A REVIEW ON RECOVERY PROCESS OF PRECIOUS METALS LIKE GOLD AND SILVER CONTAINED IN ELECTRONIC WASTE

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https://doi.org/10.1590/SciELOPreprints.9125

Submitted on: 2024-06-12
Posted on: 2024-07-01 (version 1)
(YYYY-MM-DD)

A REVIEW ON RECOVERY PROCESS OF PRECIOUS METALS LIKE GOLD AND SILVER CONTAINED IN ELECTRONIC WASTE

REVISIÓN DEL PROCESO DE RECUPERACIÓN DE METALES PRECIOSOS COMO EL ORO Y LA PLATA CONTENIDOS EN RESIDUOS ELECTRÓNICOS

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RESUMEN

El proceso siderurgia para el tratamiento del oro y la plata se mantuvo inalterado durante los primeros 70 años del siglo XX y consistió esencialmente en la lixiviación con cianuro en solución seguida de la separación sólido-líquido, siendo el lavado de los residuos sólidos de la forma más eficiente posible, y con el tratamiento de la solución lixiviante con zinc metálico para la recuperación de metales preciosos.
Este proceso es generalmente muy eficiente y bastante económico, pero tiene sus limitaciones en el tratamiento de minerales de baja ley y ciertos tipos de minerales complejos. Debido a la baja ley que se encuentra en las minas, se han reciclado residuos de otras industrias para obtener oro y plata. El proceso de reciclaje de minerales lleva alrededor de 20 años de estudio, desarrollo y aplicación. Este artículo muestra un resumen de los procesos de reciclaje más importantes como fundición, fundición alcalina, proceso electroquímico e hidrometalúrgico.

Palabras clave: *oro, plata, cianuración, desechos electrónicos, reciclaje, metales preciosos, fundición, horno kaldo, fundición alcalina, proceso electroquímico, proceso hidrometalúrgico.*

ABSTRACT

The sider-metallurgical process for the treatment of gold and silver remained unchanged during the first 70 years of the 20th century and consisted essentially of leaching with cyanide in solution followed by solid-liquid separation, with the washing of solid waste in the most efficient way possible, and with the treatment of the leaching solution with metallic zinc for the recovery of precious metals.
This process is generally very efficient and quite cheap but has its limitations in the treatment of low-grade ore ores certain types of complex minerals. Due to the low grade found in the mines, waste from other industries has been recycled to obtain gold and silver. The mineral recycling process takes around 20 years of study, development and application. This article shows a summary of the most important recycling processes like smelting, alkali smelting, electrochemical and hydrometallurgical process.

Keywords: *gold, silver, cyanidation, e-waste, recycling, precious metals, smelting, kaldo furnace, alkali smelting, electrochemical process, hydrometallurgical process.*

1. INTRODUCTION

The siderometallurgical process for the treatment of gold ores and silver remained unchanged during the first 70 years of the 20th century and consisted essentially of leaching with cyanide in solution followed by solid-liquid separation, with the washing of solid waste in the most efficient way possible, and with the treatment of the leaching solution with metallic zinc for the recovery of precious metals [1]

Gold is a rare element with a concentration of just 0.005 ppm in earth crust. This low concentration is a big challenge for gold processing due to a need of upgrading by factor of 3000 to 4000 to receive commercial concentrations. Due to its siderophile properties, gold is frequently bonded with silver, copper and other metals and it also occurs in sulfidic ores such as pyrite, tetrahedrite, chalcopyrite and arsenopyrite [2, 3].

On the other hand, there´s the silver, a characteristic white metal. Silver is the softest of all metals and the one with the highest thermal and electrical conductivity. Its symbol is Ag (comes from Latin: argentum, "white" or "bright"). It is a white, shiny, soft, ductile and malleable transition metal.
Their resistance to corrosive agents makes it ideal for the manufacture of some containers special or as a coating for other metals [3].

Today’s gold ore reserves are assessed around 51,000 tons; it means the reserves are almost 20 times the world annual primary production. Gold production numbers and the gold price are shown in Figure 1 [2, 4].

World silver production has not changed physical spaces, as it shows in the Figure 2, in the sixties were Mexico (21.2%), Canada (16.2%), United States (14.7%), Peru (14.6%) and Australia (7.2%) that together they produce more than 70% of the world's total. Today produce 27.4 miles of tons (mt), and they are the same countries producers and China that produce the percentage worldwide: Mexico (21.3%), China (14.5%), Peru (13.8%), Australia (7%), Russia (5.6%) [5].

Figure 1. Gold production amount (t) and corresponding gold price ($) [2, 4].

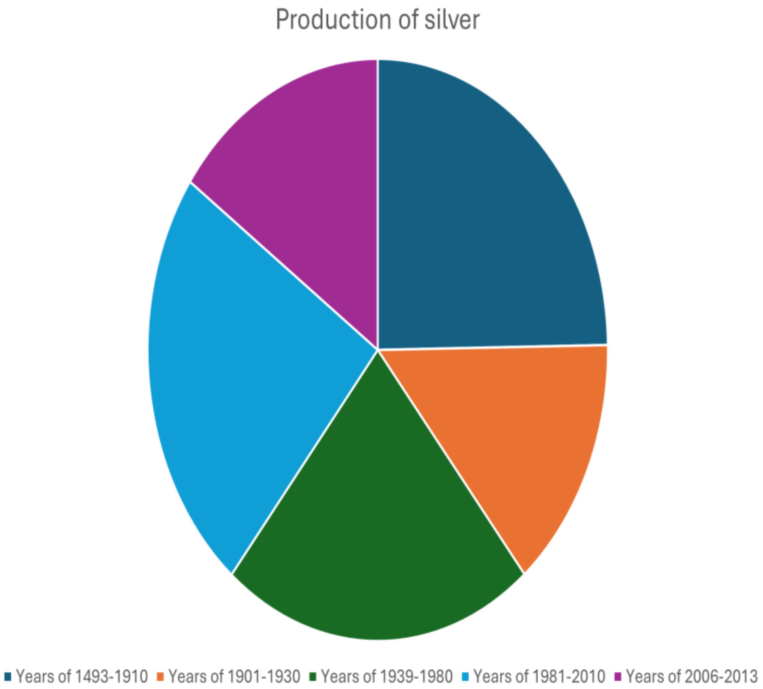


Figure 2. World silver production in thousands of metric tons [5].

The main process of obtaining gold and silver is summarized in Figure 3. Below each process is explained in a summarized way:

1. Crushing and Grinding: The ore containing gold is mined and crushed into small pieces, then ground into a fine powder to increase the surface area for the cyanide solution to react with the gold.

2. Leaching: The powdered ore is mixed with a dilute cyanide solution (usually containing sodium cyanide), which dissolves the gold into a solution. This process occurs in large tanks called leaching tanks.

3. Adsorption: The gold-cyanide complex is then adsorbed onto activated carbon particles in a process known as carbon-in-pulp (CIP) or carbon-in-leach (CIL). The activated carbon is typically made from coconut shells or other organic materials with high adsorption properties.

4. Recovery: The gold-loaded carbon is then separated from the pulp and sent to a stripping vessel where the gold is desorbed from the carbon using a hot alkaline cyanide solution, producing a concentrated gold-cyanide solution.

5. Electrowinning or Zinc Precipitation: The gold-cyanide solution is further processed to recover the gold. This can be done by either electrowinning, where electricity is used to plate the gold onto cathodes, or by zinc precipitation, where zinc dust is added to the solution to precipitate the gold.

The main disadvantage of the cyanidation process are the adverse effects of the use of cyanide and thiocyanate, such as:

1. Cyanides are relatively mobile in soil. Once in the soil, cyanide can be removed through several processes. Some cyanide compounds in soil can form hydrogen cyanide and evaporate, while others will be transformed into other chemicals by microorganisms in the soil. Consequently, cyanides generally do not leach into groundwater. However, cyanide has been detected in groundwater at a few landfills and at industrial waste disposal sites. The high concentrations of cyanide found in some landfill filtrates and in garbage stored at some sites are toxic to soil microorganisms. Because these microorganisms can no longer transform cyanide into other chemical forms, cyanide can pass through the soil into groundwater [6].
2. There is less information about what happens to thiocyanate when it enters the environment. In soil and water, thiocyanate is transformed into other chemical forms by microorganisms. This occurs in

soil at temperatures up to 86ºF (30ºC). At these temperatures, the thiocyanate in the soil does not evaporate or adhere to the soil [6].

Due to climate change, it is decided to make changes in metallurgical extraction, from the use of less aggressive reagents to the recycling of electronic waste (e-waste).

Recycling e-waste is important from an energy conservation perspective as well. Using materials recycled from e-waste to supplement virgin resources can result in major energy savings and can also lessen the environmental impact associated with the mining and refining of raw materials [7]. This could result in up to 95% energy savings for aluminum, 85% for copper and 74% for lead and steel [8, 9]. There are also considerably lower CO_2 emissions from recycling e-waste compared to processing virgin materials, which was shown in 2019, where e-waste recycling reduced global CO_2 by an equivalent of 15 Metric Ton (Mt) by providing an alternative to mining and processing virgin materials [9].

In addition to the economic benefits of e-waste recycling, it is also important to consider the impact that unrecycled or improperly treated e-waste has on the environment [7]. PCBs are composed of a range of hazardous materials, including lead, mercury, brominated flame retardants (BFR), chlorofluorocarbons and hydrochlorofluorocarbons [11]. If improperly handled and disposed of in unlined landfills, these compounds contaminate groundwater and pose a significant risk to the environment and human health [12].

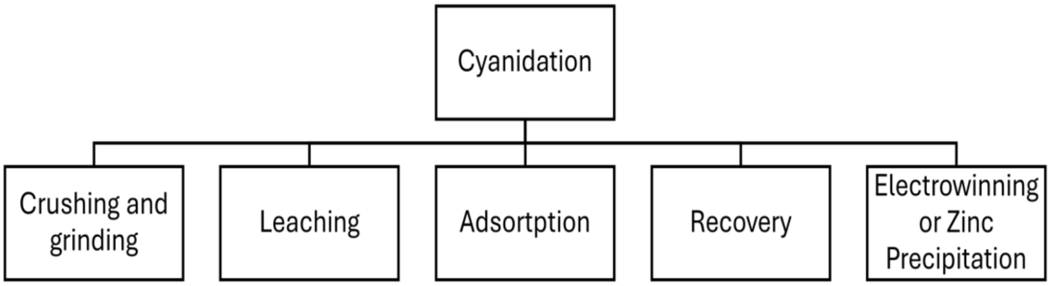


Figure 3. Process of cyanidation.

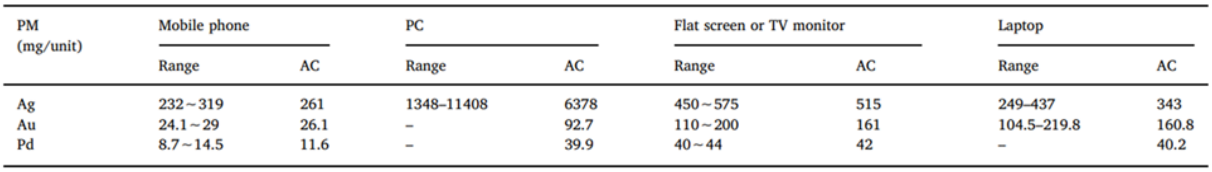
2. ALTERNATIVE EXTRACTION METHODS OF GOLD AND SILVER

2.1 RECYCLING ELECTRONIC WASTE

In electronics industry, gold and silver are used as contacts, bonding wires and switches, while palladium

In electronics industry, gold and silver are used as contacts, bonding wires and switches, while palladium is used in computer hard disk drives [13]. The content of main precious materials (PMs) in typical e-waste is shown in Table 1 [14].

Table 1. The content of precious metals in typical electronics. AC: Average Content [14].



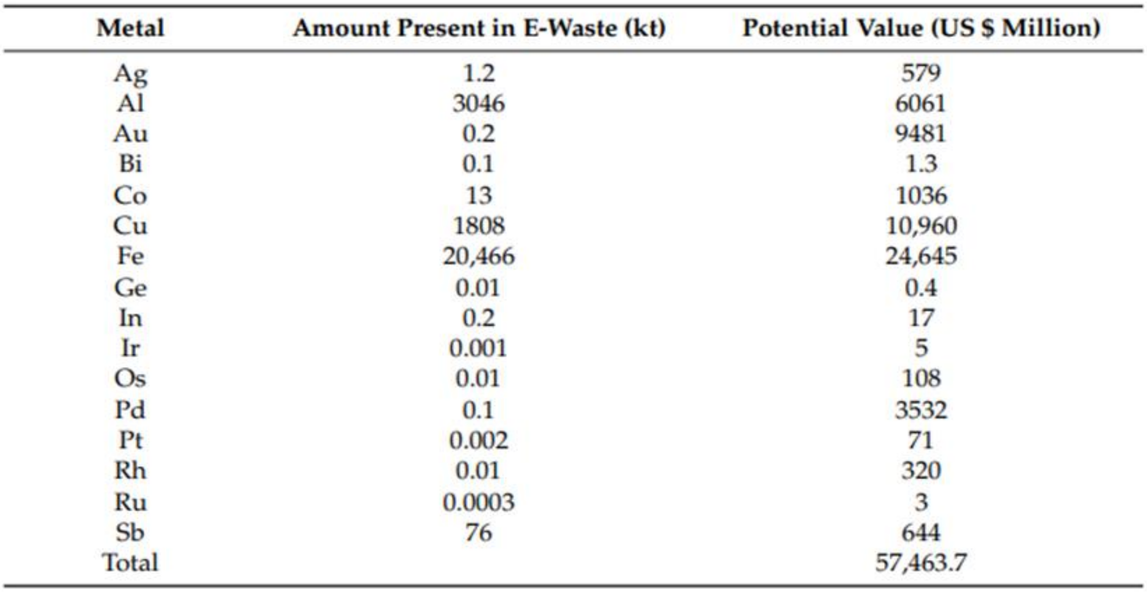
PM (mg/unit)	Mobile phone		PC		Flat screen or TV monitor		Laptop	
	Range	AC	Range	AC	Range	AC	Range	AC
Ag	232 ~ 319	261	1348–11408	6378	450 ~ 575	515	249–437	343
Au	24.1 ~ 29	26.1	–	92.7	110 ~ 200	161	104.5–219.8	160.8
Pd	8.7 ~ 14.5	11.6	–	39.9	40 ~ 44	42	–	40.2

In 2015, global demand for gold, silver and palladium in the field of electronics were 254 tonnes, 12,816 tonnes and 40.18 tonnes, respectively [15]. In recent years, huge quantities of electronic waste (e-waste) have been generated from the electronics end of life [16].Therefore, e-waste has gradually become significant source of precious metals. For example, according to National Institute for Materials Science (NIMS), over

6800 tonnes of gold (16% of the world reserves) and 60,000 tonnes of silver (22%) were found in urban mines [17]. However, only about 20% of e-waste was recycled through appropriate channels.

As primary metal resources are depleted [19], it will be critical to recovery and reuse many metals and rare earth elements from secondary resources, like e-waste. For example, the demand for copper is expected to increase by 275–300% by the year 2050, and this is unlikely to be met through mining of current virgin minerals [10]. Metals such as iron and aluminum are also in demand for the manufacture of electronic goods [20]. Based on the waste generation data for 2019, it would be possible to recover metals with a combined value of US $57 billion, which could be used to meet the metal demand created by the manufacture of new electrical equipment Table 2 [8].

Table 2. Potential value of raw materials in e-waste generated globally in 2019 [8].



Metal	Amount Present in E-Waste (kt)	Potential Value (US $ Million)
Ag	1.2	579
Al	3046	6061
Au	0.2	9481
Bi	0.1	1.3
Co	13	1036
Cu	1808	10,960
Fe	20,466	24,645
Ge	0.01	0.4
In	0.2	17
Ir	0.001	5
Os	0.01	108
Pd	0.1	3532
Pt	0.002	71
Rh	0.01	320
Ru	0.0003	3
Sb	76	644
Total		57,463.7

Generally, the flow sheet of e-waste recycling by smelting is shown in Fig. 4. Before smelting, e-waste usually needs to be treated through classification, dismantling, shredding/grinding and sorting of metals and plastics [21]. E-waste recycling through black copper smelting is feasible and economic. The recovery rates of precious metals are over 95% [22].

2.1.1 COLLECTION AND PREPROCESSING

E-waste is generally sorted by type prior to processing, as some components present in e-waste, such as batteries, cathode ray tubes (CRTs) and mercury-containing. Once e-waste is collected, the pre-processing of e-waste is one of the most important steps [23]. E-waste is generally sorted by type prior to processing, as some components present in e-waste, such as batteries, cathode ray tubes (CRTs) and mercury-containing lamps require specific measures to mitigate hazards [24]. For example, batteries need special preprocessing to prevent spontaneous discharge that can lead to combustion [25]. The next stage of pre-processing involves the systematic dismantling, disassembly and removal of components or parts prior to further processing [26]. Dismantling can be divided into manual dismantling and mechanical dismantling, depending on the construction of the equipment. Improper manual dismantling poses a significant environmental and health concern due to the release of fumes and hazardous substances should be banned if proper safety precautions are not in place [8].

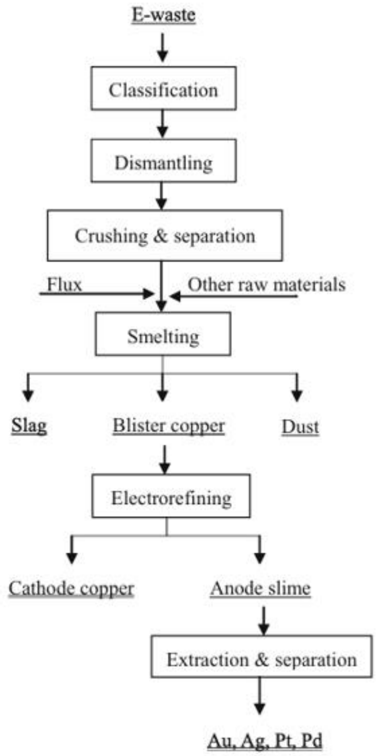


Figure 4. General flow sheet of precious metals recycling from Waste Electronic and electronic equipment (WEEE) by traditional smelting process.

The plastic recycling approach uses the properties of plastics including carbon content, binder, properties, chain structure and thermal properties, to find uses for them in manufacturing industries [91]. With this approach, it is possible to recycle plastic that is no longer suitable for reuse. Examples of this include the use of resin containing electronic waste, such as toner powder, as an alternative source of carbon in metallurgical industries [27].

Glass is another major component in e-waste, predominantly found in screens, monitors and lamps, which collectively constitute up to 12% of e-waste generated worldwide [8].
Recent investigations have focused on the removal and recovery of lead from CRTs to provide a safe recycling pathway for the glass, including the use of ultrasound to facilitate lead leaching, recovering up to 90% of the lead [28].

In addition, it has been shown that mechanical activation followed by dilute nitric acid leaching can recover up to 92.5% of lead in the glass [29]. Once the lead has been extracted, the remaining silica-rich glass can undergo additional processes for recycling. Using a combination of the above approaches might provide a sustainable pathway for the recycling of this hazardous waste.

2.1.2 SMELTING

Open burning in the blast furnace is always employed in the in formal recycling sectors. The elements form metal phase that contains 60–80% copper, as well as precious metals, lead, tin, antimony, nickel and so on [30]. The recovered black copper was further purified by electro-refining or directly leached by H_2SO4. This process generates large amounts of hazardous gases, wastewater and residues. The improper disposal through open burning pose serious risks to the environment and human health. Besides, it is difficult to recover other valuable metals except copper and precious metals. Fortunately, pyrometallurgical processes have been significantly improved with the consideration of maximum recovery of metals and minimum pollution. Generally, the flow sheet of e-waste recycling by smelting is shown in Fig. 4. Before smelting, e-waste usually needs to be treated through classification, dismantling, shredding/grinding and sorting of metals and plastics [31]. E-waste recycling through black copper smelting is feasible and economic. For example, 250,000tonnes of different waste are treated annually in Umicore, of which e-waste covers up to 10wt.%. The main processing steps contain copper smelting in Isasmelt furnace and lead blast smelting, the copper-leaching and electro winning plant, and precious metals refinery. The recovery rates of precious metals are over 95% [32]. Another application for pyrometallurgical process to recover metals from e-waste was at Boliden's Rönnskär smelter [33].

E-waste was firstly ground into powder. Then they were fed into Kaldo furnace to upgrade precious metals in copper. The process in Kaldo furnace consists in:

A typical composition of the decopperized anodic slime (DAS) processed in the precious metals plant (PMP) is (wt.%) Ag-18, Au-0.07, Pb-25.5, Bi-2.2, As-2.3, Sb-8.4, Se-4.4, Te-0.55, Ba-1.0, SiO_2-2.6 S-5.3 Cu-0.30 others (Ni, Sn, Al_2O_3, and Cl)-29.45. The DAS is processed batchwise in a Kaldo furnace, shown schematically in Figure 5 [34]. The furnace can be rotated and tilted vertically and is enclosed in a metallic casing, thus avoiding fugitive emissions. A typical operation consists of the following steps:

- Melting the DAS. The furnace temperature is held at 1100°C with the aid of the primary lance; lead oxide, sodium carbonate, silica, and coke particles are loaded into the reactor to produce molten metal and slag phases [34].
- Converting the molten metal. Silica particles are added to the molten metal to produce a slag phase at 1,150°C in which most of the lead is eliminated [34].
- Refining the molten metal. Air is injected through the secondary lance over the surface of the molten metal. The goal of refining is to eliminate the selenium as gaseous SeO_2. The furnace temperature is held at 1100–1150°C [34].
- Tellurium slagging. Sodium carbonate is added to the molten metal to produce a slag phase in which the remaining tellurium concentrates. The slag phase is tapped off leaving behind the doré with approximately 98% silver [34].

Then it was sent to the converter to remove impurities. Precious metals were finally recovered by electro-refining process [35, 36].

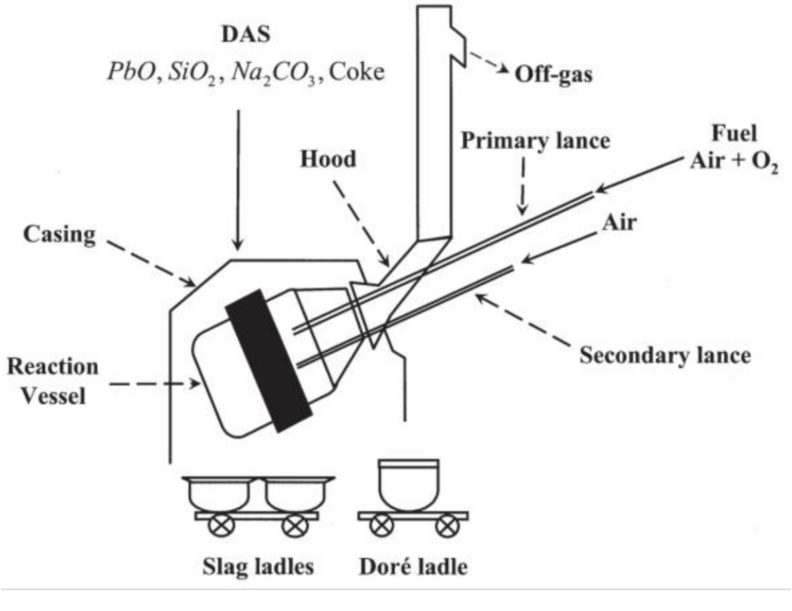


Figure 5. A schematic representation of the Kaldo Furnace at La Caridad PMP Mexican of Cuprum precious metals plant [34].

2.1.3 ALKALI SMELTING

Using $NaNO_3$-NaOH as fluxing agent [37] developed an alkali fusion-leaching-separation process to recover metals in crushed metal enrichment (CME) originated from waste PCBs. The recycling flow sheet was shown in Fig. 6. Amphoteric metals, such as Sn, Pb, Zn and Al, were oxidized and converted to soluble salts in the fusion process. The residue was leached by H_2SO_4 to recover Cu. Precious metals could not be dissolved by H_2SO_4 and were enriched in the leaching residue. The recycling rates of Sn, Zn, Pb, Al and Cu were 96.85% 91.28%, 78.80%, 98.39% and 97.88%, respectively, under optimal conditions of the fusion processes (mass ratio $NaNO_3$:NaOH:CME of 3:4:1, fusion temperature of 500°C, fusion time of 90 min). Meanwhile, the enrichment ratio precious metals were over 10 [37].

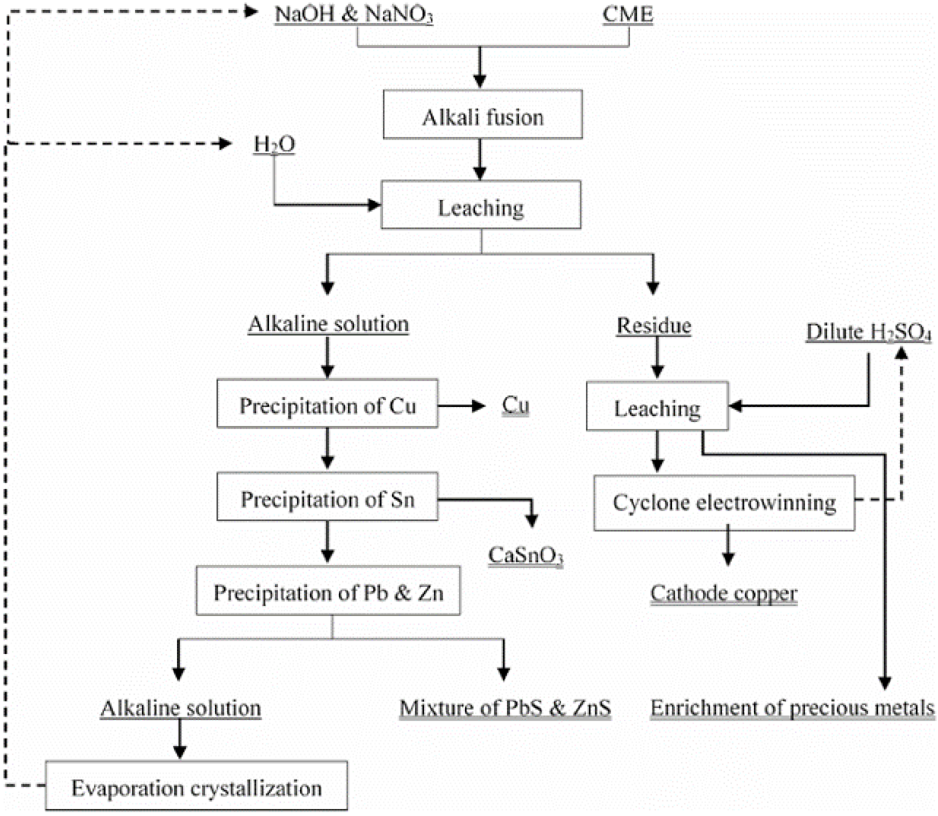


Figure 6. Flow-sheet of alkaline fusion-leaching- separation process [37].

2.1.4 ELECTROCHEMICAL METHODS

Electrochemical technology is a promising mehod of recover precious metals from e-waste due to its high energy efficiency, low environmental impact and minimal chemical usage. Have recovered gold from waste PCBs by using electro-generated chlorine as an oxidant [38]. This process is environmental friendly because it can operate in the closed system and chlorine can be reduced during the leaching of precious metals. The leaching efficiency of gold was 93% in 0.1 mol/L HCl by electro-generated chlorine at the current density of 714 A/m^2. The leaching of gold was increased with higher temperature, higher initial concentration of chlorine, and lower concentration of acid. Have developed a chemical-electrochemical process for the simultaneous recovery of copper and enrichment of gold from waste PCBs [39]. This process was performed by employing two different types of reactors coupled in series. One was for the dissolution of base metals with a perforated rotating drum, the other one was for the regeneration of the leaching solution with the parallel electro-winning of copper. After dissolution of base metals and recovery of Cu, the gold concentration in the residue was 25 times higher than in the initial waste PCB samples. The minimal chemical input to recover metals was one of the advantages of the electro-recycling process. Oxidizing agents were generated to dissolve metals at the anode while reducing dissolved metals at the cathode [40]. Two stages of electro-recycling were proposed: (1) about 97% of Cu, Sn and Ag were recovered with Fe^{3+} in sulfate, (2) then Pd and Au were dissolved using Cl_2 generated in dilute HCl solution.

2.1.5 HYDROMETALLURGICAL PROCESS

Exist methods using safer reagents, such as thiosulfate ($(NH_4)_2S_2O_3$) or with ammonium persulfate ($(NH_4)_2S_2O_8$), since they are low cost, environmentally friendly, environment, promote a high leaching rate [41], [42], [43] and enable a recovery greater than 93% of Au [44]. This chemical process is carried out in a solution of ammonium-copper (II)-thiosulfate, since it must be catalyzed by copper for it to occur [43].

The chemical reactions involved are those illustrated in (1) and (2):

$$4Au^0{}_{(s)} + 5(S_2O_3)^{2-}{}_{(aq)} + Cu(NH_3)_4{}^{2+}{}_{(aq)} \rightarrow 4[Au(S_2O_3)_2]^{3-}{}_{(aq)} + [Cu(S_2O_3)_3]^{5-}{}_{(aq)} + 4NH_3 \quad (1)$$

$$8(S_2O_3)^{2-}{}_{(aq)} + 2Cu(NH_3)_4{}^{2+}{}_{(aq)} \rightarrow [2Cu(S_2O_3)_3]^{5-}{}_{(aq)} + 8NH_3 \quad (2)$$

The chemical reaction represented by (2) not only reduces the cupric ion concentration, but also consumes thiosulfate, which are essential for the leaching of gold. Since the selectivity of each of the reactions involved in the process is unknown of gold leaching with thiosulfate and since this type of process requires quite a few resources, time and auxiliary equipment, and since inadequate treatment of the byproducts could cause serious problems for health and the environment [45], [46], we proceed to evaluate a emerging method, which uses sodium chlorate ($NaClO_3$) as a chlorination agent; sulfuric acid (H_2SO_4), as a leaching agent; sodium chloride (NaCl) is used to provide the Cl^- necessary for the formation of complexes with Au; it's used methyl isobutyl ketone (MIBK) to extract and transport gold from an aqueous phase to a organic; and oxalic acid, to reduce and recover gold. Figure 7 shows the extraction mechanism using this acetone [45].

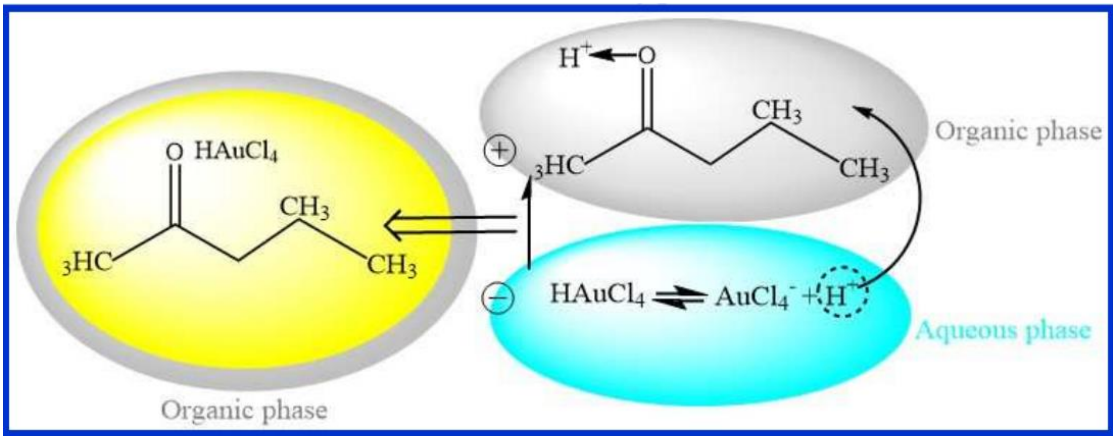


Figure 7. Process and mechanism of extracting gold from aqueous phase by MIBK [45].

The extraction process using MIBK, illustrated in Figure 7, has several advantages on conventional extraction processes [45]. During the extraction process, the The oxygen atom in the MIBK provides the electron pair to coordinate with the oxygen ion. hydrogen, and in this way, forms a cation (RH^+), while metal ions form a complex anion ($HAuCl_4^-$), which forms the hydrophobic ion pair by electrostatic action and then the association complex of ($RHAuCl_4$). These processes transport Au ions (III), ions from the aqueous phase to the organic phase, which is then taken to a process of separation by distillation to remove the organic phase from the solid enriched with Au. Finally, the solid material resulting from the distillation is subjected to a process of calcination at 500 °C for 2 hours [45], the Figure 8 describes this recovery process of Au.

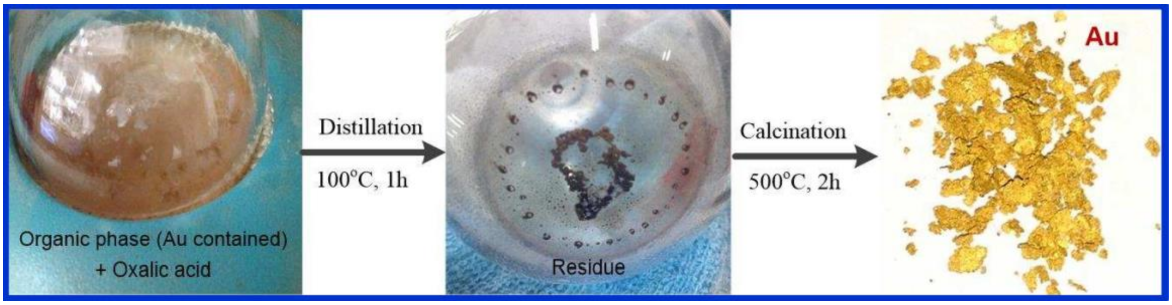


Figure 8. Production process of sponge gold [45].

3. CONCLUSIONS

Precious metals are widely applied in many fields of industries. Due to the conflicts of limited natural resources and increasing demands, as well as their economic value, it is essential to recycle precious metals from secondary resources. Based on the traditional technologies for recycling precious metals, various methods have been significantly improved. As the precious metals dominate the most value for e-waste recycling, the loss of these metals should be minimum [46].

The most suitable process for the recovery of metals from waste electrical and electronic devices is to first use a physical one, followed by a hydrometallurgical, since this process is the most friendly and efficient with the environment, with which the best performances are obtained in the recovery of metals. However, it must continue studying and investigating this process, because some reagents used during the recovery and/or dumping of byproducts are still considered toxic and harmful to the human health and the environment.

4. ACKNOLEDGMENTS

The author of this article thanks the Instituto de Administración de Riesgos (IDEAR) for allowing me to be part of the teaching body for the own professional development and teaching service for future quality engineers.

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June 12, 2024

Declaration of Conflicts of Interest

I, Ana Sofia Avila Mata, with Unique Population Registry Code identification: AIMA950729MCLVTN08, master's in metallurgical engineering sciences and Materials Engineer with a specialty in advanced materials. I declare that I do not have any real, potential or obvious conflict of interest in relation to the execution of any project.

M.C. Ana Sofia Avila Mata

Saltillo, Coahuila, México
12 de Junio del 2024

Declaración de Conflicto de Interés

Yo, Ana Sofia Avila Mata, con identificación Clave Única de Registro de Población: AIMA950729MCLVTN08, Maestra en Ciencias de la Ingeniería Metalúrgica e Ingeniera en materiales con especialidad en materiales avanzados. Declaro que no tengo ninguna situación de conflicto de interés real, potencial o evidente, en relación con la ejecución de ningún proyecto.

M.C. Ana Sofia Avila Mata

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