

## E-waste: A Review of CRT (Cathode Ray Tube) Recycling

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Received date: May 03, 2017, Accepted date: Jun 04, 2017, Published date: Jun 10, 2017

### Review Article

#### Abstract

The developments in monitor technology have accelerated in recent years, acquiring a new dimension. The use of liquid crystal display (LCD) and light emitting diode (LED) monitors has rapidly reduced the use of cathode ray tube (CRT) technology in computers and televisions (TVs). As a result, such devices have accumulated as electronic waste and constitute a new problem. Large parts of electronic waste can be recycled for reuse. However, some types of waste, such as CRT TVs and computer monitors, form hazardous waste piles due to the toxic components (lead, barium, strontium) they contain. CRT monitors contain different types of glass constructions and they can therefore be recycled. However, the toxic substances they contain prevent them from being transformed into glass for everyday use. Furthermore, because CRT technology is obsolete, it is not profitable to use CRT as a raw material again. For this reason, poisonous components in glass ceramic structures found in CRT monitors can be confined and used in closed-loop recycling for various sectors.

**Keywords:** Cathode ray tube (CRT), E-waste, Recycling, Electron gun

#### Introduction

Cathode ray tubes (CRTs) are an old technology that was globally used for over 60 years. This technology, which is commonly used in television (TV) monitors, has also been used in computers and in many technological devices over time. It is a widely applicable technology and it has been widely preferred for a long time due to its easy accessibility, price compatibility, and long life [1]. However, with the addition of liquid crystal display (LCD) and light emitting diode (LED) monitors with higher resolution fineness to the market, CRT monitors have been discontinued in many countries and have become electronic waste [2,3]. CRT technology is still in use; it is the cheapest TV product in Eastern Europe, the Middle East and in African countries that cannot acquire LCD and LED TVs [4]. CRT waste is an important part of electronic waste globally [5]. CRT wastes should be specially stored because of the harmful components they contain [6]. These components can be absorbed by soil over time, and can be passed indirectly to animals and humans [7–9]. Lead is particularly harmful to the environment and is the most commonly found heavy metal in CRT devices [10].

Most electronic waste can be recycled. The recycling of the various components contained in e-waste, such as metal, plastic, and circuit boards, is often more efficient than their production from raw materials. For this reason, e-waste is a possible source of economic benefits [11]. However, since these types of waste are often composed of different types of substances and are disposed by consumers in inappropriate ways, the additional expenditure incurred in the collection, storage, and disintegration, reduces the recycling rate. For technology products that are no longer in demand, such as CRT, it is not profitable to recycle them to be used in the production of CRT again [12]. Recycling of CRT waste is not economically profitable due to its toxicity and, at the same time, it has a limited number of reuse options. The use of recycled raw materials in new products is also limited. For this reason, poisonous components in glass ceramic structures found in CRT monitors can be confined and used in closed-loop recycling by various sectors [13]. The most recycled CRT-waste products are glass fiber [14], glass ceramic, glass-based composites [15,16], and ceramic glazes [17].

According to the Electrical Waste and Electronic Appliances Authority, 50,000 to 150,000 tons of CRT waste are emerging in Europe annually, which is expected to increase over the coming years [18]. In the United States, a significant portion of the current electronic waste is CRT waste. It is estimated that the total amount of waste at home and at work is about 7 million tons [19]. In China, 1.7 million tons of electronic waste came into being in 2006. This amount is expected to exceed 5 million tons by 2017 [20].

## CRT Structure

CRTs, now known as “old-generation” television and computer monitors, are produced using specially compounded vacuum glass [7]. It constitutes about 65% of the weight of a standard monitor [21]. It is based on the voltage difference between the electron gun and the anode. In the vacuumed structure, electrons can move freely. Thus, electrons are separated from the cathode surface by the voltage difference and strike the phosphor-coated screen.

CRT monitors contain glass structures with different structural and chemical properties in order to provide the appropriate electron flow and to generate light in different colors and tones on the surface [22]. These are: (A) front panel, barium strontium-containing glass; (B) funnel, lead-containing glass; (C) frit, low melting temperature solder; (D) neck, glass with high lead content [23]. Materials such as barium, strontium, and lead, contained in these glass types, are harmful to human health [24]. CRT monitors, according to their dimensions, contain between 0.5 kg and 2.9 kg of lead [25]. Lead in the tetrahedral glass structure can be found as  $PbO_3$ ,  $PbO_4$ , and  $PbO_6$ . These oxides cannot be easily detached from their environment due to the strong bonding energies between lead and silicon [26]. The neck and funnel parts of CRT products fall into the toxic waste category. The front panel exhibits lower toxicity due to the barium strontium content it contains. A standard CRT consists of 65% front panel, 30% funnel glass, and 5% neck glass.

**Glass panel:** It is the outermost glass layer on which the image is formed. It has the lowest lead oxide content, of about 2–3%. The primary contribution of the panel glass is in the form of barium oxide. In some countries, such as Japan and the United States, the amount of electricity consumed by electrical goods is high, so the proportion of strontium in the glass is higher than that of barium. Panel glass constitutes 65% of the total system weight. Phosphorus is present in the structure at 14–22%. In addition to the phosphor used as a cover for the panel glass, there are also cadmium and zinc in small quantities [27]. The reason for the presence of lead in the structure is that ultraviolet (UV) rays and radiation do not penetrate the human body [28]. However, its use may vary according to the manufacturer and it may also not be lead.

**Shadow mask:** It is the thin metal sheet layer behind the front panel. There are holes in this metal sheet that allow the electron beams to strike the point where they will bring the necessary color. Approximately 400,000 of these holes are placed on the mask.

**Funnel glass:** Lead oxide is most abundant in this area. This region contains 22–25% lead and it is called the lead glass [29,30]. The lead ratio can be up to 30%, depending on the CRT type, the manufacturer or the production year. This amount varies between 1.5–3.0 kg by weight. It directs the rays coming from the electron gun to the front panel.

**Frit:** Lead glass and panel glass tie together with frit solder. Frit contains about 80% lead and has a low melting point [8].

**Table 1: Weight % of chemical components in CRT glass structures [10].**

Oxides	Color CRT panel glass	Color CRT funnel glass
SiO <sub>2</sub>	55.4	49.61
PbO	0	24.17
K <sub>2</sub> O	8.13	7.79
Na <sub>2</sub> O	7.75	5.32
Al <sub>2</sub> O <sub>3</sub>	3.3	3.63
SrO	8.57	2.99
CaO	0.5	2.3
BaO	8.92	1.96
MgO	0.13	1.49
ZrO <sub>2</sub>	1.69	0.58

Fe203	0.08	0.07
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## CRT Types

CRT production has changed over time due to technological progress. The varieties formed during this change are basically grouped into two groups [8]. While the first CRT systems were simpler in black and white, the color CRT systems that were developed later are basically the same, with some differences [31].

### Black-white CRT monitors

By applying voltage to the electron gun, free electrons are generated. A voltage difference is created between the cathode and the anode. Because of this voltage difference, free electrons move towards the front panel. The beam is created by the deflection bobbin placed in front of the cathode. This bundle is routed on the screen with the diversion bobbin, resulting in a black and white image.

### Color CRT monitors

They basically have the same operating principle, but color CRT monitors have three different electron guns: red, green, and blue [32]. The electrons from the different guns reach the phosphorous surface through the metal plate called the shadow mask. As the beams pass through the shadow mask, the deflection bobbin is moved electromagnetically through the holes in the shadow mask by moving these beams [33]. Thus, a moving image occurs. Many colors are produced by operating these electron guns in different combinations.

## Generation of CRT Products

Over the years, CRT technology began to be abandoned due to the release of LCD and LED monitors in the market, which have improved image qualities and smaller volumes, depending on the technology [34,35]. Over the past 10 years, total TV-set sales have increased globally, while CRT monitor sales have declined [36].

The lifespan of almost every new technological product produced is shorter than that of a product from a previous generation. In the European Union, 7.5 million tons of electrical and electronic-equipment waste are produced annually [19,37]. Approximately 80% of monitor waste is generated by television and computer CRT monitors [23]. It is anticipated that currently available CRT products will complete 85% of their lifespan within the next 10 years. In 2000, the United States accumulated 300,000 tons of electronic waste in collection sites. CRT waste constitutes the third largest community in this type of waste [38]. Waste of electrical and electronic equipment is estimated to have increased by 30–40 million tons per year, worldwide [39].

In Thailand, CRT waste is also an increasing problem. It is estimated that 1.5 million TVs and 1.05 million computers have become waste in 2010, whereas 1.9 million TV sets, 750,000 computers, and 550,000 monitors were sold in 2004 in Thailand. Since Thailand does not yet have a comprehensive e-waste management system, it is becoming increasingly difficult to obtain information on the amount of treated waste and recovery rates [40].

Harmful substances contained in the waste, such as lead, mercury, and phosphorus, are kept in collection areas where human-health hazards develop. In some countries, such as the US and Japan, manufacturers are responsible for the collection of some electronic waste, but a large part of this waste is sent to waste collection sites [41]. Most companies have campaigns set up to prevent these wastes from being sent directly from homes and businesses to collection sites, and to, conversely, return to the manufacturer [42].

Until recently, CRT waste was used in the production of new CRTs and was introduced into systems in which the lead was melted. However, as evident from the data, the choice of this technology today necessitates the use of the waste in different areas. Nevertheless, their use is limited to different areas due to their very different and toxic content.

## CRT Waste Management in Leading Counties

In especially populous, economically developed, and developing countries, such as the United States, China, and India, rapidly accumulating electronic waste needs to be managed with appropriate procedures. Recycling operations that function very well from countries such as Sweden have recently been the subject of interest for countries like India. This technology has been discontinued in many countries, such as South Korea [43]. Many of the remaining monitor units are being delivered to less developed countries. On the other hand, unregistered collection and inconsiderate use of electrical and electronic devices, the waste of which is causing environmental destruction due to its rapid accumulation, led the administrations of the some countries to register and control this process [44]. A description of the current status and considerations of electrical and electronic waste, CRT waste in particular, in some countries is provided below.

## India

Problems with electrical and electronic waste in India have increased, especially after 1990 [45]. CRT production has stopped in India by leading companies in the monitor industry—as in many countries. CRT monitors are still in demand by low-income Indian citizens, although production has stopped. This demand is met by importing from countries that still continue to produce these devices, such as China. It can be predicted that the use of CRT will continue in this region, as India is the second most populous country in the world and most of its population is of a very low income [46].

The most e-waste producing regions in India are Mumbai, Delhi, Bangalore, Chennai, and Kolkata [47]. The total amount of waste produced is approximately 400,000 tons, and approximately 10% of this amount is glass waste [48,49]. Although glass recycling is an easy operation, producers are hesitant to recycle unknown glass. The largest recycling center in India is in New Delhi. CRT monitor waste is being collected by junk dealers due to the copper it contains. CRT monitors reach landfills with local collectors. Workers in landfills separate the monitors and the ones in better condition are put back on the market. Damaged monitors are manually separated into their components by workers. Broken or intact glass components separated from their monitors are divided according to their contents and are usually recycled to produce new products in the same sector [50].

## China

In China, almost all electronic and electrical-appliance waste is collected in small areas and is manually separated into basic parts and recycled [8]. In the research conducted, Chinese people appear to believe that recycling is the responsibility of the producers, the recycling companies, and the government [51]. 60% of this type of waste is collected by unofficial collectors. The waste collected in such manner is separated into basic components, such as metal, plastic, and glass, in collection areas; the components are stored for later reuse [52].

Since 2003, China has made a significant progress in CRT recycling, with the support of major monitor manufacturers. In 2004, Tianjin University started to work on the whole process of CRT recycling [53]. China's largest CRT-recycling center opened for use in 2008.

## United Kingdom

Although European countries have made more progress in waste management than many Asian countries, they are still far from being fully efficient. Manufacturers in the UK are obliged to comply with procedures to ensure that electrical and electronic waste is recycled and used in such a way as not to damage the environment [54]. For this reason, there are recycling centers approved in the UK [55].

Early in the 2000s, CRT recycling in the UK was particularly focused on computer monitors. This is due to the fact that recycling is costly and not enough facilities existed [56]. Waste to be recycled is generally evaluated in four different ways:

- During the production of new CRTs, the different types of glass are separated and reused. This method is not in use anymore, because there is no CRT production in Europe. However, the separated panel and funnel glass is sent to countries that are currently producing, such as China.
- For ceramic products, CRT glass is processed to a fine sand size and it is reused if it has been confirmed that the glass content was thoroughly cleaned off contaminants.
- Since CRT waste has a lower melting point than other raw materials, energy recovery and flow are used as enhancing elements in smelting processes, after some pretreatments.
- The lead is extracted from the leaded parts of CRT waste, especially at high temperatures, by the help of catalysts used to obtain raw materials to be used in the production of new glass.

## Sweden

Sweden, one of the world's leading countries in the field of recycling, is also one of the countries in good standing regarding the recycling of CRT. In Sweden, there are firms capable of separating lead from the glass [57]. The use of CRT monitors in the country has fallen very rapidly since 2004—almost to zero by 2007. For this reason, CRT waste has emerged and must be recycled in large quantities [58]. With a program that started in 1995, this situation had been foreseen and IBM started to recycle old monitors without harming the environment [8]. The front panel of the CRT glass and the funnel glass are separated from each other, on a monitor that is manually divided into basic materials, such as plastic, metal, and glass. Glass is used as an additive material in the glass and construction industries, after it has been separated from its toxic constituents. In addition, secondary raw materials produced enter the international market.

Leading CRT-recycling companies have indicated that these products will be recycled in the near future and that LCD monitors may be involved in this process [58].

## South Africa

South Africa is a developing country in waste management. One of the problems facing the development of this process in South Africa is the lack of adequate data [59]. There has not been enough past work on this subject. However, in recent years, the work of local governments has been accelerated in order to establish the amount of electric and electronic waste as a priority [60]. According to current data, 0.35 million tons of waste is generated annually in South Africa [59].

Monitors used in South Africa are imported from outside, because no local producer operates in the country. Product that completes their life can be left in the campaign when a new product is purchased. Those in good condition find their place in the second-hand market. Many are sent to collectors. Waste collectors divide the monitors into their basic components and sell them for recycling as secondary raw materials. However, CRT, which makes up the majority of the monitor, does not have an appropriate recycling facility in the country [59].

## United States of America

When compared to developing countries and considering different internal policies, CRT management in the US is different [61]. Many states describe CRT waste as dangerous [62]. It is envisaged that this type of waste will accumulate until 2026 [63]. The state system in the United States and the recycling of electrical and electronic waste differ in the various states. For example, with the California government's law enacted in 2005, consumers were asked to pay for the recycling cost of the product when they bought a new product. This fee is charged at an additional cost of \$6–10 [64].

According to a 2006 decision in Washington State, the recycling of this type of waste has burdened producers and obliged them to recycle the waste from institutions such as schools, associations, and health care facilities. In the Maine region, this responsibility is shared by the local government and the producer [65].

## Turkey

Turkey is a developing country with a significant youth population. The use of computers and TVs in the country is also increasing. In the last 10 years, the use of computers in Turkey has increased by 40% [66]. As a result, old technology products soon became electric and electronic waste. The amount of electric waste per capita in Turkey is more than 2.5 kilograms per year [67]. Although there is not enough data to determine the total amount of this waste, an easy estimation can be made by knowing the production quantity and the average lifespan of these products. [68]. The average lifespan for a TV is 5 years [69].

According to the regulation published by the Ministry of Environment and Urbanization in 2012, it is obligatory for the distributors to transfer the old products to the waste center and to set up waste-collection points in the sale areas, by purchasing the old products and free of charge for the sale of the new products by creating the collection areas according to the local municipalities for the recycling of electrical and electronic waste in Turkey [70]. In waste-storage areas, operators are required to have a radioactive measuring device, a recording system, drainage water collecting ducts, oil-absorbent material, and a fire extinguishing system [70]. Apart from these, electrical and electronic waste in Turkey is collected by companies approved by the Ministry of Environment and Urbanization. Certified companies receive transport licenses for the different types of waste. There are also individual waste collectors of local governments. Thus, the aim is to determine and record the amount of waste [71]. The biggest challenge for waste collection in Turkey is that end-users are inconsiderate when discarding waste. In recent years, advertising efforts have been put forth to raise awareness in the population.

In Turkey, 9.7 million TV units were produced in 2015, 7.7 million of which were exported abroad. Only 2 million TV units were thus sold domestically that year [72]. A TV unit of approximately 0.22 kilograms per person was collected in Turkey in 2015. This amount is projected to increase to 0.86 kilograms per person in 2018.

In Turkey, the collection and recycling of this type of waste starts by collecting the waste from private companies, public institutions, and municipal-waste licensed vehicles and transporting it to the processing plant. The processes carried out at the recycling plant are as follows:

- The outer plastic part of the monitor is removed before the CRT enters the cutting machine.
- An automatic cutting process is performed on the monitor, which is placed on the cutting machine. The cutting machine uses a heated wire method.
- The fluorescent coating is manually cleaned and filtered with a special absorbent system.
- After the lead-containing glass is separated, it is separately stored.
- Leaded glass is sent to the smelting plant.
- Electronic circuit boards are sent abroad to be treated by appropriate refineries.

## Environmental Impacts of Crt Waste

As electrical and electronic products have developed rapidly, old technology is now a waste. This waste is becoming a greater burden for the environment [73] and for human health [74,75]. Especially in populous countries, efforts have been made to destroy or recycle this type of waste [76]. In this type of waste, which is kept in a certain area for a long time, heavy metals can be mixed into the environment even in small amounts. Some studies and analyses on water samples taken from the storage areas have determined that higher concentrations of lead leach to nature in waste collection areas [77]. Soluble lead can accumulate in plant and animal cells over time.

In addition, such collection areas can be highly acidic environments. The frit region of the CRT structure is more susceptible to dissolution in acidic environments. Because of its high lead content, it can affect both soil and groundwater. Lead can cause major damages to the human central nervous system, immune system, and circulatory system [78–80], as well as in the kidneys [81]. Nickel used in electron guns and coatings can have an allergic effect [82]. Zinc may cause cytotoxicity and ischemia [83]. It has also been observed that lead in the blood of children living in areas with an amount of lead above 500–1000 mg Pb/kg in the ground has also increased [84]. For this reason, solid-waste storage facilities should be checked for leaks regularly [85]. The total amount of lead contained in CRT monitors sold in 2002 alone is 10,000 tons [86]. Given these quantities, the threat posed by electrical and electronic waste is clear. It has been observed that the amount of lead in soil samples taken from a landfill could be 5–10 times the permitted limit [77].

### CRT recycling

There are two different systems of CRT recycling [87]. With closed-loop recycling, the waste is used in new CRT production. In open-loop recycling, the waste is used in different production areas. CRT recycling is performed in two different ways, from glass to glass recycling and from glass to lead recycling. Especially in the US and Germany, waste glass is subjected to a series of smelting processes to obtain lead [88]. CRT glass is used in lead production, in the ceramic sector, and as a brick and cement additive [89]. Recycling of CRT waste is important not only for the economic gains it provides, but also for environmental reasons [90].

Waste CRT monitors are separated from the plastic, metal or wood part of the monitor before being recycled [91]. During this stage, the CRT part should not be damaged. In such a case, the mixing of glass with different compositions can render the waste non-recyclable. Therefore, the most important point in recycling such products is preventing the mixing of glass with different components.

### Separation of panel and funnel glass

Because the components of CRT monitors differ in their glass structure, the leaded and unleaded glass must be separated while unmixed, so that it can be easily and efficiently recycled. This process is one of the most important steps during CRT recycling, so that the recycled glass can be used effectively and safely [92].

### Diamond saw method

In this process, which can be performed in both dry and wet conditions, the CRT is separated from the frit zone, where the two different glass types are combined. One or two cutters are used during this process. When the diamond cutter is rotating, the CRT monitor is rotated by the action of the handle on which it is placed. Cooling fluid may be applied during cutting. Thus, a regular sorting process is performed [93]. A further advantage of this method, which can be applied to CRTs of all thicknesses and sizes, is that no additional treatment is necessary. However, the process is slow and the resulting dust during operation leads to difficulties in application.

This method is generally performed in three stages. The first operator removes the vacuum and disassembles the electron gun and the second operator separates the front panel, funnel glass, and shadow mask. The last operator cleans the coating on the front panel and the funnel glass.

### NI-Cr hot-wire cutting method

In this method, the frit region of the CRT monitor is electrically heated and then cold air is applied. At this point, a thermal stress is formed in the frit zone. The resulting stress separates the CRT from the frit zone. The laser cutting method is similar to this method. After the heating process is performed using laser beams, cold air is similarly applied. The separated parts are accumulated in different sections [94]. During this process, care should be taken not to bring lead glass from the frit part on the front panel glass.

In practice, the nickel-chrome wire is wound along the frit line to the CRT surface. The wire is heated for an average of 30 seconds. Thermal expansion occurs in the area in contact with the heated wire. Then, with a sudden cooling (cold air or water) a thin crack is formed along the line. The two sections are easily separated from each other with light bumps.

The most likely problem that may arise with the application of this method is that it does not crack and separate from the desired region by sliding the wire. For this, the area where the wire is to be placed is cut with a diamond cutting saw. In addition, cutting edges are formed in the regions separated from the crack point. Due to the different dimensions of the CRTs produced and the thickness of the glass, the application conditions of this method vary from product to product. It is easy to implement and low in the costs needed to increase efficiency.

### **Acid-leaching method**

Acid leaching is the separation of the anterior panel and funnel sections from the nitric acid binding points. Hot acid is applied to the CRT surface and it is then left in a hot acid bath. This is not an efficient method, as a lot of wastewater is generated during this process [37]. Furthermore, the treatment of wastewater generates additional costs [95].

### **Waterjet cutting method**

During this widely used method, high-pressure water is applied on the CRT. The front panel and the leaded glass are separated by the joint region being abraded. In this process, abrasive particles can be found in the applied water. The pressure of the water can be up to 50,000 psi [96]. The most important point when applying this method is to accurately set the focal point where the water is applied to ensure a good cut.

### **Front panel cleaning of phosphorus coating**

The panel glass of the CRT structure is the most suitable part for recycling. It can be easily recycled because it either does not contain lead or it contains very small amounts. However, phosphorous coatings used for different colors should be treated before recycling [97].

### **Separation of coating using a water mill**

Phosphorous coatings can be removed from the panel surface by means of a water mill. Firstly, the front panel separates the pieces of glass that are smaller than 2 cm. The shredded glass is taken into the mixer with water. The glass to water ratio is 1/3. With the added alumina balls, the process is stirred for about 2 hours. At the end of the process, there should be no noticeable coating on the glass surfaces separated into smaller pieces. If wastewater is generated during this process, it can be reused after filtering. In addition, a small amount of glass will be lost [94].

### **Separation of coating by sandblasting**

Sandblasting is a surface cleaning process used in many areas within the industry. During this process, which is also used to clean the phosphor coating on the front panel glass, the coated surface is sprayed with fine air, and fine sand or iron particles. The sprayed particles abrade the coating. The biggest advantage of this process is that no extra waste is generated during the process. The sprayed dust can be reused.

### **Closed-loop recycling**

In closed-loop recycling, the raw material obtained at the end of the conversion is used again in CRT production. During this process, the collected CRT waste is sent to the recycling company without removing the front panel and funnel part. CRT glass structures are separated according to their contents and are sent to the manufacturer. In this phase, the lead-free front panel part is separated [98,99]. Manufacturers use some recycled raw materials in the production of new products. For this reason, producers do not want the different types of glass structures to mix with each other during the recycling stage. Raw materials of unknown origin are considered to a great risk for production. A product produced with the wrong raw material ratio cannot be used again.

Appropriately recycled CRT glass has many benefits for production. Recycled CRT reduces costs and the energy consumption of the product. It also reduces emissions during production [100]. However, the ratio of recycled raw materials used in new products remains limited [101]. In closed-loop recycling, the monitors are manually disassembled and separated from their external protection. The vacuum in the CRT is then removed to prevent the CRT from breaking down during the separation process. Separating the front panel and funnel part by sawing can be done with many different methods, such as thermal shock and acid etching [94].

### **Open-loop recycling**

Pyrometallurgical and hydrometallurgical elution of lead from the funnel glass parts is possible for CRT waste that contains high amounts of lead [102]. The pyrometallurgical process is a traditional method for recovering precious metals. However, the process intermediates and by-products that can occur are numerous. Pyrometallurgical decomposition must allow for the foreign materials to come out on the surface as slag and the metal product obtained

must be pourable. Therefore, the control of pyrometallurgical processes is complicated. For this reason, in recent years, such processes have been initiated with hydrometallurgical processes [103]. Since glass constructions contain extremely strong bonds, activity-enhancement studies are being carried out before the hydrometallurgical process.

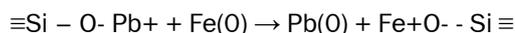
### **Lead production from waste-CRT glass**

Precious metals, such as gold, silver, and copper, can generally be recovered by electronic waste. The waste is then burned like other types of waste, where energy can be recovered [104,105]. This prevents waste accumulation in the landfill. However, it is dangerous to store a lead-containing waste, such as CRT, in such areas [106]. Due to this, some countries prohibit the storage of CRT waste in this manner [107]. Another environmental danger is the air pollution caused by burning the waste [108]. For this reason, studies have been carried out to remove harmful metals from CRT waste and reuse them [101,109].

### **Pyrometallurgical process**

Lead and other metals are present as oxides in CRT waste. These metals can be recovered by the pyrometallurgical process. The reaction medium is formed by adding to the process system substances such as carbon or iron, which are more active than lead. At the end of the reaction, the oxygen bound to the lead combines with the more active substances, leading to lead formation in the products [10]. 99% of the lead in CRT waste can be obtained with high purity. During this process, the temperature does not rise above 1000 °C, to avoid lead evaporation. The lead oxide in the CRT funnel glass is reduced with carbon. The reduction is supported by the addition of Na<sub>2</sub>CO<sub>3</sub> [110]. After the end of the metal lead reduction process, the medium is brought to 24 °C [103].

5% of TiN and SiC were used as reductants in the work of Yot et al. (2009), and the recovery of lead at 950 °C for 60 minutes reached 40% with the addition of 20% SiC by TiN [111]. X. Lu et al. [112] used iron powders as a different reducing agent in his work and tried to obtain the lead oxide in a metallic form. In this study, the mixture of iron dust and CRT, used at an 1/1 rate, was processed at different temperatures and durations. The most efficient range in these experiments was 58% at 700 °C for 30 minutes. The main reaction is as follows:



### **Hydrometallurgical process**

The hydrometallurgical process is the processing of solid material with acidic or caustic solutions. The solutions are then subjected to separation and purification procedures, such as precipitation of impurities, solvent extraction, adsorption, and ion exchange to concentrate the metals. For this reason, the control of the hydrometallurgical process and its predictability are more stable.

The strong bonds of metals in glass structures within the CRT make it difficult to recover via hydrometallurgy. For this reason, some pre-treatments have been developed to increase the solubility of lead. Researchers have tried to break the glass structures by sintering leaded glass with components such as Na<sub>2</sub>CO<sub>3</sub> and by filtering it with a lead acid solution [110].

According to one specific study, the CRT glass was milled with strong alkaline solutions (NaOH) to increase the solubility to 97% at 70 °C and make the lead more active [109].

### **Use of CRT waste in brick and cement additives**

Waste glass can be used as a cement additive [113]. Studies have investigated the removal of CRT products from waste and their reuse in beneficial applications, such as the use of CRT waste as an additive material in cement and brick making. Due to its easy preparation and low cost, many studies have been performed on this subject [114,115]. CRT glass that has been brought to the appropriate particle size can be recovered in this process in a short time and in large amounts [116].

In this type of work, panel glass was used as a contribution element after the separation of the panel and funnel glass. The funnel glass content hinders its use in this process due to the presence of lead. However, mechanistic improvements have also been achieved when working with the funnel glass [117]. It has been noted that the percentage of leaded glass should not exceed 25%, in order to prevent the lead from interfering with the environment [114]. The use of glass in concrete has a partial negative effect on its workability [118]. Reduced machinability has been observed when using more water [119].

After the broken panel glass has been dried, it is passed through the sieves according to the areas destined to be used and it is then collected in several different sizes. The classified glass particles are directly mixed as an additive without

further processing. Limestone dust is frequently used to improve the flow behavior and some of the properties of glass waste being used as a cement additive [120,121].

### **Use of CRT waste as foam glass**

Foam glass is a lightweight and handy product that is especially used where heat and sound insulation is necessary [122]. Its use has increased in recent years due to it being nonflammable, waterproof, a good insulator and having a long life. Foam glass is produced at temperatures of 700 °C and 900 °C [123]. In the production of these products, CRT glass components with a lower melting temperature can reduce the product's melting temperature in some cases [12]. Although first applications were made entirely of pure glass, the rate of these industrial waste products being used has increased to 98% today [56]. In order to improve the mechanical properties of these products, different materials have been used besides CRT [124]. Investigations have shown that the amounts of lead leaked through the glass foams are acceptable [125].

Foam glass is usually produced by adding a gas producing material to powdered glass and then baking it to trap the gas bubbles in the glass. These products are generally used as foaming agents, carbon-containing materials, organic compounds, and carbonates [126], [127]. Depending on the area to be used and the desired properties, other minerals can be added to the mixture and the mixture is then sintered. During sintering, the foaming agent content reacts to increase the volume and obtain the glass foam [128]. The foaming agent added to alter the properties of the produced glass foam varies depending on the grain size of the glass used and the cooking temperature [129].

### **Use of CRT waste in ceramic products**

There are fewer restrictions regarding ceramic industrial products that are in little contact with humans, as compared to those found for the food industry. It is therefore easier to use these type of waste in the ceramic industry. In some studies, CRT waste has been used as an additive material in ceramic glazes [18]. It has been observed that using CRT glass up to 5% does not affect the desired properties. Industrial studies have also found that the glazes using CRT glass are similar to conventional glazes [93].

The various components in the CRT may contribute to achieving certain desired properties in ceramic glazes. CRT windows can reduce energy consumption and glaze production times.

### **Nano-lead production from CRT waste**

Nano-sized metals are used in special applications for their chemical, thermal and electromagnetic properties. Lead has been specifically designed for use in a variety of composites, superconducting fiber cables and next-generation lithium-ion batteries, because of its radiation protection [130,131].

In their work, Wang Y and Zhu J [132] studied lead funnels that were pulverized and mixed with magnesium (Mg) and iron oxide ( $\text{Fe}_2\text{O}_3$ ) to form samples with different funnel-glass ratios and reacted under high temperature in an argon-cleaned environment. During the reaction, the volatilized lead was concentrated in the reactor walls and was obtained in a powder form. 90% of the lead weight was recovered in the samples containing lead up to 40%. The ambient temperature decreased significantly with the increasing funnel glass percentage, and the recovery rate of lead in the samples containing over 40% of funnel glass was reduced [132].

Xing and Zhang studied funnel-glass dust, mixed with 10% carbon dust, in an atmosphere cleaned with argon gas. Approximately 97% of the lead was vaporized in a 2–4-hour time at 1000 °C. the evaporated lead was condensed using a water-cooling system and was obtained in a powder-size range of 4–34 nm [133].

### **Barriers to the recycling of CRT**

CRT production is a complicated process and covers many sub-structures in different compositions. The amount of raw materials used is different according to various brands and models, and their quantities are not known for every product. This prevents the producers from using waste of this type as recycled raw materials. Therefore, the biggest obstacle to CRT recycling is that the exact content values are unknown [18].

In areas where glass products, such as food and household goods, are used more often, healthcare organizations limit the application of heavy metals such as lead in products, which in turn limits the use of CRT waste in this area of application. In particular, coatings containing phosphorus and cadmium in the inner surface of the lead and the panel glass of the funnel glass should be cleaned very well. This is accompanied by additional costs. Despite the fact that recycled materials are more environmentally friendly than the products produced with raw materials, costs are often at the forefront of production.

In order for the recycling to be efficient, it is necessary to efficiently collect large amounts of the product and transport it to the conversion sites. However, due to the lack of recycling awareness in many countries, the fact that such waste can be harmful is not widely known, and it is often sent directly to landfill areas. This further complicates the collection of CRT waste.

### **Non-glass CRT components and precious metal recycling**

In CRT monitors, the units that are not glass compositions are the circuit board, the electron gun, the shadow mask and the deflection yokes. Circuit boards contain the most copper and solder, but also contain many different metals in their structure. The main components of the electron gun in a standard CRT unit are glass, steel, copper, and polymer materials, and they account for approximately 1% of the total weight. The materials forming the deflection yokes are in the form of polymer and copper wire, and they constitute approximately 5% of the total weight. The shadow mask, which is a very thin and perforated sheet of plate, is made of steel.

These units are manually separated with the help of tools, after the external protection on the TV unit has been removed. After each piece is collected separately, the metal and polymers are sold to other recycling companies [52].

### **Deflection yokes**

The deflection yoke is a copper coil extending to the neck window at the beginning of the funnel region and directing the rays coming from the electron gun. The vertical and horizontal magnetic fields that make up the deflection yoke direct the beam bundles to the coated screen, scanning over the shadow mask [134,135]. This polymer and metal part contains large amounts of copper wire that can be directly recycled. Following the disconnection of the circuit board during disassembly, the deflection yoke can be easily disconnected by removing the sealing tape that connects the yoke to the neck region window. The removed coil is generally collected in the recycling zones and then sent to a copper and polymer recycling facility.

### **Electron gun**

Electron beams are formed in this region, making it the main component of the monitor [136]. The electron gun consists of cathode and anodes with different functions. The potential difference between the cathode and the anode is between 100–1000 V [137]. With the potential difference, the electrons separated from the cathode are transferred to the screen through the part in the panel, with the help of deflection yokes. The front surface of the cathode in the electron gun surrounds the control grid. There is a small opening in the anode section of the control grid. In order to collect the electrons separated from the cathode surface, a negative charge is loaded, according to the cathode.

There are two different anodes: primary and secondary. The primary anode collects the scattered beam bundles and it is also called the focusing anode. The secondary anode accelerates the incoming rays and sends them to the screen.

Steel, glass, copper, nickel, barium, and strontium are the most common materials appearing in the electron gun and they make up a very small portion of the average CRT monitor, in terms of weight and volume. In the mouth where the electron gun is combined with the funnel glass, sintered material with potassium aluminosilicate is used for crystallization [138]. The glass surrounding the electron gun contains 40% lead oxide [56]. One of the most commonly used cathodes is cesium metal because of its ability to easily release its electrons. The cesium cathodes start to emit electrons at about 950 °C.

The cathode is covered with a thin oxide layer. This is usually a mixture of barium and strontium oxides. The cathodic facing surface of the control grid and the inner surface of the cavity on the grid are electroplated with gold in a very thin manner, by use of an electrostatic method, in order to remove the effects of emulsion that can arise from these coatings when the cathode is activated. Gold alloys have also been used for this coating, but they are not as effective as pure gold.

The control grid is made of molybdenum alloy stainless steel. There are three holes, with an average diameter of 0.25 mm, passing through the rays coming from the cathode. These holes allow for the intensified passage of electrons through the emitter. The control grid, extracted from 1,000 CRT TV units, with a coating 2 mm in diameter and 0.01 inches in front of the cathode, can be recycled with 1.4 gr of gold.

TV sales in almost all of Europe and other major countries have been dominated by CRT monitors until 2004. After that time, with LCD and LED monitors developing in 2007, their market share has dropped considerably and in 2011 sales almost stopped [139]. CRT monitor usage in Europe fell by 6.3% in 2012. From 1980, when CRT monitors lost their popularity in 2007, more than 700 million CRT TVs had been sold in the United States. During this period, sales in Turkey can be estimated at approximately 100 million units. When these units are added to the use of personal computers, which became popular in Turkey after 2000, only about 2 tons of gold metal is contained within in these products.

## Printed circuit board

Printed circuit cards account for approximately 3% of the total electronic waste in the world [140]. Circuit boards, used in all areas of the electronics industry, have a market share of close to \$15 billion worldwide [141]. It is foreseen that this sector will grow together with the electronic sector.

Due to the wide variety of metals that circuit cards contain, recycling is made difficult [142]. However, most of these metals are indeed recyclable materials and their amount in circuit boards is not low. Approximately 28% of a standard circuit board is made of polymer and 23% is made of metal [143]. The most commonly used metal components on circuit boards are tin lead alloys, used in copper and solder to provide conductivity [144]. With regards to precious metals, circuit boards contain gold, silver, and platinum, as well as general-use metals, such as copper, aluminum, and iron [142]. Silver and gold are mainly used in contact areas, because they are protective and conductive [144].

These metals are found in different quantities in TV and computer units and have an average of 70% copper, 16% solder, 4% iron, 3% nickel, 2 % silver, and 0.05% gold [145-147]. However, the recycling of these metals is difficult due to their co-existence with various other metals. Different recycling methods are applied for each metal [148]. Generally, hydrometallurgical methods are applied for such purposes [149,150]. However, the waste and harmful components in these methods can increase the costs of the process [151]. Similarly, waste that is burned by pyrometallurgical methods causes pollution, because of the harmful gasses it contains [152].

Circuit cards are generally recycled for the precious metals they contain and classifications are made based on their amount of gold. Although the classification is not strictly determined by the appropriate authorities, group A is set to contain more than 400 ppm of gold, group B contains 100–400 ppm, and group C contains less than 100 ppm. The printed circuit boards used in CRT monitors are in group C [144].

Circuit boards are stripped off their assembled components by various methods before recycling, and then the coarse pieces are broken off. The very small fragmentation of the printed circuit board makes the recycling of precious metals difficult [153]. Since the metals to be recycled by these products generally fall into the class of precious metals, the hydrometallurgical process is introduced to get rid of the byproducts of pyrometallurgical processes. 76% of the gold (which is the priority in this case) can be recovered from circuit boards containing low levels of gold, such as those used in TV sets. In the early stages, cyanide was used for a long time to recover gold [154]. However, as use of cyanide is fairly toxic [155], research has been focused on the development of alternative methods to solve the gold.

Particularly in pins and connectors, the gold contained in the coating is electrolytically dissolved. Since the solution contains different metals together with gold, it is precipitated in a gold solution and then filtered. The precipitate obtained is taken to the melting pot where the gold is obtained. Gold does not directly coat the circuit board. There are copper and nickel layers between the board and the gold layer. Nitric acid can be used to separate the layers, as well as other methods. The coatings separated on the circuit board are dissolved in another hydrochloric acid and then filtered. The solution obtained therefore contains only gold. Sodium metabisulfite can be used to precipitate the gold in the solution. The sludge precipitated to obtain gold is melted in a crucible.

## Conclusions

It has been determined that the best option for environment is the recycling of CRT waste. As a result of this research, it is concluded that in many countries the infrastructure for this type of waste has not yet been established. Recycling programs should be developed worldwide. CRT products contain materials in different compositions and lead storage makes the recycling of CRT products more complicated. Because of these factors that generally increase costs, producers also avoid using recycled raw materials. However, recycled raw materials can be reused in many different areas, especially in the construction sector. As a result, the use of recycled materials will become a necessity in the future.

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