



Recovery of some economic resources from Cathode ray tube (CRT), extracting Lead

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Abstract

With diminishing primary resources, the circular economy idea developed as a replacement for the linear economy. Cathode ray tube (CRT) as an electronic commodity is considered a material intensive industry where a multitude of raw materials were consumed. At the end of life, CRT (as part of E-waste) presents a waste problem because it contains hazardous heavy metals. CRTs contain harmful substances as Lead found in the funnel glass of CRT. This waste is considered hazardous due to its content from leachable lead compounds. Lead may cause risks to human health and the environment. This work aims at valorising the potential of CRT waste as secondary material source and extracting lead from leaded glass of CRT. 250 Kg of CRT waste were manually dismantled. The product of dismantling is classified to glass, plastic, metals and weighed. The percent of glass was 57.1% (majority), sample of leaded glass were grinding and fused with sodium carbonate and adding activated carbon at 1000 °C. 80% of lead metal was recovered the other dismantling products were Couper Yoke 3.1 %, bord 9.1 %, wire 2.7 %, metals 5.5 %, plastic 15.1% and wood 5.6 % (minority). The potential use of every item is tabulated and discussed.

Keywords: Circular economy, extracting lead from CRT, Cathode ray tube glass waste, E-waste

1. Introduction

Quick technological advancements in the television (TV) industry have led to the rapid replacement of conventional TVs with new ones like plasma display panels (PDPs) and liquid crystal displays (LCDs) [1]. The lifespan of computers is also getting shorter over time. Data from the academic and business sectors in the United States suggested a 6-year lifespan from 1985 to 2000, 5–4 years in 2000, and 3 years in 2007 [2]. 65% of the weight of a TV or monitor's overall weight comes from CRTs, which are 85% glass [3,4]. CRTs are composed of several glass parts, each of which has an own chemical composition: (1) panel (65%), a glass made of barium strontium; (2) funnel (30%), a glass made of lead; (3) frit, a glaze made of lead with a low melting point; and (4) neck (5%), a glass made of very rich lead [5,6]. Studies on the CRTs' toxicity characteristics have shown that, while the panel glass shows negligible toxicity, the CRTs' funnel and neck glasses are hazardous wastes [7,8]. Therefore, if they are not properly disposed of, it

may generate serious potential environmental and health problems. Due to the vast numbers of e-waste devices imported from other countries and the sharp rise in knowledge of the possible difficulties brought on by lead leaching from CRTs, there has been a significant increase in the generation of e-waste, and at the same time, there are numerous requests for the treatment and disposal of waste to follow circular economy principles. The two main methods of recycling CRT glass are open-loop recycling (to use the glass for other uses) and closed-loop recycling (to create new CRT glass) [9]. The following outcomes can be attained by reusing recovered CRT glass: substitute raw materials, save the energy, and decrease pollution. Recycling old CRT glass to create new CRT glass is currently the preferred method of managing discarded CRT glass [10]. Essentially, it is composed of six sections: (1) electron gun, producing a slender and powerful speed electron beam with a large power to hit the screen's phosphor layer, (2) deflection coils assisted electronic beam launches, enabling the

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exceptionally quick scanning of all pixels, (3) to ensure that electronic rays hit each pixel precisely during the scanning process, a shadow mask made of aluminium film with a thickness of 0.15 mm is used, (4) panel glass with a tricolour phosphor coating that uses the excitation power of electrical beams to create images, (5) funnel glass, which has a particular percentage of lead oxide to protect against radiation [11,12]. 41.8 million tons of electronic waste were produced globally in 2014, according to study released by the United Nations University [13]. Additionally, it was estimated that by 2050, the quantity of lead-bearing glass that needed to be disposed of in the United States will be six times greater than it is today [14]. In recent years, monitor displays have been created using CRTs, which can be classified into two groups (monochrome CRT and colour CRT) [15]. Each of the four glass components that make up each type (the neck, frit junction funnel, and panel) has a particular chemical makeup and set of characteristics [16]. Due to the high lead content, the neck, frit junction, and funnel glass are categorized as hazardous items (30 wt%, 70 wt%, and 22-25 wt%, respectively) [17]. The lead content of the panel glass is minimal (0-3 wt%) but significant amounts of strontium and barium [18,19]. Numerous CRTs have gathered in landfills all over the world because of the advancement of new display technologies and the end of CRTs' useful life. Up to 150,000 tonnes of used CRTs are reportedly collected each year in Europe, and within the next five years, it is not anticipated that this amount will go down. [12,20]. Glasses among the practical recycling techniques, using CRT glass to create foam glass has received a great deal of interest [21,22]. Andreola's case study looked at the possibility of employing CRT glass in the production of glass-ceramics [23]. Glasses were heated to a melting point of roughly 1500 °C and then subjected to a variety of thermal processes to turn them into glass-ceramics (soaking times ranged from 0.5 to 8 hours at 900 °C to 1100 °C). A good degree of crystallisation has been reported to occur at roughly 1000 °C by employing the examination of thermal, microstructural, and mineralogical data and with a large percentage of glass trash (50–75%) if a MgO and CaO carrier (dolomite) of 40–45% is added. Lead-containing glass is reused by Dondi while making roof tiles and clay bricks has been explored for viability [24]. How heavy-clay products behaved technologically and performed technically under the influence of funnel and panel glasses was assessed. The viability of employing used CRT glass as the main material in porcelain stoneware tiles has also been examined in earlier research [25,26], ceramic glazes [4], applications in

shielding against X-ray radiation [27,28] and platelet composites made of glass and alumina [29]. CRT in cement, aggregate and sand alternative. The benefits of CRT glass in cement-based products are numerous, like river sand, silica content is high in waste CRT glass and pozzolanic in nature, and this makes them a suitable replacement for natural aggregates in concrete blocks or cement mortars [30-32]. Additionally, like heavy weight aggregates [33-36], because the CRT funnel glass contains a lot of hazardous metals, substituting it for natural materials can enhance the radiation-shielding properties of cement-based components [37,38]. However, Romero observed that the significant leaching of harmful metals was caused by the higher replacement of natural sand with waste CRT glass [39]. Ling and Poon stated that by using an acid pre-treatment, lead leaching might be prevented to some extent, because of the potential for lead leaching, the amount of additional untreated CRT glass should be kept at less than 25% [28,40-42]. lowering the amount of lead that is leached from waste CRT glass can be accomplished through acid pre-treatment; however, a significant amount of the acid solution tainted with leftover hazardous metals is also produced. In addition, because scrap CRT glass has a smooth surface, the interfacial connection between the cement paste and glass was compromised, significantly lowering the strength of the finished product [17,43]. Consequently, a more environmentally friendly technique for enhancing the lead immobilisation and interfacial characteristics of the waste CRT glass surface by adding cement binder should be devised. Cement-based products have employed waste CRT glass as a fine aggregate at concentrations of 30 and 60% by weight, and in the cement mortars that are produced, the graphene oxide (GO) addition was used to encourage lead immobilisation and strengthen interfacial bonding. The adoption of GO did more than only mitigate the damaging environmental impact of discarded CRT, but also improved mechanical qualities of waste CRT materials based on cement that were manufactured. Alkali-activated cement (AAC) has also been attempted to be made using scrap glass powder as a precursor since it includes significant amounts of amorphous silica and calcium [44-45]. The findings demonstrate that the fine aggregate in concrete paving blocks made from 100% CRT funnel glass not only had adequate levels of compressive strength (>45 MPa) and ASR (alkali silica reaction) expansion (0.1%), but also enhanced water absorption resistance, drying shrinkage (Ling and Poon, 2014). Lead recovery waste CRT glass has high lead level in the funnel glass (15-25% PbO). Hydrometallurgy and pyrometallurgy methods can be used to recover it

[46-47]. Silica flux in pyrometallurgy. The processes used in the smelting of lead and copper depending on operational procedures, silica flux might be very high. It may be possible to substitute silica with discarded CRT glass [46-47]. Tricolor fluorescent powders are used to create images on phosphor panel glass: green colour ZnS: Cu, red phosphor Y_2O_3 or $Y_2O_2S:Eu_3$, blue colour ZnS: Ag, besides, additionally, a relatively thin and light Al-film is present to enhance fluorescent powder's electroconductivity [48]. It has been demonstrated that waste CRT phosphor powder may successfully recover Y, Al, Zn, and Eu metals. Furthermore, the " $H_2SO_4 H_2O_2$ " system is an excellent technique with minimal environmental impact, large economic advantages. Additionally, our study offers a straightforward approach based on recovery benefits, technology consumption costs, and environment restoration costs to determine a technology's viability and sustainability in resource recycling settings [38]. Also, according to reports, using a roasting treatment to oxidise the sulphide, and a pre-treatment with 5 M NaOH for three hours at 95 °C to remove the base metals and phosphate ion, increases the amount of rare earth elements (REEs) being extracted (65% Sm, 77% Ce, 56% Y, and 68% Eu). increasing the duration of the 5 M NaOH pre-treatment from 3 to 7 hours at 95 °C, less time was needed to complete extractions of Eu, Sm, Ce, and Y totalling 90, 90, 71, and 58%, respectively. By changing the pH of the leach solution from 6 to 11, it is feasible to precipitate rare earth elements and recover them as hydroxides [49]. We can extract lead from the hazardous waste cathode ray tube (CRT) funnel glass and get Copper, Nickel, Gold, Silver, etc. Even though each of them used processing techniques that could be detrimental to both the environment and human health, they were all highly profitable.

linear Economy and Circular Economy is displayed as shown in **Figure 1**.



Figure 1: Circular Economy & Conventional linear Economy

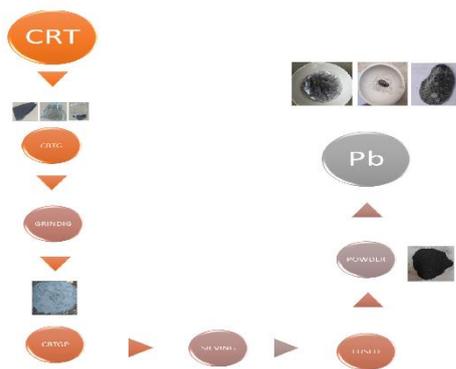
2. Material and Methods

250 kg of TV set from various brands of different size were collected. The following step were carried out: Step 1: CRT from the television or monitor was removed.

- Step 2: the vacuum from the CRT was released.
- Step 3: Crush the CRT and separate the glass from any residual metals.
- Step 4: Prepare uniform cullet and remove phosphorescent coatings.
- Step 5: Remove all non-glass components from the CRT's exterior.
- Step 6: Remove the Yoke
- Step 7: Remove the Bord
- Step 8: Remove the Wire
- Step 9: Remove the Plastic
- Step 10: Remove the Metals
- Step 11: Remove the Wood
- Step 12: Remove the Nickel masks from TV.
- Step 13: Remove the Nickel cannon cathodes from TVs.

2.1. Recovery of lead metal from CRT Leaded glass

For recovering Pb from CRT Leaded glass via chemical conversion, the flowsheet of the process is shown in Scheme (1). The suggested process consists of three main steps. In the first step the collected sample of CRT glass (CRTG) was grinding into CRT glass powder (CRTGP), then it was sieved using sieve shaker Grain size of Mesh 70 to form more homogenous mixture. The second step, 50 gm of CRTGP was mixed with 50 gm of anhydrous sodium carbonate powder and placed on activated carbon powder in silicon carbide crucible. Fusion is the third step, in which the mixture was heated at 1100 °C for 2 hrs. finally the solid material resulted after fusion with sodium carbonate was crushed by ball mill and sieved to separate solid lead metal.



Scheme (1): Schematic diagram of lead metal recovery from CRT Leaded glass.

3. Results and discussions

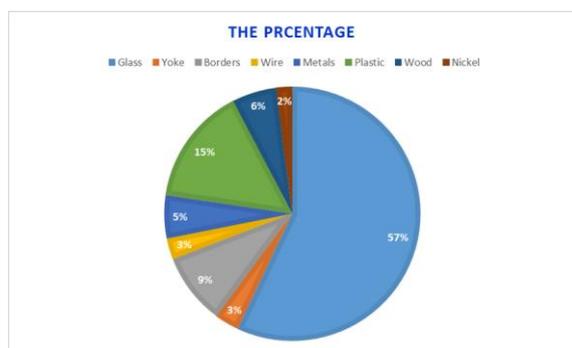


Figure 2: CRT component percentage.

3.1. The percent of CRT glass

Figure 2 represents the CRTs component which are made up of 57% glass and amount of 65% of the total weight of a monitor or TV [3-4]. Due to the high lead content, the neck, frit junction and funnel glass are categorized as hazardous items (30,70, and 22-25 wt%, respectively) [17]. Therefore, if they are not properly disposed of, there may be major potential dangers to both the environment and human health. The two main methods of recycling CRT glass are open-loop recycling (to use the glass for other uses) and closed-loop recycling (to create new CRT glass) [9]. Recycling used CRT glass to create new CRT glass is the recommended method of managing waste CRT glass [10]. Reducing pollution, switching to alternative raw materials, and saving energy are all possible with the utilization of recovered CRT glass. using the CRT glass to produce foam glass [21-22]. Like river sand, silica content is high in used CRT glass and pozzolanic in nature, and this makes them a suitable replacement for natural aggregates in concrete blocks or cement mortars [30-32]. A similar situation exists with heavy weight aggregates [33-36] because the high concentration of heavy metals

in CRT funnel glass, substituting it for natural components can enhance the radiation-shielding capabilities of cement-based components [37,38]. Lead recovery waste CRT glass has a high level of lead in the funnel glass (15-25% PbO). Recovery is possible by pyro-metallurgy and hydro-metallurgical processes [46-47]. The weight percentage of CRT glass is different from Brand to another as shown in Figure 3.

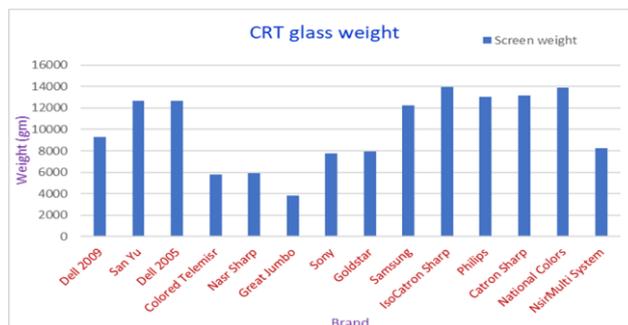


Figure 3: The percentage of CRT glass in different brands.

3.2. Glass Components

CRTs are constructed from a variety of glasses (Leaded glass & non-leaded glass), each with a unique chemical composition and set of characteristics:

(1) panel, lead-free barium-strontium glass; Two-thirds of the CRT's bulk is made up of the screen or panel, which is the front of the CRT. In more recent CRTs, barium oxide is used in place of lead oxide in the panel glass.

(2) funnel, a lead glass that contains 20 wt % lead oxide, making up nearly a third of the weight of CRT; The funnel or bell refers to the back part. Most of the lead in a CRT is found in the funnel glass, which is a leaded type of glass.

(3) neck, an electron gun is protected by a lead-rich silicate glass with PbO content of more than 25 wt %; The electron gun's neck is encased in a straight glass tube (s). Leaded glass makes up the neck.

(4) frit, the three components are joined with a lead-rich solder glass [50]. The CRT is sealed using solder glass or frit. 85% of frit is lead.

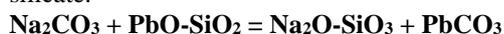
3.2.1. Characterization of solid waste (CRT Glass):

X-Ray Fluorescence (XRF) measurements at international accreditation service analysis was carried out on the leaded glass and non-leaded glass and the data obtained were listed in Table 1. We can conclude that the main constituents of leaded glass are lead oxide is about 16 Wt. %, silicon oxide is 52 Wt. %, calcium oxide is 3.5 Wt.

% and ferric oxide is 0.2 Wt. %. While in case of Non-lead glass, the main constituents are lead oxide is about 1.04 Wt. %, silicon oxide is 57.53 Wt. %, Barium oxide is 9.2 Wt. % and Strontium oxide is 8.77 Wt. %.

3.2.2. lead recovery from CRT

Ilyes, et al, 2017 reported that, when lead concentration in crystal glass mixture was less than 40%, it acts as network modifier [51]. Also, Kacem, et al 2017 reported that, lead silicate melts at 760 °C while sodium carbonate melts at 854 °C [51]. So, the developed reaction is mainly based on increasing the fusion heating temperature. The reaction was followed as lead silicates react with part of molten sodium carbonate to form lead carbonate and sodium silicate.



Then lead carbonate (PbCO_3) decomposed to form lead oxide (PbO) and carbon dioxide (CO_2) by heating (350 - 450 °C) [52].



While a part of sodium carbonate was dissociated to sodium oxide (Na_2O) and carbon dioxide (CO_2) at 851 °C [53].



Finally, Carbon dioxide generated reduced the percentage of oxygen around the reaction that increased the chance of formation carbon mono oxide.

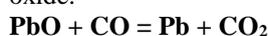


Table (1): XRF analysis for original solid waste sample (CRT).

Oxide (%) (*)	Neck glass powder	Panel glass powder
Al_2O_3	3.53	2.86
CaO	3.48	1.41
SiO_2	51.86	57.53
Fe_2O_3	0.21	0.11
MgO	1.25	0.27
K_2O	8.84	8.42
Na_2O	4.77	5.38
SO_3	0.13	0.18
Cl	0.06	0.05
L.O.I. (**)	0.9	1.38
C_3A		
C_3S		
$\beta\text{-C}_2\text{S}$		
C_4AF		
PbO	15.92	1.04
TiO_2	0.25	0.49
P_2O_5	0.04	0.06
SrO	2.62	8.77
ZrO_2	0.65	1.88
BaO	3.17	9.20
CeO_2	1.71	0.28
CuO	0.17	0.02
Sb_2O_3	0.27	0.38
ZnO	0.17	0.27
Total	99.98	99.98

*According to ASTM C 114 – 00 (standard test methods for chemical analysis)

** According to ASTM C 114 – 18

As we mentioned above the reaction of lead recovery is based on the fusion time and temperature. To evaluate the Effect of thermal energy and time on lead recovery, the fusion temperature increased gradually from 800 °C to 1100 °C for constant time 120 min and we conclude from Figure 4 that the lead recovery increased from 20% to 80% as temperature increased.

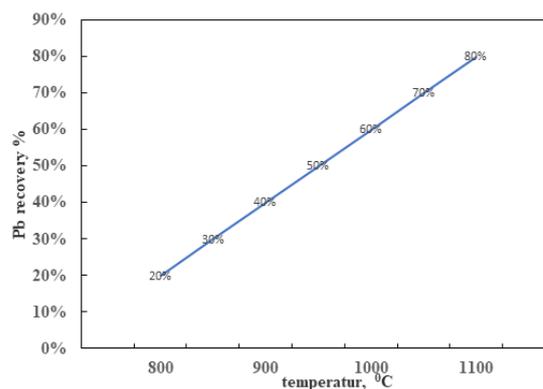


Figure 4: Effect of fusion temperature on lead recovery for 2 hr as fusion time.

The same procedure was carried out at 1100 °C fusion temperature with increasing time of fusion from 1 hr to 4 hrs as depicted in Figure 5. The maximum lead recovery 80% was attained after 4 hr of fusion and any further increase in time has no effect.

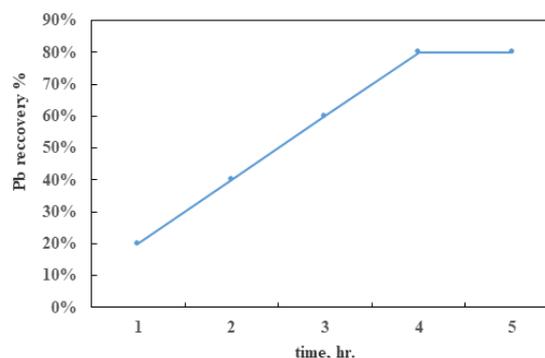


Figure 5: Effect of fusion time on lead recovery at 1100 °C as fusion temperature.

3.3. Non-Glass Components

Glass-to-glass recycling requires the removal of non-glass components.

METALS, CRTs can be used to recover small amounts of metals like copper, steel, and nickel.

Compared to older versions, newer ones produce fewer valuable metals. Hazardous waste is also assumed to include shadow masks and the copper wire yoke.

PLASTICS, most plastics are exported to foreign markets or reused into new high-value engineering plastic resins including high-impact polystyrene (HIPS), polycarbonates (PC), and acrylonitrile-butadiene styrene (ABS).

Borders Previous research has provided a straightforward way for determining the viability and sustainability of technology in resource recycling settings. This method is dependent on the advantages of recovery, the cost of technology consumption, and the cost of environmental restoration [38]. Vacuum pyrolysis in conjunction with mechanical-physical separation is used to recover valuable materials from used tantalum capacitors.

Frames consist of amounts of aluminum or metals like copper, steel, and nickel... etc.

Banding the CRT is strengthened with metal bands, before recycling, it must be removed.

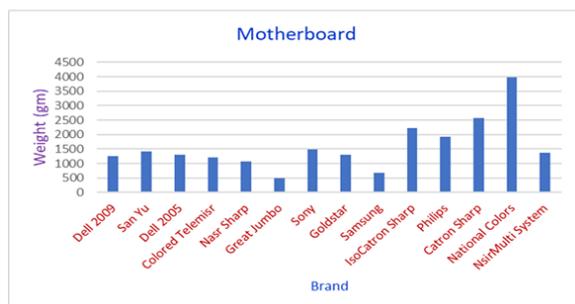


Figure 6: The percent of Motherboard in different brands.

The motherboard is the precious part which contains the precious metals (Therefore, if they are not properly disposed of, it may generate serious potential environmental and health problems as shown in Figure 6).

Electron gun, Figure 7 represents Nickel cannon cathodes from TVs (the beam of electrons is generated by a stainless-steel electron gun).

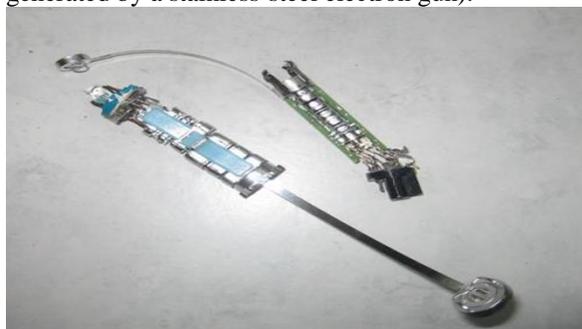


Figure 7: Nickel cannon cathodes from TVs

Nickel masks from TV (Shadow mask)

The electrons are focused on the panel's back by the shadow mask, which is a metal screen as shown in Figure 8.



Figure 8: Nickel masks from TV

The percent of Plastic material

The second large material percentage is plastics which is minimum in Nasr Sharp Brand and maximum in San YU Brand as depicted in Figure 9.

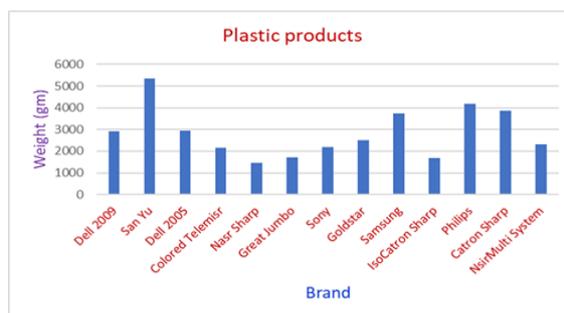


Figure 9: The percent of Plastic in different brands.

The percent of wood

From the 14 brands only 4 brands contain percent of wood as presented in Figure 10, and it was clear that the percent of wood is minimum in Goldstar Brand and maximum in National colors Brand.

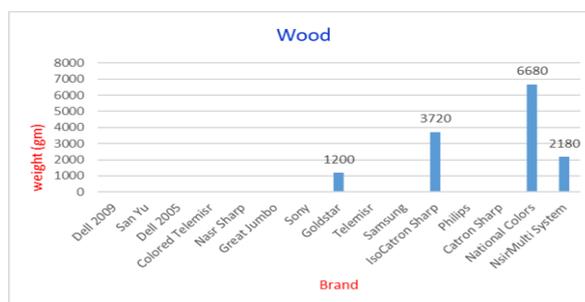


Figure 10: The percent of wood in different brands.

Copper recovery

Figure 11 shows the weight percent of copper pulp yoke in various brands. It was obvious that the minimum percent 5% in Great Jumbo Brand while the maximum one 4% in Nasr Sharp Brand.

Although the Dell 2009 represents 4.2% Yoke, the CRT's neck is encircled by coils of copper wire known as the yoke, which acts as an electromagnet to direct electrons to the correct location on the panel.

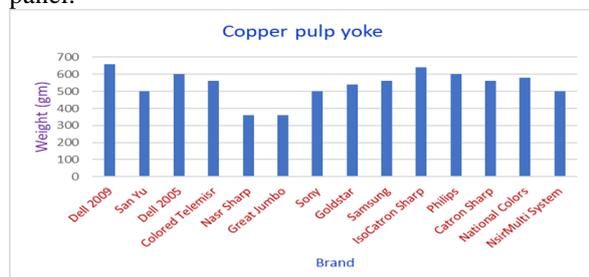


Figure 11: The percentage of Copper Yoke in different brands.

The percent of Wire

2.7 % is the average percentage of wire in 14 brands containing mainly copper metal with 30%. From Figure 12 we can conclude that Samsung Brand represents 0.5% as the minimum percent while National Colors Brand give the maximum percent 4%.

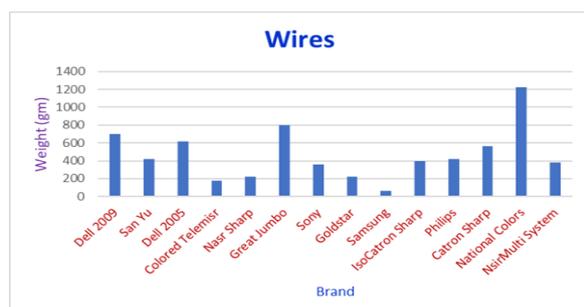


Figure 12: The percentage of Wire in different brands.

The percent of Al -with other metals

By scanning over 14 brands we found that the percent weight of aluminum with other metals is very small in Nasr Sharp and Samsung Brands while it reaches great value in Iso Catron Sharp Brand and greatest in National Colors Brand as depicted in Figure 14.

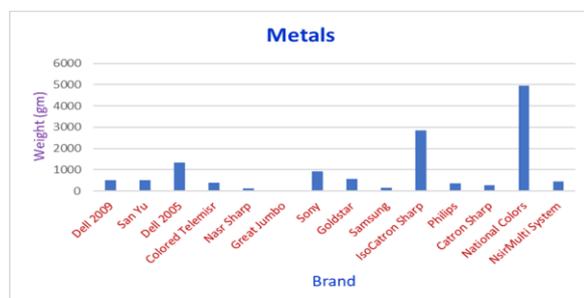


Figure 14: The percentage of metals in different brands.

Uses Of Copper

Since more than 50% of the copper consumed worldwide goes into making wire, electrical conductivity is particularly crucial. Also, utilized in the production of semiconductors. Since it is frequently plated with either gold or silver, copper is mostly utilized as an alloy of those two metals. Copper is used in building construction, electrical goods, as well as the creation of industrial equipment and transportation vehicles. The heating and cooling systems, appliances, telecommunications all depend on copper wiring and plumbing. In automobiles and trucks.

Uses of Aluminum

Because it conducts heat well, it is used to make oil and gas pipelines, medical devices, refrigeration equipment, chemical reactors, and other items. In the industrial setting, it is used to make heat sinks, heat exchangers, and cookers. It is extensively utilized in the production of electric cables, high tension bus bars, and radios. It is utilized in packaging. In addition to other aluminum products, Al-foil can be rolled into Al-strips and wire.

Uses of Nickel

Nickel resists corrosion and is used for plating to protect other metals. Also used mainly in making alloys. in toasters and electric ovens. Alloys of nickel are used in shafts and turbine blades, batteries, coins and as a catalyst. The manufacturing of ferronickel for stainless steel (66%) dominates the use of nickel. It is also employed in the manufacture of foundries (3%), non-ferrous alloys (12%), batteries (2%), plating (7%), and alloy steels (5%) as depicted in Figure 13.

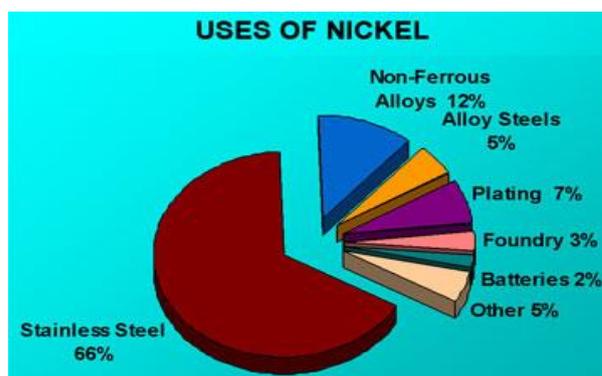


Figure 13: uses of Nickel

Conclusion

WEEEs are made up of different components, the majority is from E-waste which contains dangerous compounds that, if not properly managed, can be detrimental to both the environment and human health. A circular economy provides opportunities and reduces the environmental impact of resource consumption.

Factory waste might be used as a valuable input in another operation, and items could be repaired, repurposed, or improved rather than discarded. When waste is produced as little as possible, the value of goods, materials, and resources is preserved in the economy for as long as feasible, and people may live well, grow their businesses, and find work while lessening environmental pressures. It emphasizes recycling, restricting, and repurposing the economy's physical inputs as well as employing trash as a resource, this causes the use of primary resources to decline. The idea can, in theory, be used with various kinds of natural resources. finally applying circular economy on CRT getting the most value out of them, then reusing and recovering valuable materials, precious and rare metals. We can extract lead from the hazardous waste CRT funnel glass and get Copper, Nickel, Gold, Silver, etc. Even though each of them used processing techniques that could be detrimental to both the environment and human health, they were all highly profitable.

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