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### EXTRACTION OF GOLD BY INTENSIVE CYANIDATION AND BIO-EXTRACTION OF BASE METALS FROM ELECTRONIC SCRAP - A SEMIPILOT SCALE EXPERIENCE

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**ABSTRACT** – The accelerated growth of new technologies and considering the ever-increasing consumption of new electronic devices entails discarding jumbled up electronic scraps. Electronic waste, nowadays, can reach a significant number of different elements, with different physical-chemical characteristics, ranging from base metals, precious metals, rare earth elements and recalcitrant elements. In this study, we used the intensive cyanidation for recovering precious metals, contained specifically on printed circuit boards. Base metals, on the other hand, more specifically copper and nickel, major elements in these plates, were extracted using a biotechnological approach, on a semi-pilot scale. The bacteria *Acidithiobacillus ferrooxidans*-LR and *Leptospirillum ferrooxidans*-ATCC53992 were used whose function, in this process, was to oxidize ferrous ions, added to the leaching medium, to ferric ions in a reaction cycle, as the ferric ions act as an oxidizing agent and are reduced to ferrous ions after the oxidation of metals contained in electronic scrap.

**Key words:** Cyanidation, Bio-extraction, base metals, electronic scraps.

#### 1- INTRODUCTION

Recently, the emergence of new technologies has led to a growing variety of new electronic devices, with a consequent increase in their consumption, shortening their useful lives and generating large amounts of electronic waste, known as waste of electrical and electronic equipment (*i.e.*, WEEE).

However, the generation of this type of waste, associated with the stimulus exacerbated by the consumption, reveals a problem that is configured in an

increase in the generation of this type of residues. Due to cultural factors, consumers have preferred to discard rather than repair malfunctioning or damaged equipment. At the same time the constant launches of new technologies and modernization of old equipment also contribute to maintain this phenomenon (PUCKETT & SMITH, 2002). Due to the forecast of electronic equipment becomes obsolete, either by shortening its useful life or due to failure events and problems in their operation are classified as waste. Those wastes carries a high number of metallic elements from non-renewable primary sources (*i.e.*, ores, oil etc.) that eventually need to be recovered for producing new electronic devices making use of new technologies for the sustainable use of these mineral assets.

These electronic waste originate from the disposal of electrical and electronic devices in disused, such as cell phones, computers etc., which contain memory cards, printed circuit boards, batteries, LCD etc. in their structures, as well as various elements and chemical substances (BHUTTA, OMAR, YANG, 2011 apud JIANZHI et al., 2004; YAMANE et al., 2012)(GUO et al., 2009; VEIT et al., 2006). Such electronic waste contains in its structures primarily polymeric and metallic materials. The well-known e-waste (electronic waste) covers the following equipment: radios, televisions, computers and their peripherals, cell phones etc.

This waste is composed mainly of plastic, iron, non-ferrous metals, glass and wood. According to Oliveira and Sobral (2012), modern electronic devices can include a large amount of elements, among them are plastics, precious metals (Ag, Au, Pd e Pt), ferrous metals (V, Cr, Fe, Mn, Ni, Nb, Mo), non-ferrous metals (Mg, Al, Ti, Co, Cu, Zn, Sn, Pb), and metals for special applications (Li, Be, B, Ga, As, Se, Sr, Y, Zr, Cd, In, Sb, Te, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Hg, Tl, Bi).

The final destination of electronic waste is landfill or incineration; however, when the electronic waste is disposed of incorrectly, affects a series of environmental problems, since that can be naturally leached, producing leachate, resulting in pollution of groundwater and water bodies. In addition, when these residues are burned toxic gases are emanated (*i.e.*, dioxins and

furans) as a result of chemical reactions, due to the presence of flame retardants (GUO et al., 2010; JIE et al., 2008; KANG, SCHOENUNG, 2005). Conventional recycling processes involve hydrometallurgical and pyrometallurgical routes (Min Chen et al. 2021); however, bioleaching presents itself as an alternative route for extracting base metals (CHOI et al., 2004) and precious metals from electronic scraps (BRANDL & FARAMARZI, 2006). In this way, several techniques used for processing electronic scraps were developed reducing their characteristic volume. Figure 1 below gives a quick idea on how the electronic equipment is generated, consumed and later recycled to recover the metallic content.

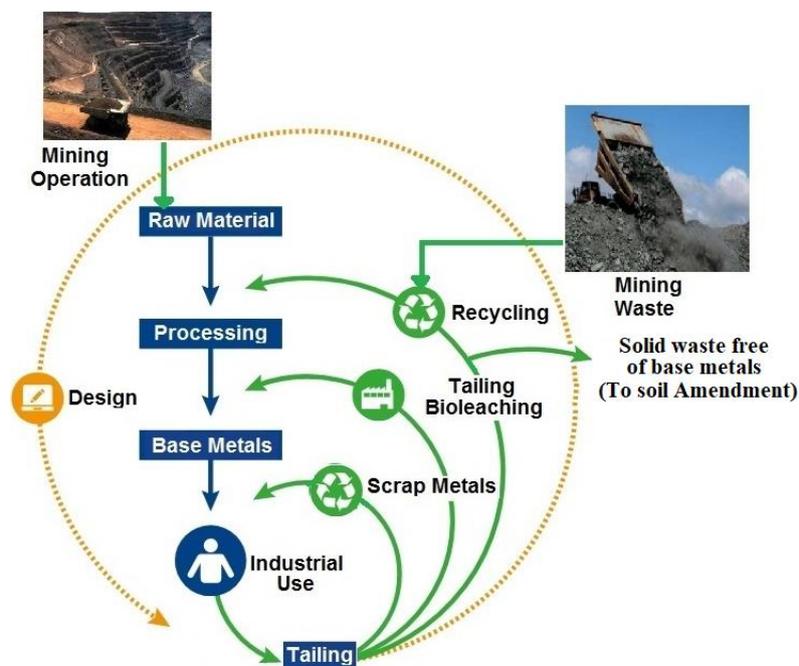


Figure 1: Production of electrical and electronic devices from different natural resources, its post-consumer discharge and recycling from the perspective of the circular economy. (Source: the authors)

This Figure shows the combination of raw materials from different industrial sectors (*i.e.*, mining, petroleum industry etc.) in the manufacture of consumables. Once produced, these goods reach obsolescence in a short period of time and are improperly discarded. However, we are dealing with goods that carry metallic elements in their constitution from non-renewable

natural resources. In the circular economy, these obsolete devices can be repaired during maintenance or can be remanufactured, which means, the undamaged electronic components can be reused and, finally, the metallic parts can be recycled, duly extracted in their soluble forms for subsequent separation and obtaining pure metals.

The hydrometallurgical processes, used in the extraction of precious metals, make use of specific reagents, such as cyanide, aqua regia, thiourea, halides, among others (CUI & ZHANG, 2008). Among the hydrometallurgical processes, cyanidation is traditionally used in the extraction of precious metals due to its effectiveness as a complexing agent in conjunction with oxygen, which acts as an oxidizing agent. The cyanide is used in the form of salts, such as sodium cyanide (NaCN), potassium (KCN) and calcium cyanide, (Ca(CN)<sub>2</sub>), the first two being the most soluble in water. According to Guzman (1999), cyanidation is carried out effectively, considering the appropriate use of different process variables, such as cyanide and dissolved oxygen concentration, pH, temperature and stirring speed. However, adjusting the pH to a value between 10 and 11, is essential for cyanide ions (CN<sup>-</sup>), when dissolving sodium cyanide in water, do not undergo hydrolysis, with formation of hydrocyanic acid (*i.e.*, HCN), as shown in Reaction 3, toxic gas, thus preserving these cyanide ions, in their free form, in solution (CIMINELI, 2009).



On the other hand, the bioleaching process is a promising alternative, as it does not require high energy consumption and low cost of implementation and operation. In the metals bio-extraction process, microorganisms are responsible for generating the oxidant agent in the reaction system (*i.e.*, Fe<sup>3+</sup> ions) from the oxidation of ferrous ions (*i.e.*, Fe<sup>2+</sup>) that can be added to the system either in soluble (FeSO<sub>4</sub>·7H<sub>2</sub>O) or insoluble (FeS<sub>2</sub> - pyrite) species. Brandl et al. (2001), demonstrated, in studies in which mesophilic and thermophilic acidophilic microorganisms, more specifically *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans* and *Acidithiobacillus thiooxidans* etc. (BRIERLEY, 2010; RODRIGUES, 2015; TAO & DONGWEI, 2014; WATLING, 2006) that metals can be recovered from printed circuit boards through microbial leaching. The

method of dissolving metals contained in electronic scraps is similar to the mechanism of dissolving sulphide minerals, such as copper oxidation (Equation 2) in which the  $Fe^{3+}$ , released into the system from the oxidizing action of bacteria, oxidizes metallic copper to  $Cu^{2+}$ . The role of microorganisms, in this case, is to re-oxidize the produced  $Fe^{2+}$  to  $Fe^{3+}$  establishing, thus, a reaction cycle.



## 2- EXPERIMENTAL

Initially, parts of the scrap from printed circuit boards were physically collected, visibly rich in precious metals. For the precious metals extraction process, a sample of the selected material was placed in an acrylic column and submitted to an ascending flow of aerated cyanide solution, in different concentrations of free cyanide (*i.e.*, this concentration may vary depending on the mass of scrap to be treated, normally ranging from 3 to 10 g.L<sup>-1</sup>), from a glass reactor, with useful volume of 1 litre (Figure 2 - reaction system used in the cyanidation tests, as well as samples of original scrap and after cyanidation of precious metals on bench scale).

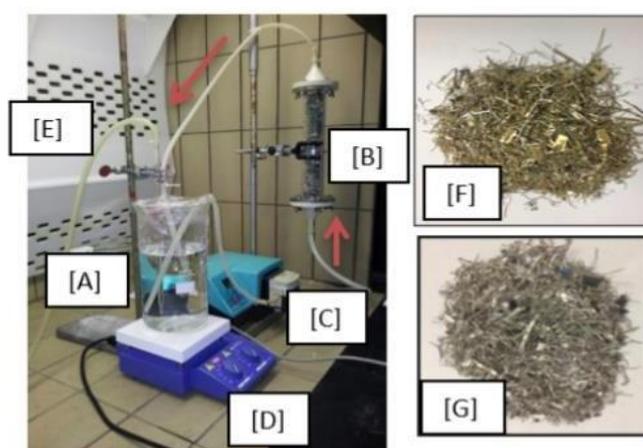


Figure 2: Reaction system consisting of: [A] Pyrex glass reactor, [B] Acrylic column loaded with electronic scrap, [C] peristaltic pump, [D] magnetic stirrer, [E] piping for air injection and, additionally, [F] and [G] scrap samples before and after carrying out the cyanidation tests, respectively.

After finishing the cyanidation process, the parts free of precious metals, now apparently exposing the base metals, were washed to remove any remaining cyanide leachate. With the recirculation of the leaching solution, the layer of precious metals, yellowish in colour, disappears in, approximately, 10 minutes indicating their total removal. A representative sample of the remaining solid phase was digested in aqua regia and the resulting leachate was analysed for the metallic constituents by Atomic Absorption Spectrometry, whose results were: Cu 64.9%, Zn 27.0%, Sn 1.8%, Al 1.4%, Ni 1.3%, Fe 1.2%, Si 1.1%, Pb 0.56%, Ba 0.34%, Ti 0.12% and W 0.11%.

Base metal bio-extraction experiments were carried out in our semi-pilot unit, shown in Figure 3, with a capacity of 20 litres of solution, containing a perforated polypropylene hexagonal drum (*i.e.*, holes of  $d < 1\text{mm}$ ) for better mass transport between the leachate and the metallic substrate, where a 100g sample of scraps were introduced. The volume of 13 litres of leaching solution consisted of MKM culture medium (*i.e.*, Modified Kelly Medium -  $(\text{NH}_4)_2\text{SO}_4$ :  $0.08\text{ g.L}^{-1}$ ;  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ :  $0.08\text{ g.L}^{-1}$ ;  $\text{K}_2\text{HPO}_4$ :  $0.008\text{ g.L}^{-1}$ ), together with a solution containing  $33.3\text{ g.L}^{-1}$  of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , pH at 1.8, adjusted with a 5M sulphuric acid solution, with the solution temperature controlled at  $30^\circ\text{C}$ , plus 750ml of culture of *Acidithiobacillus ferrooxidans* and 750ml of *Leptospirillum ferrooxidans* culture at a concentration of  $10^7$  cells/mL of each culture.

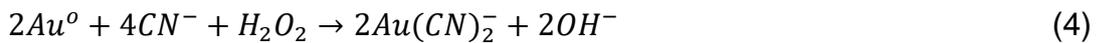
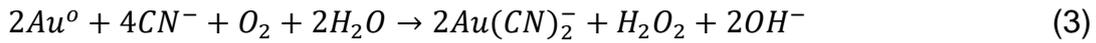


Figure 3: Reaction system used in the bio-extraction of base metals from electronic scraps.

### 3- RESULTS AND DISCUSSION

#### 3.1 Intensive Cyanidation

The reactions as shown in equations 3 and 4, below, show how the precious metals dissolution process take place, gold in particular, by the joint action of cyanide, complexing agent, and oxygen, oxidizing agent.



As can be seen, analysing the reactions 3 and 4 above, the first stage of the dissolution process of gold begins with the generation of peroxide as a reaction intermediate. With the continuity of cyanidation, this peroxide, together with free cyanide, are in charge of continuing such dissolution process. These same reactions also occur when dissolving the other precious metals. Figure 4 shows the influence of increasing cyanide concentration on the gold dissolution process in 2 hours cyanidation tests. It should be noted that the determination of the percentage of gold extraction was carried out taking into account the mass of metal solubilized throughout the experiment (determined by ICP-OES) and the content of each of the metals contained in the electronic scrap used in this study.

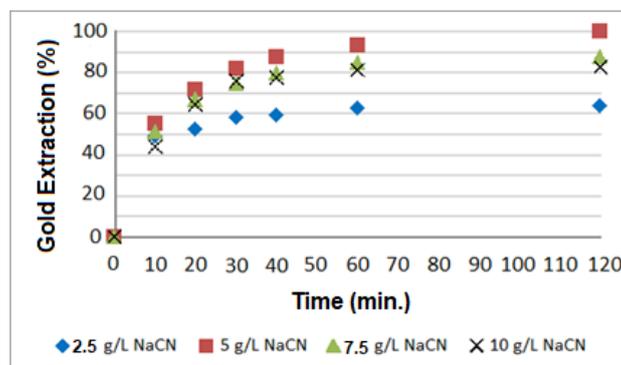


Figure 4: Gold extraction during the cyanidation test for different cyanide concentrations using only air.

As can be seen in Figure 4, there is intensification in the extraction of gold as the initial cyanide concentration is increased. However, with the continued

increase of this concentration, the extractive process significantly decreases its effectiveness since there is a decrease in the solubility of oxygen, the oxidizing agent, due to the increase of the salinity (*i.e.*, ionic strength) of the medium. Thus, it became clear that it is not advantageous to exceed the initial concentration of  $5\text{g.L}^{-1}$  in cyanide since the benefit achieved at higher concentrations, in terms of gold extraction, does not compensate for the expenses with this increase in concentration.

### 3.2 Bio-extraction of Base Metals

With regard to the bio-extraction of base metals, from the solid material remaining after cyanidation of precious metals, what can be observed is that the action of ferric ions is effective in the dissolution of these metals, via an indirect mechanism, that is, they are generated by the bio-oxidation of ferrous ions added to the culture medium. The graph of Figure 5 highlights the evolution of the copper and nickel bio-extraction processes, the most abundant metals in the sample under study. This type of tendency can be corroborated by observing the potential values of the reactions of ferric ions with these metals, also shown in Figure 5, which are positive values, a fact that demonstrates the spontaneity of the dissolution reactions of the referred metals.

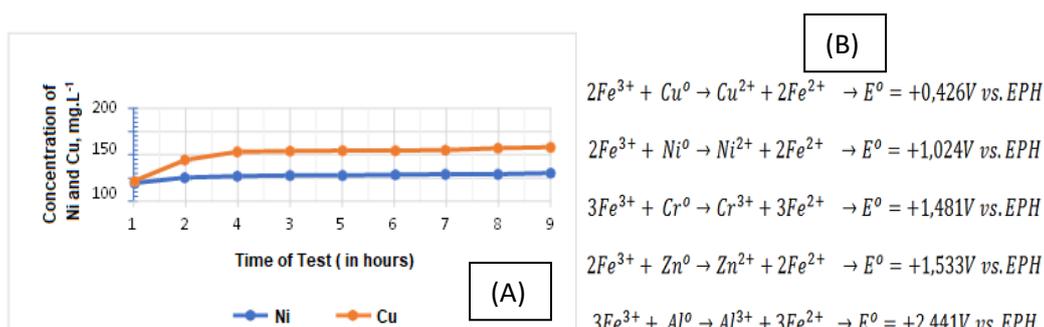


Figure 5: [A] Bio-extraction of Ni and Cu from electronic scrap, [B] Values of potential for dissolution reactions of base metals by ferric ions.

What can be observed in the graph (Figure 5) is that there is a very expressive extraction in the first four hours of the process, followed by its stagnation, possibly due to the impact of the ionic strength on the metabolism of the

microorganisms used, due to the fact that these microorganisms have not previously been adapted to the increasing concentrations of these metals.

#### **4: CONCLUSION**

During the intensive cyanidation of the gold contained in the electronic scrap sample, it was observed that the increase in the cyanide concentration was effective until the solubility of dissolved oxygen, the oxidizing agent, was compromised, which occurred after the addition of amounts higher than  $5\text{g}\cdot\text{L}^{-1}$ .

The bio-extraction of base metals by ferric ions, generated from the oxidation of ferrous ions, mediated by the microorganisms used, proved to be quite spontaneous and will certainly occur in its entirety with the continuity of this bio-extractive process.

The use of bioleaching is very promising, as it uses natural and non-pathogenic microorganisms to generate ferric ions, from reduced sources of iron, such as ferrous ions, which are sufficient oxidants for the solubilization of base metals present, copper and nickel in particular, major elements in electronic scraps.

The mixed culture composed of *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* presents itself as an attractive alternative since higher temperatures can be used, with the continuity of the bio-oxidative process, since the species *Leptospirillum ferrooxidans* is classified as thermotolerant, accelerating the dissolution process of base metals.

In the case of precious metals extraction, gold and silver in particular, they are extracted in a few minutes, by using intensive cyanidation, as these metals appear in very thin layer coatings on less noble metallic substrates (*i.e.*, copper and nickel), (*i.e.*, 2 to 3  $\mu\text{m}$ ). In the case of base metals bio-extraction, mainly copper and nickel, which are present as major elements in electronic scraps, occurs in a less accelerated way due to their high contents. However, what is used is to favour the transport of the oxidizing agent (*i.e.*, ferric ions) towards those metallic substrates using the aforementioned rotating drum.

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