)

Source: Philip H. Rieger (2009). *Electrochemistry: Second Edition* [33]

So, according to these series we have four metals to be extracted for which the electrodes selected are mentioned in the Table 2.

Table 2: Electrodes projected for the electrowinning process

Metal	Anode	Cathode
Copper	Alluminium Foil	Pure Copper Rod
Gold	Stainless Steel Mesh	Stainless Steel Rod
Silver	Stainless Steel Mesh	Stainless Steel Rod
Palladium	Stainless Steel Mesh	Stainless Steel Rod

Copper can be used as cathode; the copper extracted will be coated on the pure copper rod, enhancing it, which is more economical. Other metals use Stainless Steel as both Anode and Cathode as they are precious metals and using it as cathode would not be economical. As for the other metals the metal powder deposited on the SS Rod can be scraped out. The anode would be lined on the surface of the electrowinning chamber, so to increase the contact surface with the liquid stainless steel mesh is used. When voltage is passed through this arrangement, the anode loses electron which are gained by metallic ions in the liquid and gets deposited on the cathode. Thus the extraction of metal depends on the voltage required to lose an electron and also converting the metals in the liquid into ions. The electric potential required to reduce the metal is known as Standard half-cell potential and the series is called EMF series.

Half-Reaction	volts
$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.04
$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.68
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.41
$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.26
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.13
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	0.34
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	0.52
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	0.77
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.80
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	0.82
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	1.07
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	1.36
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	1.52

Figure 7: Standard Half Cell Potential, EMF Series

Source: James Brudenell (2000). Oxidation-Reduction Equilibria and Electrochemistry [32]

Further this Standard half cell potential is used to calculate the actual voltage required to deposit metal on cathode. This is done by Nernst Equation, which is as given below:

$$E = E^\circ + \frac{R * T}{z * F} * \ln(a)$$

Where:

E: half-cell potential of the reaction in Volts

E° : standard half-cell potential at STP and molarity of 1

R: universal gas constant, 8.314 J/mol-K

z: number of moles of electrons transferred in the reaction

F: Faraday's constant, 96,485 Coulombs/mol of electrons

a: chemical activity of the species

Here the following assumptions were made before calculating the potential

1. $V_I = E$ (standard potential).
2. Assume activities equal to concentration in mol/L.

Table 3: Calculated Electrolysis Data

	Copper	Gold	Palladium	Silver
A (ion activity)	0.000754	0.000000518	0.000000212	0.00000382
z (ionization state)	2	3	4	1
E°	0.3419	1.498	1	0.7996
E	0.2498	1.3741	0.9014	0.4793
V_I	0.2498	1.3741	0.9014	0.4793

2.5. Stage 4 (Waste Water & By-product stream treatment): After complete recovery of the metals, the waste stream contains non-soluble metals and the acid slurry. These waste streams are to be treated as per the environment, health and safety norms. Generally the acid is neutralized and the non-soluble contents are separated using a separation technique. Most common method used is Membrane separation technology.

III. EXPERIMENT, RESULTS & ANALYSIS

To check and analyze the data we have obtained, a lab scale experiment is carried. Also this experiment will give us the complete scenario of recovery by electrowinning technology and which can be further incorporated in the design. This lab scale experiment is the demonstration of the Electrowinning technology to obtain four metals; gold, copper, silver and palladium using the suggested electrodes and the calculated voltage supply.

3.1. Experiment: The experiment starts with the crushing and separation of metals from non-metals. Two type of material are being processed; RAM and motherboard. The material is crushed and powdered to an average diameter of 1.5 mm size. The metal from non-metal were separated using settling and washing which removed the lighter non-metallic solids. The denser non-metallic particles were not removed, as they are insoluble or cannot be leached in the acids and can be filtered out after leaching. Also the quantity of material processed being very small, it would not hinder the leaching process.

The material is first leached using H_2SO_4 , for every gram of sample dissolved 20 ml of acid is used. For a better convenience batches of 50 g sample are processed, so the acid required would be 1 litre. As the reaction commences gases are released, which indicates that the leaching process has started. After the reaction stops, the bubbling sojourns it can be treated with Aqua Regia. The remaining powder is filtered and washed from the solution for the next step. Aqua Regia is HCl and HNO_3 in 3:1 ratio. It is a highly corrosive reaction so it was carried outdoors. The amount of acid will be the same as in the first case; 20 ml acid per g of metal dissolved. The filtered powder is slowly added to Aqua Regia solution. This reaction requires agitation, so it is carried out on a magnetic stirrer plate. As soon as the leaching process starts yellowish green fumes can be seen which stops as the leaching process ends. There is still some powder leftover in the solution; they are the insoluble non-metallic substances which are to be filtered out from the solution. This is the final solution which will be further passed through the electrowinning chambers for metal extraction.

Now the electrowinning process is to be done. First the electrowinning for copper will be carried out, followed by gold, palladium and silver respectively. The arrangement of electrode in all the four process will be same, as shown in Figure 8. The voltage is supplied by the DC power supply which can be adjusted and regulated at the desired voltage. The voltage required for each process has been calculated earlier which will be used here. As the current is supplied the metal from the solution gets collected at the cathode. The same procedure is carried out for all the metals. Bubbling depicts that the reaction is going on which is eventually stopped with the reaction being completed. The powder deposited on the cathode end can be scrapped out. This powder can be melted to form ingots of the metal and weighed for the final results.

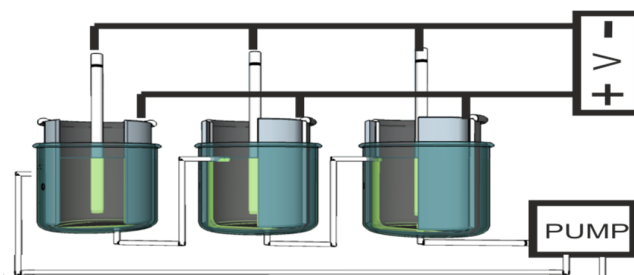


Figure 8: Electrowinning Cell arrangement

3.2. Results: In electrowinning experiment Copper, Gold, Silver were recovered from two different raw materials which were discussed; RAM and Motherboard PCB and the results for the same are presented below. Here the copper content is less due to loss of almost 2-3% in H_2SO_4 leaching.. The Gold sample was tested for its purity, which was almost 98 % pure.

Table 4: Results of recovery from Motherboard PCBs

Metal	Recovery wt. %	Estimated content wt. %	Recovery %
Copper	16.8	18.448	91.06
Gold	0.0352	0.039	90.25
Silver	0.144	0.156	92.30

Table 5: Results of recovery from RAM Boards

Metal	Recovery wt. %	Estimated content wt. %	Recovery %
Copper	23.6	27	87.40
Gold	0.0873	0.1	87.30
Silver	0.298	0.33	90.30

III. CONCLUSION

The content and purification of the metals recovered are satisfactory and also this proves that the electrowinning process is also satisfactory. Now a Plant can be developed with the same process and also the economics of the project can be considered.

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