Valorisation of a flotation tailing by bioleaching and brine leaching, fostering environmental protection and sustainable development

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ABSTRACT

Flotation tailing is a problematic mining waste, because contains sulphides that exposed to oxidising conditions generate acidic drainage and the subsequent metal mobilisation. In this study, a flotation tailing produced within an integral process for the treatment of polymetallic sulphide ores is cleaned and valorised seeking a better use of natural resources and a lower environmental impact. In this work, bacterial leaching followed by brine leaching is postulated as an alternative to the flotation tailing treatment. Bioleaching destroys pyritic matrix (99% Fe) producing biogenic ferric that can be used as oxidising agent and recycling to a hydrometallurgical process. 80-90% Cu and Zn are dissolved and critical raw materials as Sb, In and Co are recovered. Brine leaching achieves Pb and Ag extractions greater than 96% and generates a solid residue mainly composed of quartz, in which gold that initially was in flotation tailing is concentrated. A clean and easily treatable for gold recovery final residue is obtained. In conclusion, pyrite matrix has been destroyed avoiding the further acid generation and reducing dramatically waste volume, metals have been valorised, and tailing hazardousness has been removed. Therefore, the proposed process is a sustainable alternative for flotation tailing management, reducing the environmental impact, the management costs, and generating income from valorisation of metals and the production of leaching agent.

Keywords: flotation tailing, bioleaching, waste management, biogenic ferric, brine leaching

1. INTRODUCTION

Froth flotation is the most common mineral processing process for sulphide ores concentration, obtaining concentrates of a single metal, suitable for a subsequent pyrometallurgical processing (Fuerstenau *et al*., 2007; Peleka *et al*., 2018). Associated with this kind of concentration method is the accumulation of billions of tons of waste heavy metal containing all over the world for the decades of operation of mining plants (Hansen *et al*., 2005; Xie *et al*., 2013). This waste, called flotation tailing, is often stored in large piles and can cause environmental problems due to acid mine drainage (AMD), generated by the oxidation and dissolution of sulphide minerals contained. Acid water with dissolved metals can produce soil and water contamination by the seepage or run-off. Due to the water-borne transport of dissolved metals and the wind-borne dispersal of fine particles, tailing appears as great source of toxicity that can cause problems in ecosystems and residential areas (Navarro *et al*., 2008; Xie *et al*., 2013; Kefeni *et al*., 2017). In fact, the inadequate management of mining waste has already caused serious accidents, such as the one in Aznalcóllar (Spain, 1998), the catastrophe of Aberfan (Wales, 1966) or more recently the dam failure in Brumadinho (Brazil, January 2019). Bascetin *et al.* (2016), evaluated the costs of the traditional tailing dam method as well as alternative methods such as surface paste tailing disposal and geotextile or cement methods, which are gradually increasing in the world. The analysis indicated that the unit costs were 2.25 $/t, 2.29 $/t, 7.39 $/t, and 2.79 $/t respectively. In said study, the surface paste disposal method is mentioned as the most appropriate and advantageous.

The danger that involve the storage of flotation tailing, increasingly rigorous environmental regulations and the important value added that its content in metals supposes, require the proper search for technology which can successfully stabilise and recover metals from these materials. In addition, the concept of finite and non-renewable mineral resources should be integrated into future mining process. Thus, new alternatives to the current process in order to have both sound environmental protection and sustainable development are being sought.

Bioleaching can be the solution for the treatment of flotation tailing where the shortage of high-grade minerals in valuables metals hinders the use of conventional methods and, therefore, requires being landfilled (Ahmadi *et al*., 2015; Muravyov and Fomchenko, 2018). This technique is based on the solubilisation of valuable metal cations from insoluble ores by biological complexation and oxidation processes (Rawlings, 2013; Johnson, 2014). There is a large variety of microorganisms in mining sites (Panda *et al*., 2015), nevertheless, *Acidithiobacillus ferrooxidans* is one of the most widely studied and used mesophilic, chemolithotrophic and acidophilic bacteria involved in metals solubilisation from mineral deposits (Valdés, 2008). Chemical reactions involved in leaching by action of these microorganisms can be generally summarised in three basic steps (Jafari *et al*., 2018): oxidation–reduction reactions in the liquid phase catalysed by microorganisms, acid formation from organic or inorganic route, and extraction of metals from the sulphide matrix. The global bioleaching reaction of pyrite (FeS_2), the main component in flotation tailing from polymetallic sulphides, is shown below (r1).

$$4\ FeS_2 + 15\ O_2 + 2\ H_2O \rightarrow 2\ Fe_2(SO_4)_3 + 2\ H_2SO_4 \qquad \text{(r1)}$$

Many researches (Deveci *et al*., 2004; Antonijević *et al*., 2008; Mahmoud *et al*., 2017) have shown that during bioleaching, secondary copper sulphides, and zinc and lead sulphides are leached generating their corresponding sulphates and elemental sulphur. However, primary copper sulphides, such as chalcopyrite, are highly refractory and present challenges for bioleaching processes (Panda *et al*., 2013; Zhou *et al*., 2015).

Lead bioleached from lead sulphide, precipitates in bioleaching conditions due to the low solubility of anglesite ($PbSO_4$). On this matter, brine leaching is a suitable and extensively used method for its solubilisation (Frías *et al*., 2002; Ye *et al*., 2017). In the presence of chloride ions in aqueous medium, the formation of chlorocomplexes of lead gives ride to a decrease in the concentration of Pb^{2+} ions. The equilibrium of Pb^{2+} in contact with the solid phase, $PbSO_4$, is displaced, and therefore, more solid passes into solution. In addition, this technique allows the solubilisation of silver. When the total concentration of chloride ions is greater than 10^{-2} M, the solubility of AgCl increases. The dissolution of AgC1 in chloride media is because of the progressive formation of soluble chlorocomplexes of silver (Guo et al., 2010; Bahram and Javad, 2011).

This paper is focused on a flotation tailing produced in a process for the integral treatment of polymetallic sulphide ores (Fig. 1). In a first stage, a bulk flotation concentrate is obtained. Bulk flotation aims to recover jointly all the value metals in a sole concentrate for a later hydrometallurgical treatment. In this specific case, the treatment consists of a ferric leaching following by solvent extraction and electrodeposition to produce copper and zinc. Ferric leaching residue is subsequently subjected to a brine leaching for the solubilisation of silver and lead contained, which facilitates the recovery of both metals by cementation and precipitation respectively.

This piece of work is focalised on flotation tailing valorisation through bioleaching and subsequent brine leaching, obtaining a non-polluting residue. In contrast with the usual flotation tailing management, storage, the proposed process contributes to a better use of natural resources, to the protection of the environment and to the circularity of these materials, which involves the sustainability sought in the mining industry of the future.

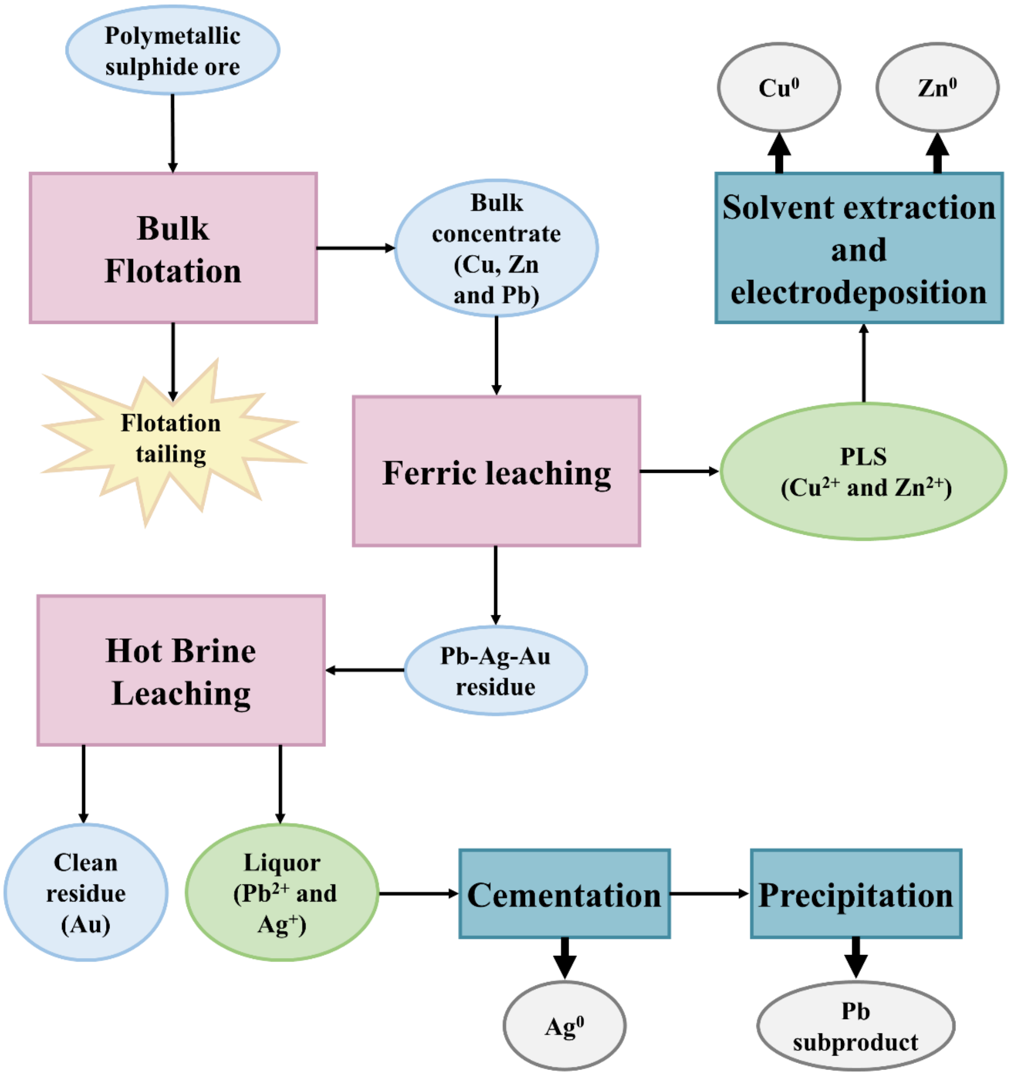

Fig. 1: Proposal for the treatment of polymetallic sulphide ores by hydrometallurgical way.

2. MATERIALS & METHODS

2.1. Flotation tailing

Flotation tailing coming from the bulk flotation of polymetallic sulphide ores from Las Cruces Mine, an important ore deposit in The Iberian Pyrite Belt (Southwest of Europe), is studied.

2.2. Microorganisms and culture

Two types of inoculums are used. The first one, called FNN-9K, is originally isolated from Rio Tinto Mine drainage waters which consisted mainly of *Acidithiobacillus ferrooxidans*, in addition of *Leptospirillum ferrooxidans* and some heterotrophic bacteria (mainly related with *Acidophilium* genus). This culture is routinely maintained by successive subculturing (20% inoculum and 31°C) on 9K medium (Silverman and Lundgren, 1959). The second inoculum used, named FNN-Py, is an adaptation of FNN-9K culture to the flotation tailing at 5% pulp density (Pd) (subcultured under the same conditions in addition to orbital agitation of 180 rpm).

2.3. Analytical methods

Two types of analysis procedures are carried out for solid characterisation. One of them lies in an acid digestion with aqua regia dissolving completely the residue to establish the total extraction. The other analysis is based on the dissolution of the solid in two steps. First, an attack with 6M HCl (30 minutes at room temperature and 180 rpm) to establish the part that has been bioleached but has been precipitated along with the undissolved pyrite matrix. The solid obtained is subjected to a second attack with aqua regia. In this second digestion, the part of the mineral that is not bioleached is determined.

The concentrations of Fe, Cu, Zn, Pb, Ag and Ca are measured by atomic absorption spectrometry (2380 spectrophotometer, Perkin Elmer) and the elements Bi, Co, Cr, Ni, In, As, W, Sb, Se y Sn are analysed by ICP-OES (715 ICP-OES, Agilent). Gold is determined by fire assay. Sulphur is measured by gravimetric analysis. Granulometric analysis is carried out through Beckman Coulter laser granulometer (LS 13 320 MW model). Crystalline phases are identified by X-ray diffraction (XRD) using $Cu_{k\alpha 1}$=1.5406 nm and scanning from $2\theta=3^{o}$ to $2\theta=90^{o}$ at CITIUS (Centro de Investigación Tecnología e Innovación de la Universidad de Sevilla) facilities.

2.4. Calculations

Solids weight loss (WL) after bioleaching or brine leaching process is calculated according to Eq1.

$$WL = \frac{(Initial\ mass - Final\ mass)\cdot 100}{Initial\ mass} \qquad \text{Eq1}$$

Fe, Cu and Zn extractions by solid (X_S) and by liquor (X_L) in bioleaching process are calculated according to Eq2 and Eq3 respectively.

$$X_S = 100 - \left(\frac{Final\ bioleaching\ solid\ mass\ after\ attack\ with\ HCl \cdot \%\ metal\ final\ grade}{Initial\ solid\ mass \cdot \%\ metal\ initial\ grade}\cdot 100\right) \qquad \text{Eq2}$$

$$X_L = \frac{g\ metal\ in\ liquor + g\ metal\ accumulated + g\ metal\ in\ jarosite}{Initial\ mass \cdot \%\ metal\ initial\ grade}\cdot 100 \qquad \text{Eq3}$$

Total extractions (bioleaching and brine leaching) for the rest of metals are calculated according to Eq4 (by the solid) and Eq5 (by the liquor).

$$X_S = 100 - \left(\frac{Final\ solid\ mass \cdot \%\ metal\ final\ grade}{Initial\ solid\ mass \cdot \%\ metal\ initial\ grade}\cdot 100\right) \qquad \text{Eq4}$$

$$X_L = \frac{ppm\ metal\ in\ final\ liquor \cdot 10000}{ppm\ metal\ in\ initial\ solid \cdot Pd\ (\%)\ initial} \qquad \text{Eq5}$$

2.5. Acid-basic accounting (ABA) test

Acid-basic accounting test (ABA) is used to predict acid drainage generation since provides a preliminary evaluation of acid generation potential (AP) and neutralisation potential (NP). This balance is expressed as neutralising potential ratio (NPR = NP/AP). AP is calculated according to the amount of $CaCO_3$ needed to neutralise a ton of sample if all the sulphur is oxidised to sulphuric acid (under the assumption that all sulphur is present as FeS_2). NP is determined by the Sobek method (Sobek et al.,1978).

2.6. Bioleaching procedure

2.6.1. Previous bioleaching tests

The performance of FNN-9K and FNN-Py inoculums are tested at 2, 5 and 10% of pulp density using the flotation tailing as substrate. All tests are carried out in sterile 250 mL-Erlenmeyer flasks at constant stirring rate (180 rpm) and temperature (31ºC) in an orbital shaking incubator. Water is added daily to compensate for evaporation losses.

Under the same conditions, control tests without bacteria at pH 1.5 are performed.

2.6.2. Bioleaching tests at constant pH

Two bioleaching tests are carried out at constant pH. In bioleaching-1, the FNN-9K culture is used as inoculum while in bioleaching-2 the FNN-Py is utilised. In both cases, a cylindrical 7L-reactor, subjected to mechanical agitation and constant temperature fixed to 500 rpm and 31ºC respectively, is used to perform the tests. A stirring rate of 500 rpm is sufficient to keep the solid in suspension. Air is injected through a 5 mm diameter spigot and pulp is kept aerated at constant flow rate of 3.5 L/min under standard conditions controlled by a rotameter. Pulp density is 5% and solution is composed of 80% of 9K medium without iron (II) sulphate, and of 20% of inoculum. pH is kept constant at 1.5 by the addition of 3 M sodium hydroxide solution (density = 1.098 g/mL) once or twice a day. Addition of NaOH solution is controlled by the mass. Loss of water by evaporation is replaced daily.

At selected time intervals sample is taken, and both phases, solid and liquid, are analysed (section 2.3). Bioleaching is considered completed when the content of Fe in the liquor and in the soluble part in the attack with HCl of the solid from the sample taken, represent jointly around 95% of extraction of this metal.

2.7. Brine leaching procedure

A study of the operating conditions for the solubilisation of silver and lead contained in the bioleaching-1 residue is performed. Tests are carried out in 250 mL-Erlenmeyer flasks at constant temperature (30ºC or 80ºC), 5% pulp density, and stirring rate of 180 rpm in an orbital shaking incubator for two hours. Variables such as acidity, concentration of leaching agent, temperature (T) and Pd are studied.

According to the best conditions for Ag and Pb extraction from the previous study, two tests at 12 and 20% pulp density are performed.

3. RESULTS AND DISCUSSION

3.1. Flotation tailing characterisation

The qualitative analysis derived from the XRD pattern (Fig. 4A), indicates the presence of gypsum ($CaSO_4 \cdot 2H_2SO_4$), pyrite (FeS_2), quartz (SiO_2), chalcopyrite ($CuFeS_2$). The chemical composition of flotation tailing is 46.32% S; 43.04% Fe; 0.81% Pb; 0,43% Zn; 0,37% Cu; 0,34% As; 0,19% Ca; 306 ppm In; 233 ppm Sb; 146 ppm Co; 106 ppm Bi; 24 ppm Ag; 21 ppm Sn; 18 ppm Cr; 17 ppm Ni; 0.9 ppm Au; less than 0.1 ppm Se and less than 0.05 ppm W.

According to 46.3% of sulphur analysed, the AP value for the flotation tailing is 1432 kg $CaCO_3$/t sample. The high value of AP and a NP=0 (absence of carbonates) indicates that the flotation tailing is a potential generator of acid drainage.

The granulometric analysis indicates a D80 = 52 μm, that is, 80% by weight of material has a size equal to or lower than 52 μm. Moreover, D50 and D20 are 29 and 11 μm respectively. This fine granulometry, typical of flotation tailing, which gives it a high reactivity and, consequently, a high capacity to generate acid effluents.

3.2. Preliminary bioleaching tests

Pyrite bioleaching (r1) produces sulphuric acid and Fe(III). In this sense, the variation of the concentration of H^+ in the medium over time allows to describe qualitatively the evolution of cultures and the dissolution of pyrite matrix. Fig. 2 shows the evolution of pH for bioleaching tests of FNN-9K and FNN-Py cultures at 2, 5 and 10% pulp density.

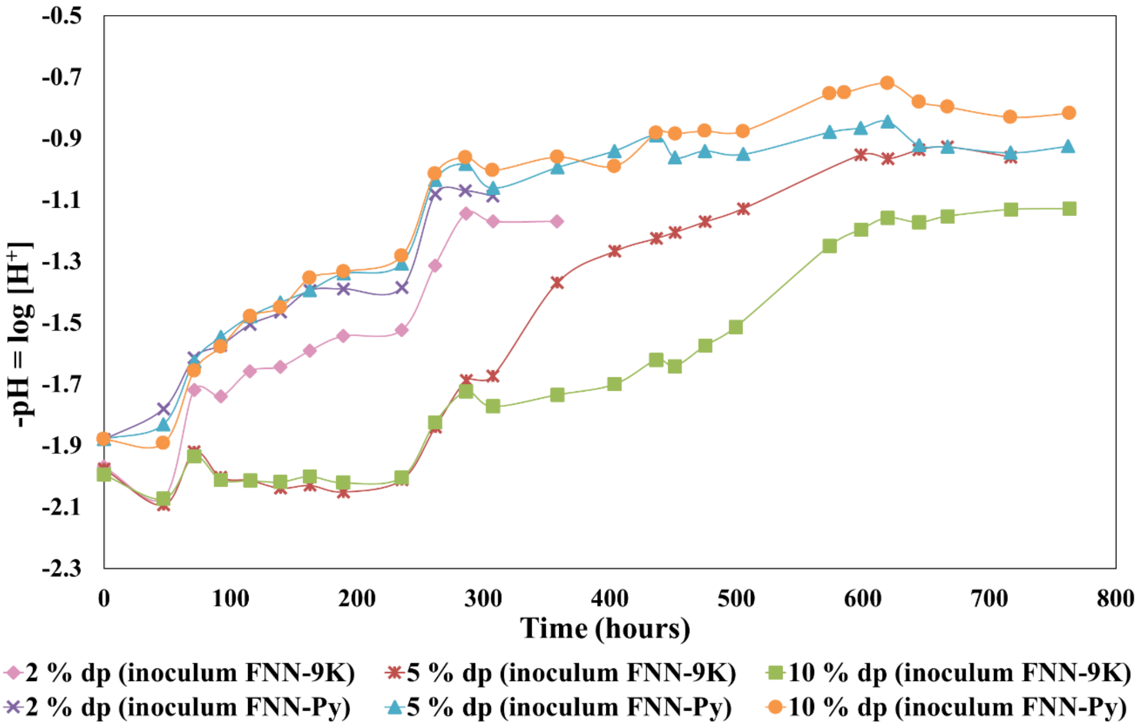

Fig. 2: Kinetics comparison of bioleaching of FNN-9K and FNN-Py cultures at different pulp densities.

The use of the inoculum FNN-Py involves to a decrease in the lag phase at 5 and 10% pulp density (Table 1) and, therefore, the beginning of the bioleaching in shorter times. In addition, this previous adaptation of the inoculum entails, unlike when the inoculum FNN-9K is used, that the concentration of substrate in the medium is not an influential factor in the inoculum lag time. The biofilm formed and adhered to the pyrite surface during this adaptation process protects the cells from the bioleaching medium, favouring the growth of the population (Bellenberg *et al*., 2015).

Given that bacteria grow using pyrite as a substrate and that flotation tailing is mostly pyrite (Fig. 4A), the final Fe balance in the medium indicates the degree of attack suffered by the matrix of the bioleached mineral. However, high acidity conditions along with the presence of iron sulphides favour the formation of Fe (III) basic hydrosulphates (r2).

$$3\ Fe^{3+} + X^{+} + 2\ HSO_4^{-} + 6\ H_2O \rightarrow X\ Fe_3(SO_4)_2(OH)_6 + 8\ H^{+} \qquad \text{(r2)}$$

In these compounds known as jarosites, with general formula $XFe_3(SO_4)_2(OH)_6$, where X = K^+, Na^+, Ag^+, Pb^{2+}, H_3O^+ or NH_4^+, a significant amount of values metals can be occluded (Ag or Pb) or immobilised by adsorption (Cu or Zn) (Daoud and Karamanev, 2006). The XRD analysis of bioleaching residue (Fig. 4B) shows potassium jarosite, as well as anglesite. Thus, to evaluate the fraction of tailing that has not been attacked by bacterial action, the previous dissolution of the jarosite by acid digestion is necessary.

Fe extractions obtained (Table 1) shows that the substrate depletion occurs at 2 and 5% pulp density. Bacterial growth is conditioned by the pH decrease in the medium. At pH values lower than 0.8-0.9, bacterial metabolic activity ceases. Thus, acidity achieved in the medium at 10% pulp density when inoculum is adapted, generates bacterial inhibition. On the other hand, there is no substrate depletion or bacterial inhibition due to the pH reached when operating at 10% pulp density with the inoculum FNN-9K, in the time interval studied.

Table 1. Lag time, final pH, weight loss, % of jarosite and total Fe extractions in bioleaching tests.

Culture	Pd (%)	Lag time (h)	WL (%)	Final pH	(%) Jarosite	Total Fe X_S (%)
FNN-9K	2	47	69.59	1.17	54.65	97.52
FNN-9K	5	235	65.76	0.96	61.31	97.46
FNN-9K	10	235	39.25	1.13	23.18	72.07
FNN-Py	2	47	76.98	1.09	49.83	98.24
FNN-Py	5	47	68.09	0.93	72.82	99.36
FNN-Py	10	47	63.95	0.82	44.66	95.04

3.3. Bioleaching tests at constant pH

The precipitation of Fe (III) depends on the acidity of the medium, therefore, an adequate pH control can be determinant to limit the extension of jarosite precipitation (Plumb *et al.*, 2008; Kaksonen *et al.*, 2014).

In tests at constant pH, the neutralisation of the acid generated, besides the evolution of Fe in the medium (Fig. 3A), provides information about the bacterial growth and the degree of mineral ore attack. On the one hand, NaOH consumption is similar in both bioleaching tests at 5% pulp density, nevertheless, an earlier addition of NaOH evidences an earlier start of the attack to ore, producing shorter lag time when inoculum FNN-Py is used (Table 2). On the other hand, the more pronounced slope of the Fe extraction curve obtained in bioleaching-2 indicates a higher pyrite dissolution rate. Total Fe extractions close to 100% indicate exhaustion of the substrate, which, in turn, marks the end of the generation of acid and therefore cessation in the addition of NaOH solution. The generation of protons during the precipitation of jarosite (r2) and the complex chemistry of the system cause that the curves of NaOH added and % Fe extracted after the matrix dissolution (r1) are not coincident.

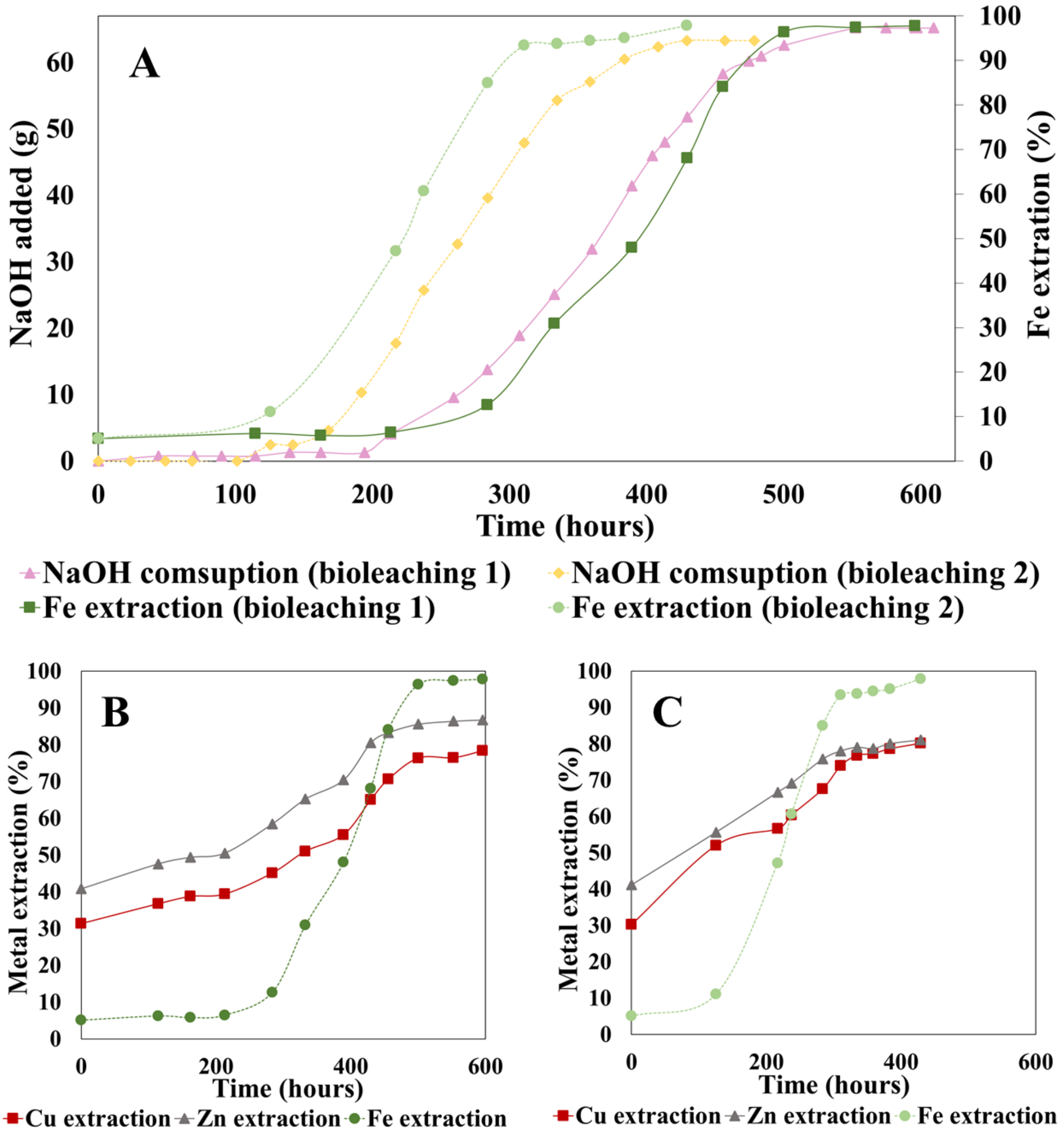

Fig. 3: (A) Relationship between Fe extraction (taking into account the precipitate as jarosite) and the NaOH consumption for bioleaching-1 and bioleaching-2; (B) Fe, Cu and Zn extractions bioleaching-1; (C) Fe, Cu and Zn extractions bioleaching-2.

At the beginning of tests (Fig. 3B and Fig. 3C) extractions of Cu and Zn of 30 and 40% respectively are observed. This fact is in accordance with the extractions obtained in control test at pH 1.5, which evinces that material is partially weathering. In bulk flotation tailings, large part of Cu, Zn and other metallic species are occluded in the pyritic matrix. Bioleaching allows the recovery almost entirely of Cu and Zn. However, the curves obtained indicate the need for the previous matrix attack for the solubilisation of the metals. Unless a significant fraction of pyrite has been attacked, high extractions of both metals are not achieved. The early dissolution of the pyrite matrix in the bioleaching-2 liberates the occluded species more quickly and, therefore, high extractions of Cu and Zn are achieved in fewer hours.

Table 2 summarises of the most relevant results obtained in bioleaching-1 and bioleaching-2. Independent of the nature or preparation of the inoculum used, the weight loss after bioleaching process is 60% and a solid composed of 75-80% of material soluble in 6M-HCl is remained. After treatment with 6M-HCl, the resulting residue represents 10% in weight of flotation tailing and is composed of around 50% of insoluble material that has been concentrated throughout the process from the starting material. This indicates that bioleaching achieves the destruction of more than 97% of the pyrite matrix in every case, leaving a minimum amount of pyrite or material non-bioleached. Final Cu and Zn extractions are also independent of the inoculum used, reaching extractions higher than 78% in all cases (Tables S.1-S.10, in supplementary data).

On the other hand, due to its low solubility of $PbSO_4$, Pb remains retained in the solid (Table 2) as shown by the XRD analysis in Fig. 4C. Lead sulphide has been leached but has been precipitated as anglesite. The bioleaching process also achieves the release of 40.6±2.5% of antimony, 74.3±4.2% of the indium and 77.8±1.3% of cobalt from flotation tailing (Table 2), three strategic elements of great importance for the European Union (*"Critical Raw Materials"*, 2018). Furthermore, Ag, Pb and Au, elements with great value in the market, remain in bioleaching residue

Table 2. Initial conditions and results of bioleaching tests at constant pH.

BIOLEACHING-1
Initial mass 175.03 g - Weight loss in bioleaching 60.17 %
Consumption of 0.3714 g NaOH/g flotation tailing - Lag time: 214 h

Metal	**Flotation tailing grade (%)**	**X_S (%)**	**X_L (%)**	**Percentage retained in jarosite (%)**	**Final grade in clean residue (%)**
Fe	42.15	98.89	97.78	22.19	6.40
Cu	0.36	79.83	78.35	22.66	0.93
Zn	0.39	89.17	86.73	15.55	0.58
Metal	**Flotation tailing grade (ppm)**	**X_S (%)**	**X_L (%)**	**Bioleaching residue grade (ppm)**	
Pb	8095	5.0	4.3	19300	
As	2483	81.6	79.5	1148	
In	172	71.3	79.4	124	
Sb	269	42.3	37.0	390	
Co	183	78.7	68.4	98	
Ag	24	2.7	1.0	59	
Ni	20	73.0	79.1	14	
Au	0.9	-	-	2.3	

BIOLEACHING-2
Initial mass 175,03 g - Weight loss in bioleaching 59.89 %
Consumption of 0.3599 g NaOH/g flotation tailing - Lag time: 192 h

Metal	**Flotation tailing grade (%)**	**X_S (%)**	**X_L (%)**	**Percentage retained in jarosite (%)**	**Final grade in clean residue (%)**
Fe	42.58	99.34	97.88	19.99	2.75
Cu	0.35	82.42	80.09	23.30	0.60
Zn	0.39	86.85	81.04	16.62	0.50
Metal	**Flotation tailing grade (ppm)**	**X_S (%)**	**X_L (%)**	**Bioleaching residue grade (ppm)**	
Pb	8100	2.6	2.3	19676	
As	2534	78.9	87.59	1336	
In	190	77.3	79.97	108	
Sb	310	38.8	45.68	474	
Co	192	76.8	73.64	111	
Ag	24	4.0	1.7	58	
Ni	23	74.7	86,06	14.4	
Au	0.9	-	-	2.2	

3.4. Brine leaching tests

The chemical composition of the bioleaching residue used as starting material (Bioleaching-1 residue) in brine leaching tests (tests 1-7) is 29.46% Fe; 1,93% Pb; 0,37% Cu; 0.26% Zn and 59 ppm Ag. Table 3 shows the variables studied in the recovery of silver and lead from the bioleaching residue.

Table 3. Conditions studied for the extraction of silver and lead at 5% pulp density.

Tests	**T (°C)**	**Pd (%)**	**HCl (M)**	**NaCl (g/L)**	**Cl^- (M)**
1	30	6.68	6	0	6
2	80	5	6	50	6.86
3	80	5	6	0	6
4	80	5	0.5	250	2.14
5	80	5	1	50	1.85
6	80	5	1	0	1
7	80	5	1.85	0	1.85

Table 4 shows the final grade of Ag, Pb, Cu, Zn and Fe, extractions data and the weight losses in brine leaching tests at 5% pulp density.

Table 4. Composition of residues obtained, metal extractions and weight losses in tests 1-7.

Test	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Final grade Ag (ppm)	26	7	7	15	16	21	14
Ag X_S (%)	92.00	98.31	98.31	93.92	94.94	92.32	96.03
Final grade Pb (%)	0.55	0.01	0.01	3.31	2.28	4.63	0.19
Pb X_S (%)	94.85	99.94	99.91	58.52	78.00	47.49	98.37
Final grade Cu (%)	0.93	0.71	0.65	0.89	0.78	1.13	0.66

Cu X_S (%)	53.60	71.40	73.36	40.96	60.26	32.06	70.11
Final grade Zn (%)	0.58	0.10	0.08	0.35	0.48	0.80	0.39
Zn X_S (%)	59.18	94.33	95.43	67.22	65.79	32.12	75.30
Final grade Fe (%)	6.40	3.31	3.28	11.41	4.90	8.29	3.13
Fe X_S (%)	96.04	98.35	98.34	90.62	96.90	93.84	98.23
WL (%)	81.80	85.32	85.06	75.77	81.35	78.10	83.38

The results from tests 1-7 indicate the need for acidity in the medium for the dissolution of precipitates formed during the bioleaching. A supply of complexing agent as HCl higher than 1.85 M is enough to achieve high extractions of Ag and Pb when operating at 5% pulp density. In spite of the shortage of Cu and Zn in the initial solid, an added effect of extraction of both metals is observed. Cu and Zn species oxidation is favoured by the increased activity of Fe (III) in chloride medium. Ferric chloride is a leaching agent more oxidising than ferric sulphate, in a way that enhances the attack by Fe (III) ion of pyrite and other sulphides or species that were not released in the previous stage. Extreme conditions of acidity and complexing agent involve the material matrix destruction and therefore high extractions of all metals. However, these conditions are not feasible on an industrial scale because they would lead to serious corrosion problems.

The XRD analysis (Fig. 4D) indicates that, according to the high weight losses allowed to foresee, the residue is practically constituted in its totality by insoluble material (mostly quartz), which has been concentrated since the beginning of the bioleaching.

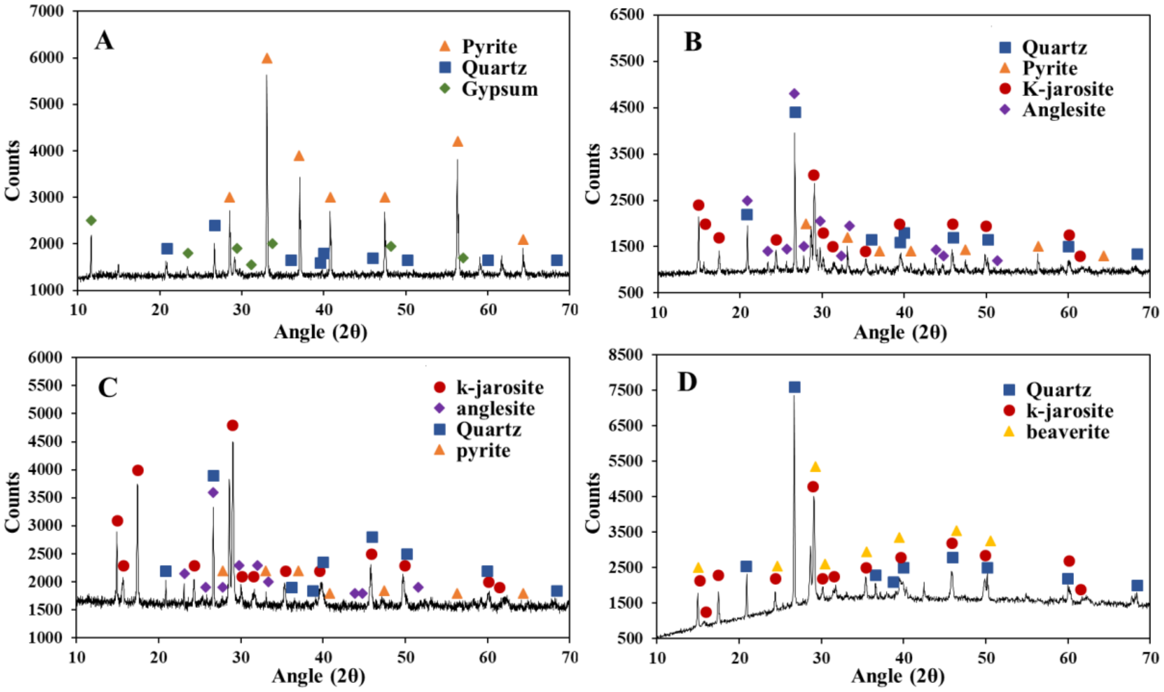

Fig. 4: XRD patterns of (A) flotation tailing (B) bioleaching residue at low pulp density (C) bioleaching-2 residue (D) brine leaching residue.

3.4.1. Influence of pulp density

In tests at 12 and 20% of pulp density, the same proportion of Cl^- consumption is maintained, adding the amount of HCl needed so that at the end there is a free HCl concentration equivalent to that of the 5% pulp density test. In test 7 it is established that, for brine leaching of 5 g of bioleaching residue composed of jarosite in 75.80%, the concentration of Cl^- consumed was 0.473 M, leaving a concentration of 1.377 M of free chloride. The chemical composition of the bioleaching residue used as starting material in tests 8 and 9 is 22.20% Fe; 1,74% Pb; 0,27% Cu; 0.24% Zn and 50 ppm Ag. Table 5 shows the conditions in tests 8 and 9.

Table 5. Conditions studied for silver and lead extractions at 12 and 20% pulp density.

Test	**T (ºC)**	**Pd (%)**	**HCl (M)**	**NaCl (g/L)**	**Cl^- (M)**
8	80	12	2.51	0	2.51
9	80	20	3.27	0	3.27

Table 6 shows final grades of residues from tests 8 and 9 and extractions and weight losses obtained.

Table 6. Final residues composition, extractions and weight losses for tests 8 and 9.

Test	**8**	**9**
Final grade Ag (ppm)	24	24
Ag X_S (%)	89.12	89.16
Final grade Pb (%)	0.22	0.41
Pb X_S (%)	97.21	94.74
Final grade Cu (%)	0.32	0.31
Cu X_S (%)	73.47	74.56
Final grade Zn (%)	0.20	0.15
Zn X_S (%)	81.86	86.28
Final grade Fe (%)	1.19	1.13
Fe X_S (%)	98.80	98.87
WL (%)	77.82	77.91

Given the sufficient amount of acidity and complexing agent, both from HCl, according to the results reported in Table 6, pulp density does not appear to be a significant factor in silver and lead extractions.

3.5. Global evaluation of results

This research work is framed in a new process for the treatment of Cu-Zn-Pb polymetallic complex sulphide ores, aimed to recover valuable metallic content in its entirety and reduce the environmental impact of waste generated in the mining operation. Fig. 5 shows a flow sheet of the proposed process.

Present work proposes bioleaching with extremophile microorganisms as treatment for the valorisation of waste obtained in flotation stage. In relation to the operating conditions, it is deduced that the previous adaptation to flotation tailing as a substrate of the strain used in bioleaching favours the kinetics of the process. On the other hand, when operating at constant pH, the inoculum used in this study has not influence on the degree of attack suffered by the pyrite matrix (99% pyrite dissolution) or the efficiency of Cu and Zn extractions (80-90%), and generates high extractions of critical raw materials such as Sb, In and Co.

The bioleaching liquor, due to its content in ferric sulphate, can be directly used as leaching agent in the hydrometallurgical process for treating bulk Cu-Zn-Pb concentrate (Fig. 5), giving savings in the process due to the high demand for Fe^{3+}. In addition, it contributes significant amounts of Cu and Zn put in solution during the bioleaching. If it were introduced in the line of bulk concentrates treatment, the recovery of both would be carried out by the traditional solvent extraction process and subsequent electrodeposition.

Although the destruction of the pyrite matrix eliminates the refractoriness of the flotation tailing (Lazer et al., 1986; Lorenzo-Tallafigo et al., 2019), bioleaching process does not produce the dissolution of Ag, Pb and Au, requiring a subsequent treatment for complete recovery. Results for brine leaching tests indicates that said treatment is suitable for the solubilisation of Ag and Pb contained in the bioleaching residue, obtaining an inert and clean residue, constituted mostly by quartz (Fig. 4D) and concentrated in Au (gold solubilisation requires more extreme conditions (Sandberg and Huiatt, 1986; Dutrizac, 1992; Frías *et al.*, 2002)). On this sense, bioleaching residue could be introduced in brine leaching stage for its valorisation and the complete elimination of the danger (Fig. 5).

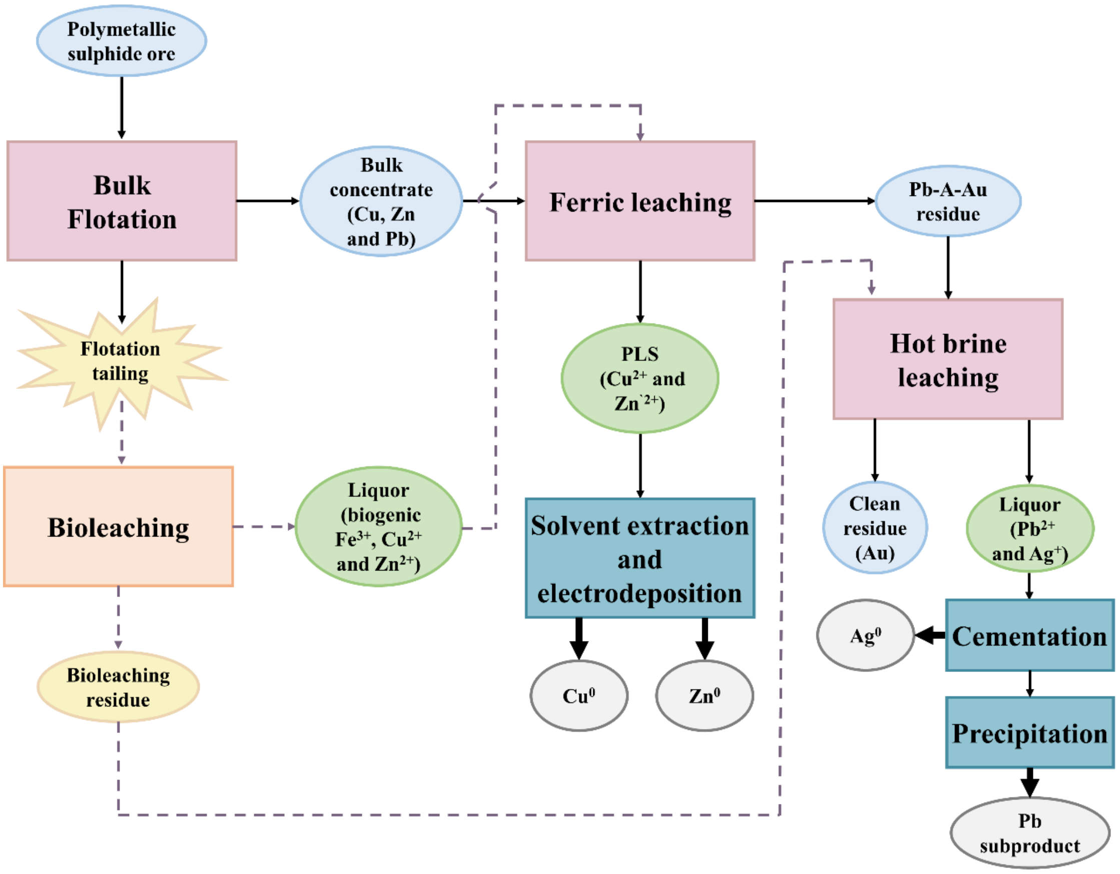

Fig. 5: Treatment of Cu-Zn-Pb polymetallic complex sulphides in pyrite matrix proposal.

Economic and mass balance of the process proposed in Fig. 5 are found in a spreadsheet as supplementary data. In mass balance can be observed the value added of Cu and Zn recirculated and Pb, Ag and Au recovered, just as savings of leaching agent in the hydrometallurgical process. The economic balance was used in this study for economic assessment of the incorporation of the new stage of residue treatment. In order to estimate the profitability of the project, the Fixed Asset Turnover Ratio is used. This coefficient equals annual sales divided by the value of fixed assets (FA). The annual sales consider, in addition to the income from the sale of metals such as Cu and Zn, the savings that the amount of Fe^{3+} recirculated with the bioleaching liquor would imply in the annual cost, as well as the savings in the annual management of the flotation tailing currently stored in piles. These sales forecasts do not take into account the potential profit from remaining metals (Ag, Pb, Au and CRMs) contained in the bioleaching residue due to the imprecision in predicting the extra cost that the addition of said metals to the initial integral process would entail. For calculations of the net present value (NPV) and the internal rate of return (IRR), it is estimated an interest of 15%, that the fixed asset represents 85% of total investment and a project lifetime of 15 years. The applicable tax rate is the general rate for the industry (25%), although it should be highlighted as a favourable argument from the tax point of view that tax incentives apply to mining companies have not been considered. On the other hand, production costs (PC) are calculated according to the Eq6. In this process, raw material (RM) to be used is a polluting residue that would be recycled, assuming no cost. Auxiliary services (AS) include energy required in the bioleaching reactor, in addition to extra costs in electrodeposition and solvent extractions stages for Cu and Zn recovery incorporated in the process. Direct labour (DL) costs have been estimated according to Wessel method.

$$PC = RM\ costs + AS\ costs + 2.5 \cdot DL\ costs + 0.25 \cdot FA \qquad Eq6$$

Table 7. Data for the economic balance.

Fixed Asset Turnover Ratio	0.85
Total mass bioleached (t)	5,250,000.00
Net Annual sales (€/year)	28,531,790.00
Cu and Zn recovery (€/year)	6,815,204.96
Savings in tailing management (€/year)	721,350.00
Saving Fe^{3+} (€/year)	20,995,235.04
Fixed assets (€)	33,566,811.76
Investment (€)	39,490,366.78
Working capital (€)	5,923,555.02
Amortization (€/year)	2,237,787.45
Production costs	14,603,648.21
RM costs (€/year)	0.00
AS costs (€/year)	210,670.75
DL costs (€/year)	2,400,509.81

Table 8. Economic balance.

Years/€	**0**	**1-14**	**15**
Fixed assets	33,566,811.76		
Working capital	5,923,555.02		
Sales revenue		28,531,790.00	28,531,790.00
Production costs		14,603,648.21	14,603,648.21
Amortization		2,237,787.45	2,237,787.45
Tax rate		2,922,588.58	2,922,588.58
BB		11,690,354.34	11,690,354.34
NB		8,767,765.75	8,767,765.75
NCF	-39,490,366.78	11,005,553.20	11,005,553.20

Based on the assumption of a credit granted at 15% interest to 15 years by a bank, an IRR of 27.11% and a NPV of 24,863,175.95 € are obtained, so it is a profitable project.

4. CONCLUSIONS

Finally, it is concluded that bioleaching followed by brine leaching is an alternative for the waste management of the flotation process. Bioleaching destroys pyritic matrix (99% Fe) and dissolves 80-90% Cu and Zn and critical raw materials as Sb, In and Co. Brine leaching achieves Pb and Ag extractions greater than 96% and generates a rich in gold clean solid residue.

The incorporation of bioleaching stage in the proposed hydrometallurgical process allows for obtaining a positive balance between the economic growth, the environmental care and the social welfare, due to it drastically reduces its environmental impact and generates income.

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