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DEPARTMENT OF CHEMICAL ENGINEERING

CP301: DEVELOPMENT ENGINEERING PROJECT

PROCESS DESIGN FOR THE EXTRACTION OF COPPER FROM E-WASTE

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## Abstract

One of the major problems our country is facing is the lack of technology in treatment of e-waste. The rate of generation of e-waste is greater than the rate at which e-waste is treated. Since e-waste contains lot of economically valuable and toxic metals, there is an urgent need to treat and handle the e-waste. This study investigates about the process that can be used for the extraction of metals from the e-waste. A number of methods like physical treatment methods, pyrometallurgy, hydrometallurgy etc. were studied. As per the investigation, we found out that pyrometallurgy is the most efficient method for the extraction. Economic analysis is also performed to check the feasibility of the process.

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## 2 Introduction

Electronic waste, commonly known as e-waste, refers to discarded electronic products such as computers, televisions, laptops, mobile phones, and so on. It contains a wide range of components, including metals like copper, nickel, iron, gold, silver, platinum, palladium, lead, mercury, cadmium and arsenic, as well as non-metals, such as plastic, ceramic and rubber [17].

The disposal of e-waste is a rapidly growing problem which has increased significantly in the past decades. According to the UN's Global E-waste Monitor 2020, a total of 53.6 million tons of e-waste was generated worldwide in 2019, of which India, the third largest contributor, generated 3.2 million tons [13]. In most cases, this massive amount is dumped without suitable treatment, due to a lack of a proper recycling facility. This leads not only to a critical loss of valuable precious metals, but also pollutes the environment with several toxic substances which can cause serious health hazards.

Table 1: Toxic metals present in Electronic devices, and their effects [4]

Metal	Impact
Lead (Pb)	Damage of nervous and circulatory systems in adults, skin damage, headaches, nausea
Cadmium (Cd)	Respiratory system issues, kidney bones problems, carcinogenic, defect in neurodevelopment of fetus and young children
Mercury (Hg)	Affects brain and central nervous system, causes tremor, depression and behavioral disturbances
Chromium (Cr)	Defects in neurodevelopment, multiple organ failure, carcinogenic, and leads to oxidative stress
Arsenic (As)	Cardiovascular diseases, breathing difficulties, gastrointestinal disturbances, liver and renal disease

The metal content in e-waste may be upto 60%, because of which recycling and recovery of metals from e-waste is a study of great importance, especially for nations which are unable to mine precious metals. This requires enforcing of rules for proper collection, dismantling and treatment, the right infrastructure, an efficient reporting process, and more awareness among consumers on the hazards of improper disposal of e-waste.

Over the years, certain laws have been published for e-waste management. Most recently, the E-Waste (Management) Rules, 2022, has been introduced for compulsory authorisation of the dismantling and recycling units from the concerned State Pollution Control Boards (SPCBs)/ Pollution Control Committees (PCCs). It mandates that every producer of Electronic and Electric Equipment shall ensure that their products do not contain hazardous components like lead and mercury above the maximum permissible composition. It also provides for skill development, monitoring and ensuring the safety and health of workers involved in the recycling process.

### 3 Literature Survey

From various analysis and studies, we understood that E-Waste management is one of the major issue that we all are facing today. For the upcoming years, India will generate e-waste of 5.25 million tons by the year of 2026 which is shown in the figure 1. One of the most efficient ways to use e-waste is to extract metals from it. For that, it is essential to have a thorough awareness of the composition of different metals that make up e-waste, as well as the proper extraction techniques that must be used. Various metallic constituents in the e-waste is shown in the figure 2 below.

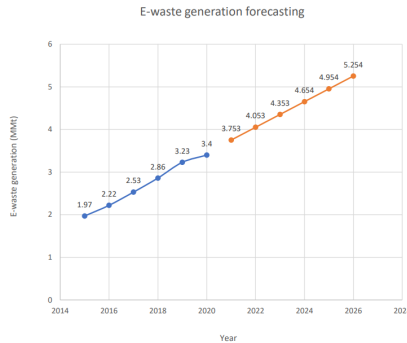


Figure 1: Generation of E-waste in India

Metallic Constituents of E-waste

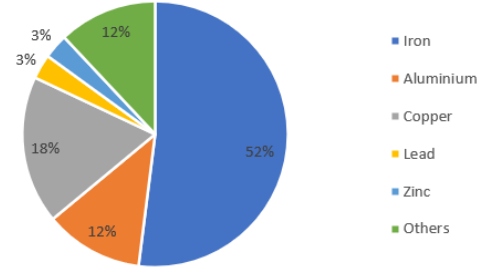


Figure 2: Metal constituents of e-waste [3]

Almost all of the waste electrical and electronic equipment (WEEE or e-waste) contains waste printed circuit boards (WPCBs), which make up 4-7% of its weight [11]. PCB is a crucial part of every electronic device since it mechanically and electrically connects all other electronic components [8]. Waste PCBs (WPCBs) contain more than 40 different types of metals in a variety of amounts, including those that are detrimental to the environment (like Pb, Cr, As, Cd, and Hg) and others that have commercial value (like Cu, Sn, Au, Ag, and Pd) [10]. In conclusion, we can consider WPCB as an alternative source for the extraction of metals other than natural resources.

Table 2: Metal composition of PCBs in different electronic equipment [18]

Metals(Wt%)	Computer PCBs	Laptop PCBs	Mobile PCBs	TV PCBs
Cu	19.40	20.13	18.4	10.31
Zn	1.90	1.89	1.27	1.15
Fe	1.60	1.52	1.54	6.64
Pb	1.60	1.74	0.46	2.26
Ni	0.037	0.064	0.1	0.05
Cd	0.081	0.071	0.077	0.014
Cr	0.005	0.0055	0.0099	0.0057
Mn	0.005	0.0045	0.0094	0.0039

From the understanding of Table 2, Cu is the metals which have highest composition in all the PCBs. Various studies are showing that we can extract around 20% of Cu from PCBs but it is only about 0.2-0.7% from Cu ores [14]. Also the market value of metals which are extracted from 1000 kg of PCB is shown in the Table 3. The economic effectiveness of extracting copper from PCBs is evident from the table.

Table 3: Market value of the metals recovered from PCBs [19]

Recovered metals	Weight	Approximate cost(in Rs)
Gold	279.3 g	Rs.14,51,183 (Rs.51,95,782/kg)
Precious metals (Pd,Pt,In)	93.31 g	Rs. 3,15,595
Copper	190.512 kg	Rs. 1,22,497 (Rs. 643/kg)
Aluminium	142.152 kg	Rs. 31,273 (Rs. 220/kg)
Lead and Tin	30.844 kg	Rs. 11,811
Silver	450 g	Rs. 35,535 (Rs. 72,300)

### 3.1 Methods for the extraction of Cu from E-waste

In the present world, industries use several different methods to extract Cu from E-waste/PCBs. First, a pre-treatment is done by physical processes in order to increase the surface area and to concentrate the metal content in PCBs. Subsequently, chemical processes such as pyrometallurgy or hydrometallurgy are used to extract Cu.

#### 3.1.1 Physical Extraction process

The physical extraction process is considered as the pre-treatment method for the extraction of various metals from E-waste. The main purpose of this process is to separate metals from non-metals in E-waste/PCB, on the basis of physical properties of the material such as size, magnetic properties, electrostatic behaviour etc.

##### 1. Sorting

Sorting is the initial step for the extraction process which arranges and categorizes the E-waste into different components like printed circuit boards (PCBs). It can be done both manually and automatically(AI sorting system).

##### 2. Shredding/Crushing

Shredding or Crushing is the stripping of metals from the base plates of waste PCBs[4]. The PCB is first subjected to a reduction in size using a crusher (eg. hammer crusher, rotary crusher, shredder), and then pulverized further using a ball mill or hammer mill [8].

##### 3. Magnetic separation

Magnetic separation is used to separate metals which have magnetic properties (ferrous) from non magnetic metals (non ferrous). This process is usually carried out by a magnetic separator, which can easily separate fine particles which have poor magnetic properties [4].

##### 4. Froth flotation

Froth flotation is a method which selectively separates materials based on their hydrophilic and hydrophobic nature. In this technique, particles of interest are physically separated from a liquid phase due to a difference in the ability of the froth to selectively adhere to the surface of the particles, which is based upon their hydrophobicity.[4]

##### 5. Electrostatic separation

In electrostatic separation, the material is separated on the basis of their electric conductivity and resistivity properties. This method has many advantages including less environmental impact, less energy requirement and easier operation [24].

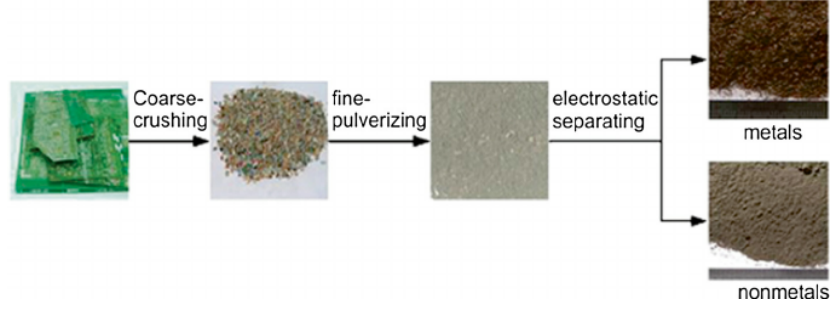
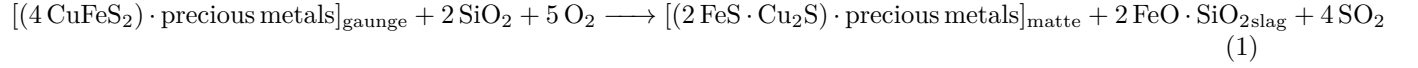


Figure 3: Physical pre-treatment process[2]

### 3.1.2 Pyrometallurgical method

Pyrometallurgy is the conventional method used to recover non ferrous and precious metals from electronic waste. It involves a series of steps which require high amounts of temperature. In this process, dried powder feed is liquefied in a furnace or in a molten bath to remove impurities such as plastics and other metals. The reactor operates at 1250 C. The feed entering the reactor will get heated up beyond its melting point by the action of air and coke. This process is known as smelting. In Cu recovery from e-waste, some precious metals with Cu and iron sulfide form liquid matte while other metal sulfides oxidized to metal oxides and produced slag, after undergoing this process. [20].



The matte produced in the above equation is further oxidised and converted to blister copper in conversion process which is happening in the converter [20].

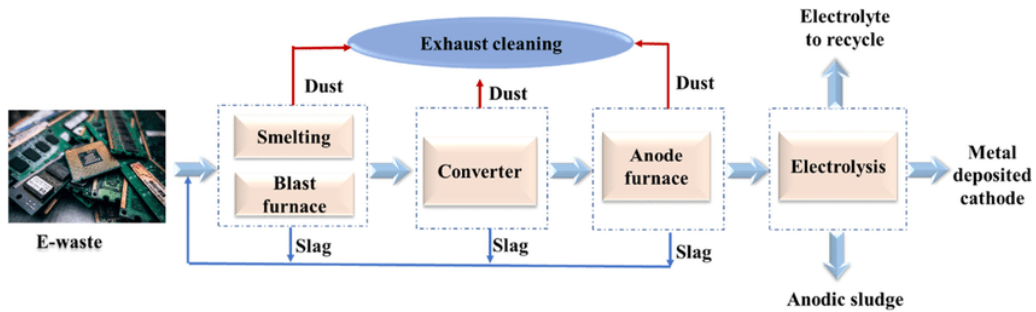
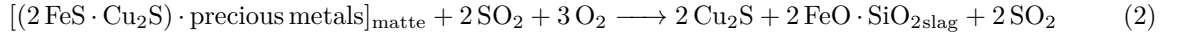


Figure 4: Process flow diagram of pyrometallurgy process [4]

As per studies, pyrometallurgy is considered to be a highly popular and economically efficient process which has the capacity to handle several tons of e-waste per year. However, this process also has some disadvantages such as high investment, high energy demand and release of toxic fumes to the environment.

### 3.1.3 Hydrometallurgical method

In hydro-metallurgical processes, leaching is done to extract metals as soluble salts using various solvents as acid, alkali, and ionic liquids. Some of the commonly used leaching agents are thiosulphate, thiourea, cyanide and halide. The leaching ability of metals from waste PCB are in the order  $Pb > Cu > Zn > Al > Ni > Cd > Se > As > Ba$  [4]. Different hydrometallurgical processes are shown in the figure below. The safety concern for hydrometallurgy is very high because of the use of various leachates which are highly toxic and corrosive, such as the cyanide leachate.

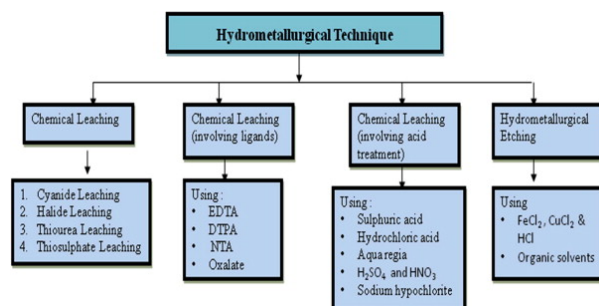


Figure 5: Different types of hydrometallurgical process [17]

### 3.1.4 Biological methods

The biological extraction approach for recovering metals has grown in popularity during the past ten years. Because biometallurgy has the potential to revolutionize the mineral industries, a wide range of sectors have expressed a strong interest in this new technology. Microorganisms (e.g., *Thiobacilli* sp, *Pseudomonas* sp, *Aspergillus* sp., *Penicillium* sp, etc.) are used in this method to extract metals from e-waste, taking advantage of their natural ability to transform the solid metallic components to the extractable or soluble form [4]. Although this is a promising and environmental friendly method for Cu extraction from PCBs, it has some limitations as well. Studies and research need to be done for the estimation of optimal pH, nutrients requirements and temperature for the growth of microbes. Since we are using microbes, the biological method also requires a lot of time to complete the process.

## 4 Problem Statement

From the literature review, we understand that copper is present in highest amounts in PCBs. There are several different processes for extraction of copper, such as the hydrometallurgical method, pyrometallurgical method, biological and hybrid methods. For industrial purposes, pyrometallurgical method is most efficient method. The goal of our project is to **design complete process for extraction of copper from PCBs**.

## 5 Methodology

The main aim of our project is to extract copper from PCBs of the e-waste through pyrometallurgical process. In our process, we are assuming 10 tons of e-waste as feed. E-waste will go through a series of processes/operations: Dismantling, shredding, milling, drying, smelting and converter.

### 5.1 Pre treatment analysis

First, in order to calculate the amount of PCBs present in e waste, we took four major e-waste equipment that are being generated by industries or households: Laptop, TV, Mobile and Computer. We have assumed 2500 kg of each equipment is present in 10 tons of e-waste.



Table 4: Average weight of PCB present in 2500 kg of each equipment

E-waste	Laptop	TV	Mobile	Computer	Total
Weight of PCB in 2500 Kg	400	192.3	500	111.1	1203.4

From our calculation, we obtained 1203.4 kg of PCB from 10 ton of e waste after dismantling. The 1203.4 kg of PCB is sent to the Double shaft waste PCB shredder. The shredder reduces the size of PCB. The output from shredder then goes to miller (Hammer mill) as feed for further reducing size to powder form. By converting the waste PCBs to powder form, we are concentrating the metal content present inside it and reducing the energy requirement for melting process. The 1095.8 Kg output of miller is fed to the dryer. The dryer reduces the moisture content of feed coming from miller as per the moisture requirement of smelter (around 10-15 %). Based on feed particle size, feed category and production rate, the continuous rotary dryer is considered.

## 5.2 Design of dryer

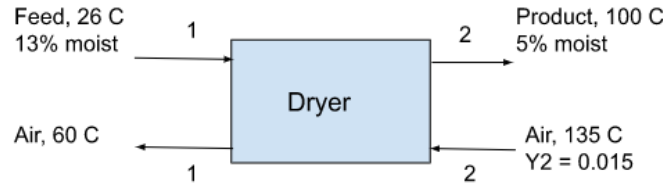


Figure 6: Dryer

Basis is taken as 1 hr. The feed enters the dryer at  $T_{F1}=26$  C and leaves at  $T_{F2}=100$  C whereas the air is entering at  $T_{A2}=135$  C. The operation occurs in counter current mode. It is assumed that the outlet temperature of air stream is  $T_{A1}=60$  C. The specific heat capacity for solid PCB,  $C_p$  is 0.396 kJ/kgK.  $Y_1, Y_2$  represent absolute humidity of air.

Mass of feed = 1095.8 kg

Mass of dry solid,  $L_s = 1095.8(1-0.13) = 953.346$  kg

Mass fraction of water in feed (on dry basis),  $X_1 = \frac{13}{87} = 0.1494$  kg  $H_2O$ /kg solid

Mass fraction of water in product (on dry basis),  $X_2 = \frac{5}{95} = 0.05263$  kg  $H_2O$ /kg solid

Mass of water evaporated =  $L_s(X_1 - X_2) = 92.255$  kg

Amount of product from dryer =  $1095.8 - 92.25 = 1003.545$  kg

Enthalpy of input feed to the dryer,  $H_{F1} = (C_p + 4.187X_1)(T_{F1} - T_o) = 26.56$  kJ/kg

Enthalpy of output coming from the dryer,  $H_{F2} = (C_p + 4.187X_2)(T_{F2} - T_o) = 61.636$  kJ/kg

Enthalpy of air stream entering the dryer,  $H_{A2} = (1.005 + 1.88Y_2)(T_{A2} - T_o) + 2500Y_2 = 176.98$  kJ/kg

Enthalpy of air stream leaving the dryer,  $H_{A1} = (1.005 + 1.88Y_1)(T_{A1} - T_o) + 2500Y_1 = 2612.8Y_1 + 60.3$  kJ/kg

In above calculations, reference temperature  $T_o$  is taken 0. The Overall Mass balance and Enthalpy balance

can provide the value of  $Y_1, G_s, L_s$  represent mass flow rate of dry air and dry solid respectively.

$$L_s(X_1 - X_2) = G_s(Y_1 - Y_2)$$

$$G_s(Y_1 - 0.015) = 953.346(0.1494 - 0.05263)$$

$$G_s = \frac{92.55}{Y_1 - 0.015}$$

$$L_s(H_{F2} - H_{F1}) = G_s(H_{A2} - H_{A1})$$

$$953.346(61.636 - 26.56) = G_s(176.98 - 2612.8Y_1 + 60.3)$$

Substituting the expression of  $G_s$  in terms of  $Y_1$  in above equation, we get,

$$Y_1 = 0.04104$$

$$G_s = 3542.819 \text{ kg/h}$$

Humid volume of air entering dryer,  $v_{H2} = (\frac{1}{28.97} + \frac{Y_2}{18.02})22.4(\frac{T_{A2}+273}{273}) = 1.183 \text{ m}^3/\text{kg dry air}$

Humid volume of air exiting dryer,  $v_{H1} = (\frac{1}{28.97} + \frac{0.04104}{18.02})22.4(\frac{60+273}{273}) = 1.0054 \text{ m}^3/\text{kg dry air}$

Maximum volumetric gas flow rate,  $Q = G_s v_{H2} = 1.1642 \text{ m}^3/\text{s}$

Maximum air velocity,  $v_a = 1.2 \text{ m/s}$

$$(A_c)(v_a) = Q$$

$$(\frac{\pi d_c^2}{4})(1.2) = 1.1642$$

$$d = 1.1114 \text{ m}$$

Energy added through the air stream to the dryer =  $(H_{A2})G_s = 627.01 \text{ MJ}$

Energy released through the air stream from the dryer =  $(H_{A1})G_s = 593.5 \text{ MJ}$

Before calculating length of dryer, number of transfer units are determined for three different temperature zones of dryer.

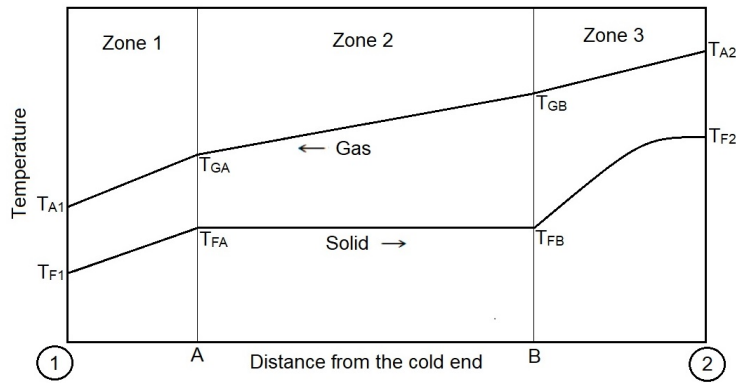


Figure 7: [Temperature Profile in Dryer](#)

The values  $T_{GA}, T_{GB}$  represent the gas temperature and  $T_{FA}, T_{FB}$  represent the solid temperature at zone boundaries.

### Zone 3

In zone 3, the amount of water left for vaporisation is very low. The temperature of solid,  $T_{FB}$  is considered as wet bulb temperature of air. Let's assume  $T_{FA}=T_{FB}=41$  C.

Enthalpy of solid at inlet to zone 3,  $H_{FB} = (C_p + X_2(4.187))(T_{FB} - T_o) = 25.271$  kJ/kg dry solid

Humid heat of gas entering zone 3,  $C_{HB} = 1.005 + 1.88Y_2 = 1.033$  kJ/kg K

The  $C_{HB}$  will remain constant in zone 3 as change in humidity is negligible.

Heat balance over zone 3,

$$\begin{aligned} L_s(H_{F2} - H_{FB}) &= G_s(C_{HB})(T_{A2} - T_{GB}) \\ 953.346(61.636 - 25.271) &= 3542.819(1.033)(135 - T_{GB}) \\ T_{GB} &= 125.53 \text{ C} \end{aligned}$$

Temperature of gas/air entering zone 3,  $T_{GB} = 125.53$  C

From psychrometric chart, for  $Y = 0.015$ , Adiabatic saturation temperature of air = 40.5 C

This comes close to the assumed value of  $T_{FB}$ , 41 C.

At boundary B,  $\Delta T_B = T_{GB} - T_{FA} = 125.53 - 41 = 84.53$  C

At end 2,  $\Delta T_2 = 135 - 100 = 35$  C

Log mean temperature difference in zone 3,  $\Delta T_m = \frac{84.53 - 35}{\ln(\frac{84.53}{35})} = 56.172$  C

Number of heat transfer units,  $(N_{tG})_3 = \frac{T_{A2} - T_{GB}}{\Delta T_m} = 0.1686$

## Zone 2

To calculate number of transfer units,  $(N_{tG})_3$ , first  $T_{GA}$  value is determined through enthalpy balance.

$$\begin{aligned} L_s(H_{FB} - H_{FA}) &= G_s(H_{GB} - H_{GA}) \\ H_{GA} &= 171.665 \text{ kJ/kg} \\ H_{GA} &= (1.005 + 1.88Y_A)(T_{GA} - T_o) + 2500(Y_A) \\ T_{GA} &= 63.82 \text{ C} \end{aligned}$$

The  $T_{GA}, T_{GB}, T_{FA}, T_{FB}$  values are used to find out the no. of transfer units.

Number of transfer units,  $(N_{tG})_2 = 1.3094$

The validity of assumed value of exit gas temperature,  $T_{A1}$  is checked by doing energy balance over zone 1.

$$\begin{aligned} L_s(H_{FA} - H_{F1}) &= G_s(H_{GA} - H_{A1}) \\ 953.346(41.883 - 26.56) &= 3542.819(171.665 - H_{A1}) \\ H_{A1} &= 167.542 \text{ kJ/kg} \\ H_{GA} &= (1.005 + 1.88Y_1)(T_{A1} - 0) + 2500(Y_1) \\ T_{A1} &= 60.02 \text{ C} \end{aligned}$$

The  $T_{A1}$  value is close to the assumption of  $T_{A1} = 60$  C. Similarly, for zone 1, the no. of transfer units is determined as  $(N_{tG})_1 = 0.1355$ .

Total number of heat transfer units =  $(N_{tG})_1 + (N_{tG})_2 + (N_{tG})_3 = 0.1355 + 1.3094 + 0.1686 = 1.6135$

Average gas mass flow rate,  $G = (G_s(1 + Y_1) + G_s(1 + Y_2))/2 = 3642.09$  kg/h

Gas mass flow rate per area,  $G' = \frac{G}{3600(\frac{\pi d^2}{4})}$

Volumetric heat transfer coefficient [7],  $Ua = \frac{237(G')^{0.67}}{d} = 209.37 \text{ W/m}^3\text{K}$

Humid heat at ends,

$$\begin{aligned}C_H &= 1.005 + 1.88Y \\C_{H1} &= 1.033 \text{ kJ/kg K} \\C_{H2} &= 1.082 \text{ kJ/kg K}\end{aligned}$$

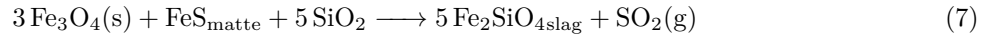
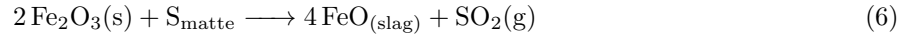
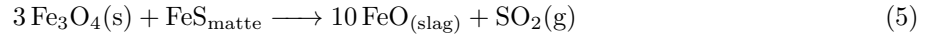
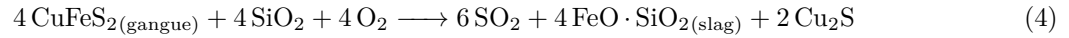
Average humid heat,  $C_H = (1.0332 + 1.082)/2 = 1.0576 \text{ kJ/kg K}$

Length of heat transfer unit [7],  $L_T = \frac{G'(C_H)}{Ua} = 5.268 \text{ m}$

Length of dryer,  $L = (N_{tG})(L_T) = 1.6135(5.268) = 8.4999 \text{ m}$

### 5.3 Smelter analysis

The major reactions that are taking place in smelter are [23] :



The overall reaction is formed by combining above equations. This represents one mole of feed:  $4 \text{ CuFeS}_2 + 6 \text{ Fe}_3\text{O}_4 + 2 \text{ FeS} + 2 \text{ Fe}_2\text{O}_3 + \text{S}$ ,  $\text{SiO}_2$  represents flux and C is the fuel. The amount of feed for the smelter is 1003.522 kg.

Molecular weight of feed = 2648.4 kg/kmol

No. of moles =  $1003.522 \text{ kg} / (2648.4 \text{ kg/kmol}) = 378.916 \text{ moles}$

Material balance for Smelter:

1 mol of feed = 2 moles of  $\text{Cu}_2\text{S}$

378.916 moles of feed = 757.83 moles of  $\text{Cu}_2\text{S}$  = 120.495 kg  $\text{Cu}_2\text{S}$

Energy balance for Smelter:

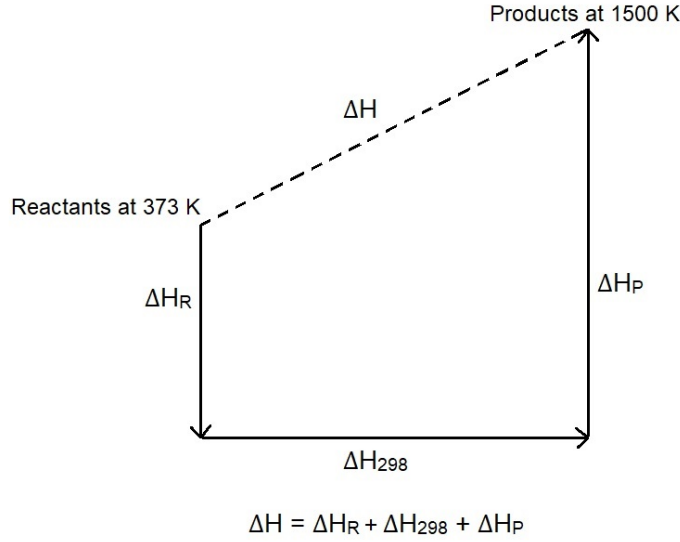


Figure 8: Reaction Path for Smelter

The smelter is operating at 1500 K. A path is devised for the purpose of energy calculations to proceed the reactants at 373 K to products at 1500 K. Because data are available for standard heats of reaction at 298 K, the most convenient path is the one which includes the reactions at 298 K [9]. This is shown schematically in the figure 8.

#### Path 1

Temperature of the reactants is brought down from 373K to 298K.

$$\Delta H_{reactants} = \sum n_i C_{pi} (T_f - T_i)$$

Specific heat capacity values [15, 6]:

$$\begin{aligned} C_{pCuFeS_2} &= 100.416 \text{ J/molK} \\ C_{pSiO_2} &= 47.973 \text{ J/molK} \\ C_{pO_2} &= 29.68 \text{ J/molK} \\ C_{pFe_3O_4} &= 155.91 \text{ J/molK} \end{aligned}$$

$$\begin{aligned} C_{pFeS(l)} &= 62.09 \text{ J/molK} \\ C_{pFe_2O_3} &= 110.114 \text{ J/molK} \\ C_{pS(matte)} &= 30.792 \text{ J/molK} \\ C_{pC} &= 9.639 \text{ J/molK} \end{aligned}$$

For reaction(4),

$$\begin{aligned} \Delta H_{reactants} &= \left[ \frac{4}{15} (C_{pCuFeS_2}) + 4(C_{pSiO_2}) + 8(C_{pO_2}) \right] (T_f - T_i) \\ &= \left[ \frac{4}{15} (100.416) + 4(47.973) + 8(29.68) \right] (373 - 298) \end{aligned}$$

$$\Delta H_{reactants} = -34.208 \text{ kJ}$$

Similarly,

$$\text{For reaction(5), } \Delta H_{reactants} = -2.649 \text{ kJ}$$

$$\text{For reaction(6), } \Delta H_{reactants} = -1.255 \text{ kJ}$$

$$\text{For reaction(7), } \Delta H_{reactants} = -20.638 \text{ kJ}$$

$$\text{For reaction(8), } \Delta H_{reactants} = -2.949 \text{ kJ}$$

$$\begin{aligned}
\text{Net energy} &= -34.208 - 2.649 - 1.255 - 20.638 - 2.949 \\
&= -61.7 \text{ kJ} \\
&= -6.17 \times 10^4 J
\end{aligned}$$

### Path 2

Heat of formation values [15, 6]:

$$\begin{aligned}
H_{fCuFeS_2}^0 &= -173.1 \text{ kJ/mol} & H_{fFeS(l)}^0 &= -68.81 \text{ kJ/mol} \\
H_{fSiO_2(s)}^0 &= -910.86 \text{ kJ/mol} & H_{fFeO(l)}^0 &= -249.53 \text{ kJ/mol} \\
H_{fO_2}^0 &= 0 \text{ kJ/mol} & H_{fFe_2O_3}^0 &= -824 \text{ spkJ/mol} \\
H_{fSO_2(g)}^0 &= 13.1 \text{ kJ/mol} & H_{fS(matte)}^0 &= -1.8 \text{ skJ/mol} \\
H_{fFeSiO_3}^0 &= -217.972 \text{ kJ/mol} & H_{fFe_2SiO_4}^0 &= -34.651 \text{ kJ/mol} \\
H_{fCu_2S(l)}^0 &= -56.488 \text{ kJ/mol} & H_{fC}^0 &= 0 \text{ kJ/mol} \\
H_{fFe_3O_4(s)}^0 &= -1120.89 \text{ kJ/mol} & H_{fCO_2}^0 &= -393.5 \text{ kJ/mol}
\end{aligned}$$

$$\Delta H_{reaction} = \Sigma H_{products} - \Sigma H_{reactants}$$

For reaction(4),

$$\begin{aligned}
\Delta H_{reaction} &= 2(H_{fCu_2S}^0) + 4(H_{fFeO.SiO_2}^0) + 6(H_{fSO_2}^0) - 4(H_{fCuFeS_2}^0) - 4(H_{fSiO_2}^0) \\
&= 2(-56.488) + 4(-217.972) + 6(-296.84) - 4(-173.1) - 4(-910.86)
\end{aligned}$$

$$\Delta H_{reaction} = 1569.936 \text{ kJ/mol}$$

Similarly,

$$\text{For reaction(5), } \Delta H_{reaction} = 639.34 \text{ kJ/mol}$$

$$\text{For reaction(6), } \Delta H_{reaction} = 351.59 \text{ kJ/mol}$$

$$\text{For reaction(7), } \Delta H_{reaction} = 7515.689 \text{ kJ/mol}$$

$$\text{For reaction(8), } \Delta H_{reaction} = -393.5 \text{ kJ/mol}$$

$$\begin{aligned}
\text{Net energy added} &= 1569.936 + 639.34 + 351.59 + 7515.689 - 393.5 \\
&= 10076.551 \text{ kJ/mol} \\
&= 3818166.02 \text{ kJ} \\
&= 3818.166 \text{ MJ}
\end{aligned}$$

$$\begin{aligned}
\text{Net energy released} &= -393.5 \text{ kJ/mol} \\
&= -149103.446 \text{ kJ} \\
&= -149.103 \text{ MJ}
\end{aligned}$$

### Path 3

Temperature of the products is raised from 298K to 1500K.

$$\Delta H_{products} = \Sigma n_i C_{pi}(T_f - T_i)$$

Specific heat capacity values [15, 6]:

$$\begin{aligned}
C_{pSO_2} &= 48.455 \text{ J/molK} & C_{pFeO(l)} &= 68.199 \text{ J/molK} \\
C_{pFeO.SiO_2} &= 51.374 \text{ J/molK} & C_{pFe_2SiO_4(slag)} &= 207.723 \text{ J/molK} \\
C_{pCu_2S} &= 81.446 \text{ J/molK} & C_{pCO_2} &= 47.76 \text{ J/molK}
\end{aligned}$$

For reaction(4),

$$\begin{aligned}\Delta H_{products} &= [6(C_{pSO_2}) + 4(C_{pFeO.SiO_2}) + 2(C_{pCu_2S})](T_f - T_i) \\ &= [6(48.455) + 4(63.735) + 2(87.446)](1500 - 298)\end{aligned}$$

$$\Delta H_{products} = 866.116 \text{ kJ}$$

Similarly,

For reaction(5),  $\Delta H_{products} = 877.995 \text{ kJ}$

For reaction(6),  $\Delta H_{products} = 386.144 \text{ kJ}$

For reaction(7),  $\Delta H_{products} = 1306.658 \text{ kJ}$

For reaction(8),  $\Delta H_{products} = 57.407 \text{ kJ}$

$$\begin{aligned}\text{Net energy} &= 866.116 + 877.995 + 386.144 + 1306.658 + 57.407 \\ &= 3494.32 \text{ kJ} \\ &= 3.49 \times 10^6 J\end{aligned}$$

$$\begin{aligned}\text{Total energy added due to all the three paths} &= 3494.32 + 3818166.02 \\ &= 3821660.34 \text{ kJ} \\ &= 3821.7 \text{ MJ}\end{aligned}$$

$$\begin{aligned}\text{Total energy released due to all the three paths} &= -61.7-14910.446 \\ &= -149165.146 \text{ kJ} \\ &= -149.2 \text{ MJ}\end{aligned}$$

## 5.4 Converter analysis

The reactions that are taking place in converter [20]:



Molecular weight of  $\text{Cu}_2\text{S} = 159 \text{ kg/kmol}$

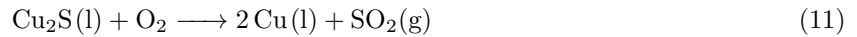
No. of moles =  $120.495 \text{ Kg}/(159 \text{ kg/kmol}) = 757.83 \text{ moles}$

Material balance for Converter:

1 mol of  $\text{Cu}_2\text{S} = 2 \text{ moles of Cu}$

757.83 moles of  $\text{Cu}_2\text{S} = 1515.66 \text{ moles of Cu} = 96.244 \text{ kg Cu}$

The overall reaction for the converter is:



Energy balance for Converter:

### Path 1

Temperature of the reactants is brought down from 1500K to 298K.

$$\Delta H_{reactants} = \sum n_i C_{pi} (T_f - T_i)$$

Specific heat capacity values [15, 6]:

$$C_{pCu_2S} = 81.446 \text{ J/molK}$$

$$C_{pO_2} = 32.972 \text{ J/molK}$$

For reaction(11),

$$\begin{aligned}\Delta H_{reactants} &= [(C_{pCu_2S}) + (C_{pO_2})](T_f - T_i) \\ &= [(87.446) + (32.972)](298 - 1500)\end{aligned}$$

$$\Delta H_{reactants} = -144.742 \text{ kJ}$$

$$\begin{aligned}\text{Net energy} &= -144.742 \text{ kJ} \\ &= -1.45 \times 10^5 J\end{aligned}$$

### Path 2

Heat of formation values [15, 6]:

$$\begin{aligned}H_{fCu_2O(l)}^0 &= -112 \text{ kJ/mol} & H_{fSO_2(g)}^0 &= 13.1 \text{ kJ/mol} \\ H_{fCu(l)}^0 &= 13.1 \text{ kJ/mol} & H_{fCu_2S(l)}^0 &= -56.488 \text{ kJ/mol} \\ H_{fO_2}^0 &= 0 \text{ J/mol}\end{aligned}$$

$$\Delta H_{reaction} = \Sigma H_{products} - \Sigma H_{reactants}$$

For reaction(9),

$$\begin{aligned}\Delta H_{reaction} &= 2(H_{fCu_2O}^0) + 2(H_{fSO_2}^0) - 2(H_{fCu_2S}^0) - 3(H_{fO_2}^0) \\ &= 2(-112) + 4(-296.84) + 6(-296.84) - 2(-56.488) - 3(0)\end{aligned}$$

$$\Delta H_{reaction} = -704.704 \text{ kJ/mol}$$

Similarly,

For reaction(10),  $\Delta H_{reaction} = 62.248 \text{ kJ/mol}$

$$\begin{aligned}\text{Net energy added} &= 62.248 \text{ kJ/mol} \\ &= 47173.4 \text{ kJ} \\ &= 47.173 \text{ MJ}\end{aligned}$$

$$\begin{aligned}\text{Net energy released} &= -704.704 \text{ kJ/mol} \\ &= -536319.322 \text{ kJ} \\ &= -536.319 \text{ MJ}\end{aligned}$$

### Path 3

Temperature of the reactants is raised from 298K to 1500K.

$$\Delta H_{products} = \Sigma n_i C_{pi}(T_f - T_i)$$

Specific heat capacity values [15, 6]:

$$C_{pCu} = 31.38 \text{ J/molK} \quad C_{pSO_2} = 48.455 \text{ J/molK}$$

For reaction(11),

$$\begin{aligned}\Delta H_{products} &= [2(C_{pCu}) + (C_{pSO_2})](T_f - T_i) \\ &= [2(31.38) + (48.455)](1500 - 298)\end{aligned}$$

$$\Delta H_{products} = 133.68 \text{ kJ}$$

$$\begin{aligned}\text{Net energy} &= 133.68 \text{ kJ} \\ &= 1.34 \times 10^5 J\end{aligned}$$



Total energy added due to all the three paths =  $47173.4 + 133.68$   
 = 47307.08 kJ  
 = 47.3 MJ

Total energy released due to all the three paths =  $-144.742-536319.322$   
 = -536464.064 kJ  
 = -536.46 MJ

## 6 Results and Discussion

### 6.1 Overall Mass and Energy balance

The below figure represents the process flow diagram with the overall mass flow.

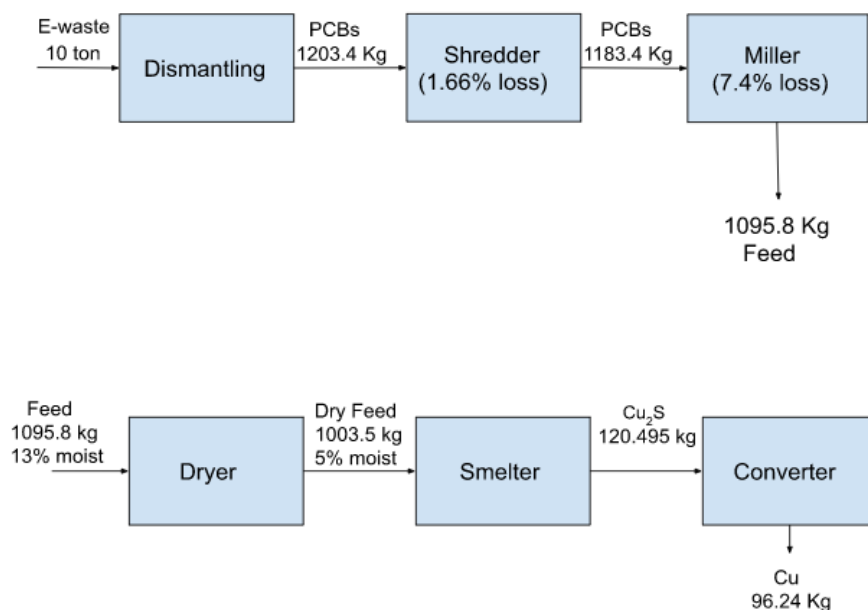


Figure 9: [Process Flow Diagram](#)

The energy balance for dryer, smelter and converter was done. The below figure shows the results of energy flow.

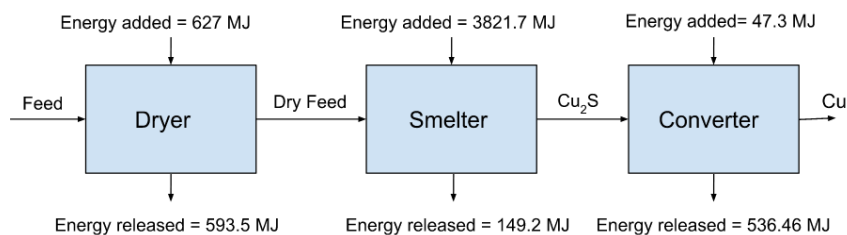


Figure 10: [Energy Flow](#)

## 6.2 Economic Analysis

Costing was done for the entire process. Capital costs of the equipment used in physical processes, as well as that of smelter and converter, were found from various sites, while that of the dryer was calculated based on the equipment area using the chart available from literature. In the following analysis, L denotes lakh while Cr denotes crore.

1. Dismantling: Cost = Rs. 35 L

2. Shredding: Cost = Rs. 13.64 L

3. Milling: Cost = Rs. 4.55 L

4. Dryer:

Diameter of dryer =  $2m$

Area of dryer =  $\frac{\pi d_c^2}{4}$

$= \frac{\pi 2^2}{4}$

$= 3.14m^2$

From chart [12], purchase cost of dryer = \$ 9000 = Rs. 7.38 L

5. Smelter: Cost = Rs. 8.2 L

6. Converter: Cost = Rs. 0.985 L

Total Capital Cost =  $35 + 13.64 + 4.55 + 7.38 + 8.2 + 0.98 = \text{Rs. } 69.75 \text{ L}$

Cost of utilities and working capital will typically be 40% and 15% respectively of total capital cost, while taxes account for 2% of this value[21].

Total Operating Cost =  $0.57 \times 69.75 = \text{Rs. } 39.76 \text{ L per month} = \text{Rs. } 477.1 \text{ L per annum}$

Total Cost per annum =  $69.75 + 477.1 = \text{Rs. } 546.85 \text{ L}$

By the end of our treatment of e-waste, we are able to extract 96.24 kg of Cu per hour. Total annual revenue generated is calculated by taking the plant to be operating for 8000 hours per year, which is the benchmark for maximum efficiency.

Market value of 1kg of Cu [22] = Rs. 751.60

Total revenue =  $751.60 \times 96.24 \times 8000 = \text{Rs. } 55.64 \text{ Cr per annum}$

Total profit generated =  $55.64 - 5.4685 = \text{Rs. } 50.17 \text{ Cr per annum}$

Break Even point analysis has been done as follows.

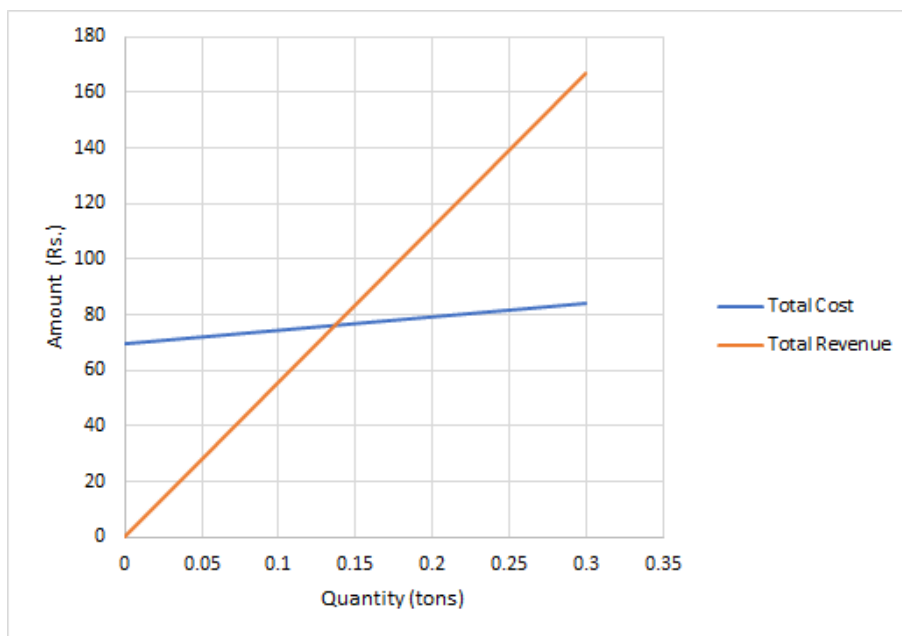


Figure 11: Calculation of Break Even point

From the above graph, break even point occurs when the quantity of e-waste considered for processing is 0.137 tons. As our input is greater than this value, our process is profitable.

In the design project, we tried to determine the energy requirements of smelter and converter. We used the thermodynamics concepts to get the results. For the smelter and converter analysis, finding  $C_p$  values for given phase and temperature range was challenging. For some compounds, the  $C_p$  values are only available for solid phase not for liquid phase. So we considered some assumptions there. As the data for the composition of various components in the feed for smelter and converter is not available, we did the calculations by assuming that components are present in stoichiometry. In smelter and converter, while calculating enthalpy for products, we didn't consider the latent heat for phase change because of lack of resources. As the percentage of ferrous content in PCBs was very low (2.68%), magnetic separation unit was not included after the milling process. The presence of magnetic separator will increase the capital expenditure and the operating cost that will lead to the rise in total cost.

## 7 Future Scope

### 7.1 Heat Recovery Unit

In recent years, there has been growing interest into the recovery of the heat contained in the flue gases emitted by the smelter. Recovery and reuse of this energy will reduce the primary energy requirement for the smelter because more power output can be achieved with the same amount of fuel, leading to improvements in energy management and efficiency.

Depending on the process fluid used, the cycle may be the Steam Rankine Cycle or the Organic Rankine Cycle.

Steam Rankine Cycle (SRC) - Heated steam at high pressure is passed through a steam turbine to turn it. The turbine then rotates a generator to produce electricity. The exhaust steam water is then cooled to restart the cycle and further preheated in the boiler to produce steam.

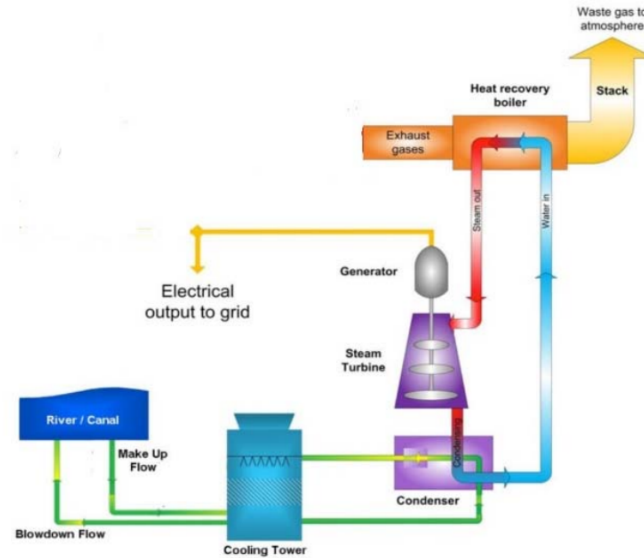


Figure 12: Steam Rankine Cycle [16]

Organic Rankine Cycle (ORC) - A lower boiling working fluid is used as the heat transfer medium, which allows heat recovery at temperatures as low as 100°C. However, energy is reduced at lower temperatures. May be Direct or Indirect.

Direct cycle - The working fluid directly exchanges heat with the flue gases.

Indirect cycle - The working fluid is indirectly heated due to energy exchange with the flue gases.

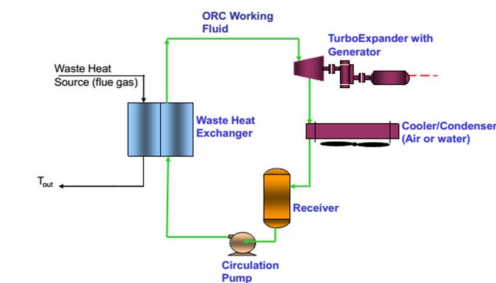


Figure 13: Direct Organic Rankine Cycle [16]

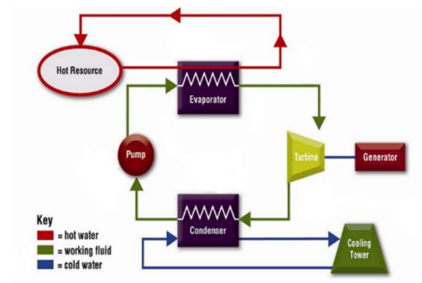


Figure 14: Indirect Organic Rankine Cycle [16]

## 7.2 Refining

In the process, we neglected the presence of precious metals such as gold, silver, platinum, antimony etc which are present in PCBs. After conversion process we are getting almost pure copper as per our process design. If we are considering precious metal, the blister Cu (98-98.5% pure) from converter will undergo further refining in anode furnace and electrolysis process to get 99.9% pure copper [5].

### 7.2.1 Anode furnace

Anode furnace is also called reverberatory furnace, in which oxygen or air will pass through the impure liquid metal. The working principle of this furnace is similar to the converter. The impurities will get oxidised as slag and volatile gases. This furnace can oxidise the metal content such as zinc, tin, lead, arsenic and antimony. If sulphur is present, it will get oxidised as sulphur dioxide. The copper that we get from anode furnace is called anode copper which have the purity of 99% [1].

### 7.2.2 Electrolysis process

In the final stage which is called electrolysis process, 99% copper is further refined to get 99.9% or above pure copper. The anode copper from reverberatory furnace is taken as anode and highly pure copper is taken as cathode in  $H_2SO_4 - CuSO_4$  electrolyte system. When a potential difference of 0.2-0.4V is applied, copper and other precious metals will dissolve in electrolyte from anode. The metals such as gold, silver, platinum, selenium and tellurium will deposited as anode mud below the anode. Copper(II) will get transfer through the electrolyte and deposited as pure copper at cathode. 99.9% copper that we get from electrolysis process is called cathode copper which is considered as highly pure form of extracted copper [5].

## 8 Conclusion

In the development project, we designed the the process for the extraction of copper from e-waste. Starting from the dismantling till the converter, we learnt about the various equipments used in entire process and their role in reaching to the desired product. Different concepts of thermodynamics, separation process and chemical reaction engineering were used to perform material and energy flow to get the estimate of products and the energy requirements of the process. From the research, we found out that the slag that is being produced in the smelter and converter can be utilised for the production of cement. We can also treat the flue gas  $SO_2$  for producing sulphuric acid. Also we observed that a lot of heat is produced in both smelter and converter. The heat can be recovered from these units and utilized it for pre heating of feed.

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