Environmentally Sound Recycling Technology of Scrap Printed Circuit Boards for Developing countries

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Abstract

From the use of renewable resources and environmental protection viewpoints, recycling of waste printed circuit boards (PCBs) receives wide concern as the amount of scrap PCBs increases. However, treatment for waste PCBs is a challenge due to the fact that PCBs are diverse and complex in terms of materials and components makeup. Disposing electronics waste (E-waste) in landfills, burning in incinerators or exporting abroad for disposal are no longer the options due to the strict environmental regulations. This paper presents the first results of research carried out on industrial scale smelting of *exclusively scrap PCBs* in an indigenously designed and developed pilot plant of 1 ton scrap PCBs per day capacity for the recovery metals. Initially 'Black copper' is produced, then 'fire refined copper' using Top Blown Rotary Furnace (TBRF) and finally electro refined Copper. The process also extended to recover silver and gold. Innovative processing of scrap PCBs ensures the savings of water, energy and environmentally acceptable emission like carbon dioxide, sulphur dioxide and also compares the parameters available for the extraction of copper from naturally occurring ore. Emission of oxides of sulphur, Nitrogen dioxins and furans are prevented from polluting the atmosphere with the help of an indigenously designed gas cleaning system. Low cost technology ensuring significant reduction in the carbon foot print can be easily replicated in the E-waste generating cities of India and also other developing countries.

.**Key words:** Metals recovery, Resource utilisation, Recycling Technology, Solid waste Disposal, Scrap PCBs, Sustainability Urban mining,

1 Introduction

Printed circuit boards (PCBs) are integral part in majority of electronic systems and are commonly found in consumer electronics, defence applications and medical equipments etc. PCBs are the core element in all electronic units. The rapid innovation in technology has resulted in availability of cheaper and better electronic products in the market making products obsolete faster and shortening the product life. As a result electronic system gets outdated anc obsolete much earlier than expected. PCBs constitute to about 3% of the total electronic scrap by weigh [1].Handling of PCB waste is a serious problem due to the toxic nature of materials present and problems associated with the landfill. Manufacturers government agencies and users are now looking fo environmentally sound recycling technology of E waste. Besides proper disposal, economical recovery of precious and exhaustible materials is also a matte of interest. E-waste generated should be utilised a valuable source of metals and also source of energy PCBs though a small portion of the entire E-waste contain high value metals. Recovery means physica recycling of materials plus energy recovery as heat afte feeding the organic parts of waste in the smelte [2].Scrap PCBs contain metals, non-metals organic compounds. Each of the above is approximately 33% o the mass of PCBs. PCBs are mainly epoxy resins in board laminate and other elements such as Carbon 18.1%, Hydrogen1.8%, Nitrogen 0.32% Oxygen 6.03% Bromine 5.07%, Antimony 0.45%. Epoxy resin is also filled with brominated flame retardants such as Tetra bromobis phenol-A (TBBPA) to decrease the flammability and to increase the temperature resistance Antimony (Sb) is also used due to its additiona effectiveness in reducing flammability. Scrap PCBs on an average can generate 421MJ/kg of energy [3].

1.1 Global Scenario:

E-waste management through traditional methods such as disposing in landfills, burning in incinerators or exporting abroad for disposal are no longer options due to the strict environmental regulations. Fortunately, the presence of valuable metals in scrap PCBs of the E-waste and increasing demand for the metals as well as complexities of the currently available primary raw materials make recycling an attractive and viable option both environmentally and economically [4]. Recycling of scrap PCBs has been paid attention as metals including precious metals are present concealed with the organic matter containing about 5% Bromine. Recovery of metals from scrap PCBs is not as easy as these metals extracted from their corresponding naturally occurring ores. Because during pyro metallurgy of scrap PCBs by-products like Hydrogen Bromide, toxic brominated polycyclic aromatic hydrocarbons released not only damage the quality of metals recovered but also the environment[5].Since the environmentally unsound and unscientific methods are being practiced predominantly in informal sector to recover metals from E-Waste in the last about two decades has created a global challenge, especially in the developing countries [6] [7] [8]. Methods practiced by informal sector to recover metals and non metals from E-waste have been the cause of exposure to toxic chemicals reported from various developing countries including China [9][10]India [11][12][13] Vietnam [9] [10] [14][11]Philippines [13] and Ghana [14][15] [16].

1.2. Indian Scenario

India is emerging as one of the world's major electronic waste generators and projected to grow at the rate of 30% annually posing grave concerns to public health and environment alike. Status of E-waste recycling by informal sector in India is not different from that of China and Vietnam. In India, about 2 million tons of E-waste is generated each year and is growing exponentially. Unfortunately about 90% of this is recycled by the informal sector which involves mainly incineration in the open air. Moradabad (Uttar Pradesh), is known as hub of informal E-waste recycling operations.

Every family in the town is specialised in one or the other process to extract metals from PCBs. Scrap PCBs are depopulated in open area using a gas torch (Fig.1). Workers do not use Personal Protection Equipments (PPEs) and thereby they are exposed to hazardous materials. Many other cities in India including Delhi, Mumbai and Bangalore also witness e-waste recycling environmentally unsound methods **[17] [18] [19]**.Exhaustive study conducted on environmentally unsound methods practiced by informal sector in Bengaluru has revealed that workers adopt hazardous and dangerous method of amalgamation to recover precious metals from segregated components of E-waste **[20]**[21]**[22] [23]**.The amalgamation process involves recovery of precious metal by heating the amalgam on a hot frying pan in open air, when inhaling of hazardous mercury vapours by the workers is inevitable. Even children are involved in the recovery of small amount of precious metal by heating the amalgam on a hot frying pan without their knowledge that they are inhaling hazardous mercury vapours.

1.3. Need for the present study:

Due to non-availability of low cost furnace to extract metals exclusively from the scrap PCBs, hitherto *'end to end'* recyclers in India have been exporting

Fig.1 Unscientific depopulation of PCBs

PCBs to Belgium and Japan for the recovery of concealed metals. To make the metal recovery process economical, profitable and also to run the furnaces round the clock, blend of PCBs and the ore concentrate is smelted together in the developed countries. Such an arrangement is however not possible in India as the supply of PCBs to an approved recycler is a challenge. This is mainly because 90% of E-waste generated is reaching the informal sector in spite of enactment of E-waste Rules in India **[24]**.The way electronic equipments are produced, used and disposed is unsustainable and thereby rapidly depleting our planet's natural resources**.** India producing about 2 million tons of E-waste annually ranks fifth amongst other nations worldwide. Recovery of mainly copper from scrap PCBs gains importance for the following reasons.Primary copper production is a major activity in the mining sector, consumes more water than any other major metal **[25]**.

- Recovery of copper from the secondary like scrapPCBs considerably reduces carbon foot prints, no solid residues (tailings) are left behind which might cause disposal problems [26].

To address the environmental problems caused by unscientific methods of recovering metals from PCBs, to conserve earth resources for sustainability and to bring the informal sector to the formal, an innovative solution of environmentally sound method of E-waste recycling carried out is presented in the study. Metals recovered from scrap PCBs can be recycled any number of times without changing their intrinsic properties can be put back in the cycle to enhance the life span of left over natural metal resources.

2.Materials and Methodology: Depopulated shredded PCBs (Fig,2) Dried cow dung briquettes lased with depopulated shredded PCBs, fluxes, low ash, low sulphur (0.6 %) containing metallurgical grade coke as fuel and oxygen enriched air have been used in the process.

2.1. Smelter: Use of smelter furnace is the first step in the recovery of metals operations from PCBs. Innovative, In India this is the first time indigenously designed and fabricated; low cost equipments have been used for a capacity of smelting one ton of PCB per day. The smelter used at present is of steel, lined inside with insulation and rightly chosen refractory bricks suitable exclusively for the smelting of scrap PCBs (Fig.3).

Fig.2.Depopulated, shredded PCBs

2.2. Gas cleaning system:

Specially designed and fabricated in-house 'gas cleaning system' ensures reducing hazardous gases allowing only clean air to be let out through the chimney. This integrated gas cleaning system coupled with the furnace makes the entire process of recovery of metals from PCBs environmentally sound.

2.3 Methodology:

Methodology of extracting electrolytic grade copper from shredded scrap PCBs involved the following stages

2.3.1 Smelting to produce black copper
2.3.2 Stack analysis
2.3.3 Fire Refining of 'black copper' using TBRF to 'anode grade' copper
2.3.4 Conversion of 'anode grade' copper to' cathode grade' copper by electrolytic refining

2.3.1 Smelting to produce 'black copper':

Functioning of the indigenously designed furnace is similar to the traditional Blast furnace. Preheated furnace was fed with, briquettes lased with shredded scrap PCBs, coke as fuel and oxygen enriched air blown to attain a temperature of about 1200^0C-1300^0C.

Fig.3.Indigenously designed & fabricated smelter

Once the free flow of molten metal and slag from the outlet of the smelter was noticed, a sample of the metal collected separately was sent for analysis mainly to estimate % purity of copper, gold and silver.

Fig.4 Ingots of 'Black copper'

This molten metal and slag associated are collected in to moulds and the ingots were allowed to cool to room temperature. Each trial furnace ran nonstop for at least 10-12 hours. The separation of the solid metal (ingot) from the slag continued. Solid metal so collected was labelled as 'black copper" (Fig.4). Data of consumption of raw materials, quantity of black copper & slag produced, energy consumed, etc. have been recorded for every smelting trial.

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To make the entire process economical, furnace had To be run nonstop for at least 12-15 hours.

Fig. 5 Fire refined copper poured out from TBRF

2.3.2 Stack Analysis:

The very objective of the present study on the extraction of metals exclusively from PCBs was to ensure a robust, sustainable and environmentally sound process. Therefore, the study of emissions during smelting has been viewed more seriously than the extraction of metals. The stack analysis therefore was conducted. These vital experiments were out sourced to laboratories approved by the Central Pollution Control Board (CPCB) of India. Literature survey done indicated that *there are no* references for the emissions and the permissible limits of particulate matter SOx, NOx, CO, CO_2 and Non Methane Hydrocarbons (NMHC) during the extraction of metals from PCBs. Therefore, in the present study stack analysis was also simulated with a small batch of shredded PCBs without gas cleaning system. The observations have been separately recorded for both the trials. Flue gas analysis for dioxins and furans also has been conducted before feeding briquettes in to the furnace and also during smelting.

2.3.3. Fire Refining:

Black copper obtained by smelting was subjected for ‘fire refining’ in a TBRF with suitable fluxes (Fig.4). A sample of molten metal collected was analysed mainly for the purity of refined copper, silver and gold. Remaining bulk of the molten metal was poured in to rectangular shaped moulds to get ’Refined copper’ bars (Fig.5).

Fig. 6 Bars of ‘fire refined’ copper

2.3.4 Electrolytic refining:

Fire refined copper bars were subjected to electrolytic refining with copper sulphate as an electrolyte taken in a tank of capacity 1000 litres. Number of stainless steel cathodes, each of dimension 900 mm x 900 mm x 1.6 mm and bars of fire refined copper have been used as anodes. Electrolysis was carried out at 200 amps and voltage ranging from 1V- 1.6 V. Copper deposited on all the cathode sheets was harvested once in fortnight and quantified (Fig.7). Concentration of copper in the electrolyte and pH to be maintained for optimum efficiency was monitored. Anode slime collected has been stored separately for the recovery of precious metals like gold and silver.

Fig.7 Electro refining of Copper

3. Results and Discussion:

Sample buttons of 'black copper' 'fire refined copper' and cathode copper have been analysed using PANanalytical Epsilon-1 EDXRF Equipment and are presented in (Fig.7).The labelled peaks indicate presence of Cu, Au and Ag respectively in black copper. EDXRF results presented in (Table 1) reveal that fire refining of 'black copper' with suitable fluxes in TBRF not only enhanced the purity of Copper from 87.8% to 98.9% ('anode grade), but also enriched gold from 0.10454% to 0.16%.

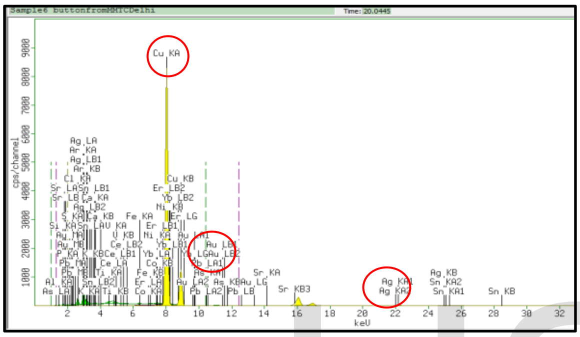

Fig.8. EDXRF spectrum of 'fire refined' copper showing Cu, Au and Ag

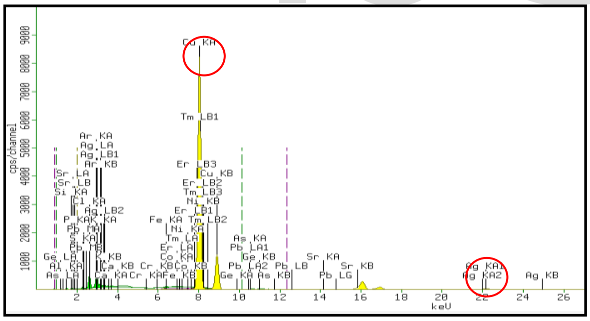

Fig.9 EDXRF spectra of electro refined copper showing, 99.4% copper 0.1% Ag. Energy peak for Au absent.

Table1. EDXRF results showing Cu, Ag and Au in fire refined copper

Metal	Black copper (Produced by smelting) (%)	Anode copper (Fire Refined Copper) (%)	Electro refined copper (%)
Copper	87.6120	98.6	99.4%
Silver	0.354	0.36	Collected In 'anode slime'
Gold	0.104	0.16	

Table2.Stack Analysis conducted during smelting

Parameter	Stack analysis with gas cleaning system coupled with the smelter (During smelting)	Simulation
Particulate matter in mg/Nm3	90.7	11.0
SOx in mg/Nm3	Less than 0.1	256
NOx in mg/Nm3	0.27	59.5
CO in ppm	Nil	Nil
CO_2 in %	Nil	0.15%
Non Methane Hydrocarbons (NMHC) in ppm.	Nil	94ppm

Table 3 Monitoring of Dioxin &Furan

Emission	Before feeding briquettes in to the smelter at a Temp. of about 1250^0 C	Smelting with briquettes fed in to the smelter at a temp. of about 1350 ^{0} C
Dioxins: 2,3,7,8 TCDD (2,3,7,8-tetra chloro dibenzo) (1,4) dioxine	< 2.5 µg/Nm3	< 2.5 µg/Nm3
Furans , 2,3,7,8 TCDF (2,3,7,8,Tetrachloro Di Benzeno Furan)	< 2. 5 µg/Nm^3	< 2.5 µg/Nm^3

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At 200 amps and voltage ranging from 1V to 1.6 V, 0 .4492 kg/Ah of copper was found to be deposited over cathode. EDXRF spectral analysis of electro refined copper deposited on the cathode indicated the purity of 99.4 % where as the energy peak corresponding to gold was absent. Electro refined copper was found to contain still 0.1% silver. This clearly showed that the precious metals like silver and gold present in the bars of fire refined copper have been collected in the 'anode slime' (Fig. 8)

.Smelting scrap PCBs, copper of 87.8 % purity could be recovered in an environmentally sound manner.

A small amount of copper still trapped in the 'slag' could be recovered by resmelting the same with the fresh batch of the 'charge' which makes the process more resource recovery efficient and economical. (Table2) presents the stack analysis results recorded during smelting and 'simulation' process conducted without gas cleaning system.

Table 4. Environmental benefits of recovery of copper from scrap PCBs over that recovered from primary source-ore

Traditional Mining Open cast mining; One ton Cu Produced (Ore with 3% Cu) Established Bench mark parameters)		**Urban Mining** One ton Cu Produced (From scrap PCBs with average 25% Cu) (present study)	
Process	**Consumption/ Envi. Burden**	**Process**	**Consumption/ Envi. Burden**
Rich grade Ore required	33.2 tons	Scrap PCBs required	4 tons
Mining & Beneficiation	33000 MJ	shredding	750.35 MJ
Fire refining	2800 MJ	Fire refining	1700 MJ
Electro refining	3500 MJ	Electro refining	1700 MJ
Total Consumption	**49900MJ**		**39687.85 MJ**
Water	3115 k litres	Water	Required only for Electro refining- Depends upon bath capacity
Environmental Burden			
CO_2 emission	1250 tons	CO_2 emission	0.44 ton
SO_2 emission	2100 kg	SO_2 Emission	21.6 kg (scrubbed)
Solid residue left Behind	32.3 tons Copper Ore Tailing(COT	Solid residue left behind	No residue left behind

Flue gas analysis conducted revealed that the emissions of NOx, SOx, CO particulate matter are within the permissible limits.SO_2 released by burning of coke containing 0.6% sulphur is all scrubbed in the gas cleaning system. Quantity of Dioxin & Furans (Table 3) before introducing the briquettes and during smelting with briquettes containing PCBs being the same suggested that there are no emissions of Dioxins and Furans during smelting and therefore the method practiced is environmentally sound. Data presented in (Table 4) suggests several benefits recovery of copper from scrap PCBs such as-

- For the production of 1 ton of copper, 33.2 tons of primary source (ore) obtained by deep mining/pit mining is required where as in the present study only about 4 tons PCBs available right on the surface are enough. This proves that present recycling technology helps mineral substitution.

- Savings on energy of 10212.15MJ(20.5% savings) makes the process more economical. 3115 k litres of water (100 % saving) per ton of copper produced from scrap PCBs as compared to copper produced from its corresponding ore is the significant saving. Water in the present process used during scrubbing is recycled and reused. Only small amount of water (non recurring) is needed for electro refining stage.

- Significant reduction in carbon foot print from 1250 tons to 0.44ton (1249.66 tons) is recorded in the process of recovery of copper from scrap PCBs as compared to extraction of Cu from the primary source respectively proves environmentally sound method practiced in the present study.

- In the traditional mining of copper from primary source about 32.33 tons of tailing left behind occupies valuable space and poses disposal problems. It is significant to note that there is no tailing dump, no botheration of effluent treatment in the present technology of recovery of copper from scrap PCBs smelting.

4. Conclusion:

Present **t**echnology developed using local skill to recover copper, with substantial saving on energy and water boosts resource recovery and conserves limited left over non renewable mineral resources for long term sustainability. Becomes the technology becomes more profitable when silver and gold from 'anode slime' collected during electrolytic refining of copper recovered chemically. Therefore, there is an urgent need to introduce the present technology for recovering metals from PCBs not only in India but also in the other developing countries. Smelter coupled with gas cleaning system is a crucial part of E-Waste recycling chain, which can further increase in the future.Helps in bringing informal sector to the formal stream for a better society adhering to environmental practices, reversing the harm that has been already caused.

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