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NON-FEROUS METALS RECOVERY

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Abstract: Non-ferrous metals are among the few materials that do not degrade and do not lose their chemical or physical properties in the recycling process. The most frequently recovered metals are: lead, gold, silver, aluminum, copper and platinum. Therefore, studies are being carried out aimed at developing new processes for the separation of metals, mainly from industrial waste by-products. The handling of e-waste including combustion in incinerators, disposing in landfill or exporting overseas is no longer permitted due to environmental pollution and global legislations. Compared to other waste components, such as plastics, wood or textiles, non-ferrous metals exhibit better reusability and higher market values. In future, new strains have to be identified to improve the metal recovery from solid waste.

Keywords: non-ferrous, recovery, recycling, waste

1. INTRODUCTION

The demand of electrical and electronic equipment (EEE) increased considerably with technological advances. Significant innovations on electric and electronic technologies have their lives shortened, thus increasing generation of waste from electrical and electronic equipment (WEEE) or electronic waste (e-waste). Global production of electrical and electronic equipment is growing rapidly and it is expected to accelerate in the near future. At the global level, latterly there are generated between 20 and 25 million tons of electronic waste per year, with a high share in Europe, USA and Australia. However, it is expected that Eastern Europe, China and Latin America to become a major producer of e-waste in the next ten years [1].

It is expected that, in Europe, electronic waste production to increase by 45% between 1995 and 2020. Therefore, a three-pillar strategy of prevention, recycling and reuse of waste is necessary to minimize environmental impact and to promote the use of wasted resources efficiently [2].



Figure 1. Suggested activities in waste management [3]

2. GUIDE LINES

Considering the Waste Framework Directive (Directive 2008/98 / EC), the treatment of municipal mixed solid waste (MSW) in Europe has become

mandatory. Most electronic waste ends up in landfill. According to the US Environmental Protection Agency report on electronic waste in 2008, 19% of them are burnt and 81% are eliminated through storage [4]. Underground removal of e-waste has several disadvantages, including the contamination of groundwater, soil, and loss of potential sources of valuable metals. In the last decade, many countries have issued legislation on electronic waste. Underground storage of e-waste incinerators or burning is not permitted without isolation of hazardous materials. Moreover, the export of e-waste in underdeveloped countries is not permitted in accordance with international [5].

Underground removal of e-waste has several disadvantages, including the contamination of groundwater, soil, and the loss of potential sources of valuable metals. In the last decade, many countries have issued legislation on electronic waste. Underground storage of electronic waste or incinerators burning is not permitted without isolating hazardous materials. Moreover, the export of e-waste in underdeveloped countries is not permitted in according to international regulations.

Until 2020, it should be prepared for reuse and recycling at least paper, metal, plastic and glass from household waste and possibly from other origins as far as these waste streams are similar to waste coming of household waste to a minimum of 50% of the total weight. Also, by 2020 should be achieved preparing for reuse, recycling and other material recovery, including operations using waste to substitute other materials, non-hazardous construction waste and demolition waste to a minimum of 70% of weight, excluding naturally occurring material.

The treatment methods aimed to reduce the organic carbon content must be in order to meet the final disposal criteria. Unlike storage, the new processing modes allow the recovery of materials contained in solid waste. This focuses on the recovery of non-ferrous metals. Compared to the other used components, such as plastic, wood or textiles, NF metals are easier to recycle with high market values. NF metal production from

primary resources is limited and it is a high energy process. Therefore, recycling of metals can contribute greatly to energy saving, reducing carbon dioxide emissions. [6].

Table 1. The energy saved by recycling compared with those of extraction of primary resources [7]

Crt. iss.	Material	Saved energy (%)
1	Aluminium	95
2	Copper	85
3	Iron and Steel	74
4	Lead	65
5	Zinc	60
6	Paper	64
7	Plastic	>80

The overall potential of NF metals from incineration ash and mechanical-biological treatment plants (MBT), depends on the design of the recovery process, employed technologies and efficiency. Many components of the NF concentrate can be extracted by means of eddy current separators, whether incineration ash or during processing in mechanical-biological treatment plants. The separation should be such as to produce metal of sufficient purity to be used as a secondary raw material. The currently used techniques present weaknesses, such as the generation of wastewater and high prices for manual sorting in the European Union. This requires the development of new approaches in accessing resources in waste, while technical requirements depend on the origin of NF concentrate.

Optimised and adapted automated sensor based sorting systems able to identify different nf-metals are considered an applicable solution. However, their application varies considerably depending on the origin of non-ferrous concentrate. This is due to the different distribution of particle size.

Mostly effective screening can be performed automatically, and staff can be used more effectively for manual quality control. Mineral dust layer covering the debris and various metals contained in incineration ash reduce visual selection mode between minerals and metals at a point where manual sorting is not possible.

E-wastes are classified as hazardous materials, therefore, should be managed properly. However, precious metals (PMS) of e-waste, such as gold, silver, platinum, gallium, palladium, tantalum, tellurium, germanium and selenium make them attractive for recycling. In industry there are various metallurgical processes to extract precious metals from e-waste.

3. ANALYSIS

Metal fractions separated from the e-waste during preprocessing may be further processed by hydrometallurgical, pyrometallurgical, electrometallurgical, biometallurgical methods, and combinations thereof. Hydrometallurgical and pyrometallurgical processes are the most important ways of processing waste electrical and electronic equipment. These routes can be followed by electrometallurgical/electrochemical processes (eg electrowinning or electrolysis) to a particular metal separation and recovery. Currently, trials for processing

electronic waste through biometallurgical pathways are not confined to the laboratory, for example, bioleaching of e-waste. However, this route has potential for further development.

E-waste preprocessing is not always necessary in pyrometallurgical route. For example, complex electronic equipment such as mobile phones and MP3 players can be treated directly during the melting process [8]. However in hydrometallurgical processes, pre-processing is required to separate the metal from other fractions. This increases the efficiency of each step associated with hydrometallurgical processes. Each route has advantages and disadvantages that must be taken into account in selecting a suitable recycling process.

Non-ferrous metals, including aluminum, copper, lead, nickel, tin, zinc and others are among the few materials that do not degrade and do not lose their chemical or physical properties in the recycling process. Consequently, nonferrous metals have the ability to be recycled an infinite number of times. Currently, precious metals are used in a wide range of applications, not only in the electronic and communications equipment, spacecraft, jet aircraft and engines, but also in mobile phones and catalytic converters. The most frequently recovered metals are:

- ≡ lead: batteries, nuclear technique, typography, nonferrous metallurgy;
- ≡ gold: jewelry, electronics;
- ≡ silver: electronics, industrial applications (catalysts, batteries, glass / mirror), jewelry;
- ≡ aluminum: nonferrous metallurgy, energy, construction, transport, metallurgy, agriculture etc;
- ≡ tin: nonferrous metallurgy (bronze), food, solders, etc;
- ≡ copper: energy, electronics, nonferrous metallurgy (brass), food, transportation of electricity and heat;
- ≡ chromium and iron alloy (eg stainless steel), nonferrous alloys, superalloys, etc;
- ≡ nickel: cast iron and alloy steel (eg stainless steel), super alloys etc;
- ≡ niobium: alloy and super alloy high / low resistance;
- ≡ manganese cast iron, alloy steel, nonferrous alloys, superalloys, etc.

Recycling for platinum, palladium, rhodium, gold and silver recovery is made from:

- ≡ catalytic converters
- ≡ catalysts for oil refineries
- ≡ industrial catalysts
- ≡ nitric acid manufacturing plants
- ≡ carbon catalyst
- ≡ electronic waste

Considering that precious metals are rare and have a high price, they continue to be recycled at a high rate of recovery. US Geological Survey estimated that 240 tons of gold wastes (new and old) were recycled in 2012 in the United States, which is more than the total domestic consumption of gold reported. In addition, Census Bureau data indicate that about 14,000 tons of scrap precious metals were exported in 2012 worth US \$ 5.5 billion. [9].

Gold recovery

Gold is widely used in computer components. Motherboards and the terminal computers are containing precious metals. Although computers and laptops contain more gold, precious metals are found in everything from coffee makers to cars. Gold of older or obsolete devices can be recovered, but if left in landfills is considered dangerous. Obvious gold deposits from technological and household items can be fragmented.

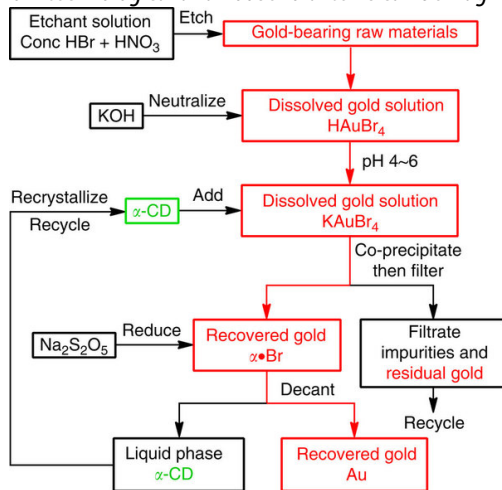


Figure 2. Processing flow gold recovery. [10].

However, gold is very finely layered to be easily removed. CBX solution can be used to extract gold from computer motherboards. CBX underlying material dissolves gold. StripFree is an electrolyte solution using an external source of electricity to remove gold layers with a stainless steel base. StripFree works in the opposite way of galvanization in which electricity is used to cover an object with gold. An old solution for gold recovery is the royal water. A mixture of hydrochloric acid and nitric acid dissolve gold. Gold material is placed in acid and then precipitated using ferrous sulfide.

Platinum recovery

The catalytic converter is a device used to reduce the toxicity of emissions from an internal combustion engine. Widely used for the first time in mass car production on the US market in 1975, to comply with tightening EPA regulations regarding the discharge of gas, catalytic converters are still most commonly used in automotive exhaust systems. A catalytic converter provides an environment for a chemical reaction of combustion and the products are converted to less toxic substances. Opel is the first European producer of catalytic converters mounted on the standard versions of gasoline engines. [11].

The catalytic converter consists of several components:

- ≡ The nucleus or core. In modern catalytic converters, the core is often a ceramic honeycomb, but there are also used stainless steel combs. Honeycomb increase the available surface area for catalyst support, and, therefore, is often referred to as a support "catalyst".
- ≡ Auxiliary layer. The auxiliary layer is used to make more efficient converters, often with a mixture of silica and alumina. Layer, when added to the nucleus, forming an irregular surface, tough, with a much larger area than the base, which then allows for for multiple places to deposit substances catalysts.

- ≡ The catalyst itself is often a precious metal. Platinum is the most active catalyst and it is widely used. This is not suitable for all applications because of unwanted additional and / or costs. Palladium and rhodium are two other used precious metals. Platinum and rhodium are used as a reduction catalyst, platinum and palladium while used as oxidation catalyst. Cerium, iron, manganese and nickel are also used, although each has its own limitations. For example, nickel is not legal for use in the European Union (due to reaction with carbon monoxide), while copper can be used, but its use is illegal in North America due to the formation of dioxin. [12]

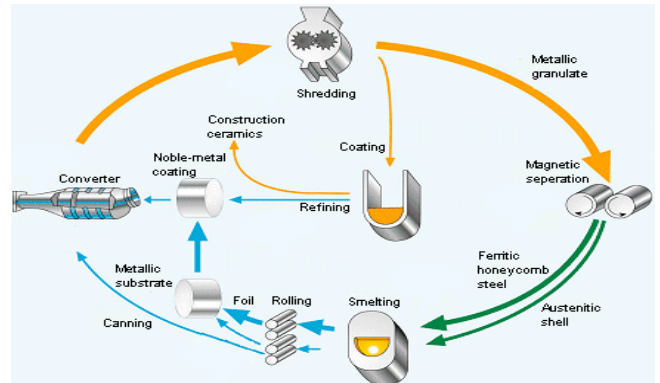


Figure 3. Processing Flow Catalytic converters [13]

While gold is common in electronics because of its superior ability to conduct electricity, platinum is an essential component of catalytic converters. A ceramic honeycomb coated with platinum uses the car engine heat to capture these pollutants. Platinum is the catalyst in a chemical reaction.

A typical catalytic converter contains 1.5 grams of platinum and other metals. The exact amount of platinum depends on the formula used. At the laboratory level, aqua regia dissolution is an excellent way to leach alts of platinum. Salts of platinum can then be further refined to pure platinum. In another technique, sulfuric acid dissolves the ceramic honeycomb, leaving platinum.

Ceramics can be also volatilized and converted to a gas or liquid, a process that may leave behind platinum. Recovery of platinum from catalytic converters and electronic components is much more costly and more difficult than gold recovery. At scrapped, damaged or recovered auto catalysts, from the dismantling car:

- ≡ The amount of platinum can range from 1 g to 15 g (or more for high power machines)
 - ≡ Catalysts for gasoline cars contains about 5 grams of platinum
 - ≡ Catalytic converters for diesel cars even contain 3 times more platinum than gasoline cars, meaning 15 g or more
- Gasoline cars, especially the new generations are equipped with catalysts containing platinum in addition with palladium or rhodium, or both, in different combinations. Diesel engines catalyst contains mainly platinum, palladium and rhodium because they need higher temperatures to become effective or because of chemical reactions that take place. Globally, there is a tendency to remove the platinum catalyst, in particular for gasoline vehicles with new car catalytic converters

containing less platinum and palladium becoming more and rhodium. For diesel versions, platinum will be replaced with gold because pollutants will decrease by 40% compared with platinum and especially the lower price of gold. Platinum is not as pure metal, palpable, it is as an alloy (Platinum, Palladium and Rhodium) and it is dispersed in a kind of ceramic honeycomb (sponge), through which gases are exhausted away. [14].

Lead recovery

The recovery of lead from used batteries is a vast field of research. Lead batteries contain lead alloy, lead sulfate, micro-porous paper and plastic. Every year industry produces about 2.5 mega tonnes of lead worldwide. The most part is used for batteries. The rest is used to cover wiring, plumbing, ammunition and fuel additives. Other uses are as pigments for the paint and plastics from PVC, protection against X-ray, crystal and pesticide production.

Primary lead is produced from sulfide ores containing iron, zinc, copper and other trace elements. The concentrate from the ore and e-waste is treated for the extraction of lead and precious metals. Basically, the process consists in sintering, reduction and refinement. Sintering is carried out to reduce the sulfur content of the material, which is composed of pyrite, limestone, silicon and lead in a high concentration. The reduction is carried out in a blast furnace using the coke in the molten lead by about 85% purity being withdrawn from the bottom of the furnace. The plastic fraction of electronic waste can partially replace coke as a reducing agent during the reduction step and metal fraction reaches the metal phase. In the refining stage, lead dross is processed by adding wood chips, fine coke and sulfur. The sulfur slag produced is separated and transferred into the furnace. The heating of furnace slag separates lead ingots (rich in lead), sulphide copper and other metals.

In the last stage of processing electronic waste by melting method of lead, precious metals and other elements are separated from ingots of lead. The precious metals are separated by Parkes process, in which the zinc forms an intermetallic compound insoluble gold and silver. Other impurities include antimony, tin, arsenic, bismuth, as well as the elements are also separated during the refining step. The end products of the refining stage a concentration of 99.99% lead, precious metals and other elements [15].

Copper recovery

Since the mid-1960s, global demand for refined copper rose by 250% (from 5 million to 18 million tons). Outputs from ores remain vital in order to meet this growing demand. Providing quantity of copper to meet the future society need, means recovery and recycling widespread and substantial investments in the mining industry. Copper is ubiquitous in modern life equipment, high-tech products, electrical installations or engines.

In 2011 the reused amount of copper was 2.1 million tons - an increase of 12% in one year, from end of life products and waste directly recycled manufacturing (direct melting). The increasing percentage of recycling is due to the increasing demand of copper industrial metal worldwide.

According to the report published by Copper Study Group International (International Copper Study Group - ICSG) 41.5% of the copper used in Europe comes from recycling. This reveals that the requirement of recycling of copper is provided, at a rate gradually. Increasing resources meet the growing demand for this metal (250% more than in 1960), while reducing environmental impact of production and ensuring availability for future generations. A computer contains about 1.5 kg copper, a typical home about 100 kg and a wind turbine 5 tons. As the copper can be recycled and reused infinitely without the loss of performance, we must ensure that products and copper waste are processed correctly when they reach the end of their useful life. [16]

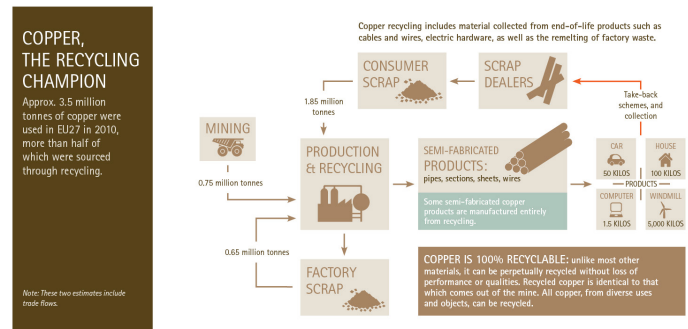


Figure 4. Copper recycling activities [18].

Copper smelting is an environmentally friendly process compared with the melting of lead generating toxic gases.

Copper smelting facilities to minimize transportation costs of e-waste and therefore recycling will be improved, allowing copper smelters to be installed near cities where electronic waste is generated. In these processes, precious metals are recovered through conventional electrowinning process, where they are separated from the sludge. [17].

Silver recovery

Silver recovery from waste solutions such as those produced by conventional processing of medical and industrial X-ray films, photographic films and pictures has been practiced for over 100 years. However, the economic viability of the process has changed radically in recent years. Silver is consumed in various ways, from eyedrops lubricants for jet engines. It is used by each hospital, medical clinic and dentist, and photo department processors, printers and anyone achieves photo processing of a wet solution.

Modern methods of recovery offer the opportunity to earn a quick payback, which means faster profits. Different methods are used to recover silver:

1. Electrolysis – most commonly used. A stainless steel drum with current attracts the silver. The silver is stripped off the drum and the by-product called flake is sent for refining – usually 90% - 95% pure.
2. By adding chemicals, which cause the silver to form sludge – this is then dried and refined. The sludge is usually 30% pure.
3. Silver Traps – are also used to extract silver. This is a container with a cartridge – the fixer filters through the container and the Silver is trapped in the cartridge
4. Researchers have also developed methods for the extraction of silver, using bacteria and enzymes that "eat" the emulsion of gelatin, silver run. This method is not widely used (since 2011).

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X-ray films contain an average of 7.5g per kilogram while negatives have 9g / kg and camera film 2g / kg. Fixer varies according to how the film is processed but average at 3.0 grams per liter.

The legislation states that hospitals and clinics to follow certain rules regarding the disposal of X-ray films. X-ray films are considered private information so they must be completely destroyed, while silver and other chemicals in the film are toxic to the environment. Recovery of silver prevents penetration of metal into the environment, but other products used in the process must be carefully withheld or destroyed. [20, 21]

Aluminum recycling

One of the basic characteristics of aluminum is its versatility, allowing the use of the metal and its alloys in a wide range of sectors, from transportation to construction, electronics, packaging, furniture and industrial installations. For these final destinations, aluminum is used in the production of durable goods, excluding packaging. At end of life, it turns into waste products which are either stored or, alternatively, recycled or reused. In market economy a possible recycling is directly related to the recovery of residual value, in the sense that it will be directly proportional to the capability to strive for such a process. In terms of recycling, aluminum and its alloys are exceptional materials, because as with other non-ferrous metals recycling can be done without significant deterioration of quality.

Almost all of the absorbed energy in the first stage of metal production, namely 95%, is preserved in material and ready to be reused when remelting. As a result, the production of a kilogram of recycled aluminum requires energy equivalent to 5% of the electrolytic production of one kilogram of metal. Secondary aluminum is the equivalent of primary aluminum, even after several cycles of life, so that recycling can:

- ≡ recover valuable material without loss of quality;
- ≡ save energy compared to primary production;
- ≡ reduce emissions and gas producing greenhouse;
- ≡ reduce mining activities;
- ≡ reduce waste. [22]

4. CONCLUSIONS

Collection of waste from electrical and electronic equipment is a key step for recycling and efficient management of resources. The main options for collecting post-consumer goods are at the municipal level, to retailers, manufacturers and individuals. The economic policies of each country dictate the balance between different ways of collecting. The collection can be improved by raising awareness and increasing investment in well-organized collection facilities.

WEEE contains limited quantities of precious metals; therefore a long-distance transport is unprofitable. Transport is a significant obstacle and overcome this barrier is to develop preprocessing centers near cities. Such centers could perform sorting, dismantling, shredding and metal fractions from the release of other waste material. The conveyance of metal fractions is the only way to minimize transport costs, which can improve the economy of recycling electronic waste.

The lack of the centers for separation the metal from complex e-waste material is one of the barriers in the extraction of precious metals from e-

waste, the issuance / separation during mechanical machining. Initial processing and release of metals are essential for recycling electronic waste.

Preprocessing steps, including sorting, dismantling, crushing and isolate the issue metals, alloys and other material values of a complex of e-waste. Some of the technical difficulties during the melting and refining processes can be reduced to a minimum during the delivery stage. Insulating of precious metals from e-waste is a challenge due to interconnections with other metals from computer motherboards.

Another barrier that affects the potential of electronic waste recycling is the incomplete knowledge of methods underlying melting and refining processes. It is crucial to have knowledge about the composition of the feedstock, and its possible side finished product. Recovery of PMS from e-waste using technologies similar to those applied natural ore is a challenge. [23]

However, according to the Belgian company Umicore (one of the largest recyclers in the world, heavy metals from electronic waste and industrial waste), urban mining could result in 200-250 g gold / tonne of integrated circuit cards and 300-350 g / tonne of mobile phones. This contrasts with the concentrations obtained in the mining of gold core, about 5 g / tonne of crude ore.

Output products contains metals in a higher concentration than primary sources, meaning that it takes typically less energy to extract the same amount of metal. The Umicore recycling unit in Hoboken, Belgium, produces, for example, 70,000 tonnes / year of metal and issues with a megaton of CO₂ less than if the amount of metal was made from raw ore. In Romania, nearly 18,000 tons of electronic waste resulting from the IT, electronics and home appliances were collected in 2008. Using the average of 250-300 g / t, would result between 62 and 70 tonnes of gold that could be recycled in a single year from this source of waste. For example, in Rosia Montana, the Canadian company RMGC aims to extract 314 tons of gold in 16 years. [24]

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