The reprocessing of hydrometallurgical sulphidic tailings by bioleaching: the extraction of metals and the use of biogenic liquors

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Highlights

Sulphides dissolution reactions were controlled by mass transfer

Cobalt extraction was directly related to the grade of pyrite dissolution

About 40% Ag and 60% Pb were dissolved under moderate brine leaching conditions

The use of biogenic liquors made economically feasible the reprocessing of tailings

Abstract

Mineralurgical and metallurgical processes generate a large amount of harmful residues. These wastes usually contain a considerable fraction of sulphides and a low percentage of target metals. Due to their characteristics, the main environmental issues concern the acid mine drainage generation and the release of metals. The bioleaching of these tailings can be considered as a win-win process due to the controlled oxidation of sulphides avoids the main environmental issues, while target metals can be recovered. In this work, a residue composed of pyrite (50.4%) and quartz, containing various non-ferrous metals, was reprocessed by bioleaching and brine leaching. Copper and zinc sulphides exhibited a refractory behaviour in bioleaching due to these tailings were previously leached, being the dissolution rate controlled by mass transfer. Cobalt is directly related to the pyrite matrix, requiring the removal of pyrite to extract it. Pyrite dissolution was also controlled by mass transfer, increasing the dissolution rate when the bioreactor conditions were improved. After 10 days of bioleaching in a stirred tank reactor, 87.2% Co, 43.6% Zn, 40.4% Cu, and 96.0% FeS_2 were dissolved. In addition, after bioleaching, 55.9% Pb and 37.9% Ag were dissolved through chloride leaching with moderate conditions (100 g/L NaCl, 10 g/L H_2SO_4, 60 ºC, and 1h). Considering the metals extraction and the saving in management costs of tailings, the reprocessing of these tailings was not economically feasible due to the low grade of target metals. Nonetheless, during bioleaching, a great amount of ferric ion and sulphuric acid was released that could be used in the hydrometallurgical circuit as leaching liquor. This saving increased the revenues from tailings reprocessing, obtaining an internal rate of return of 10% with a feed rate of 260 t/d.
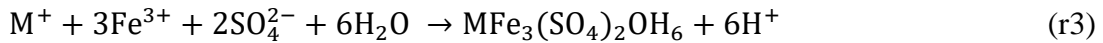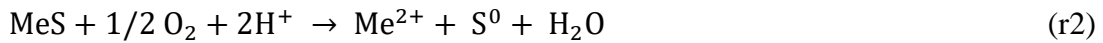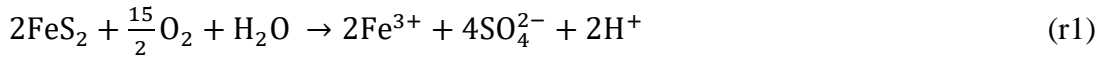
1. Introduction

Annually, approximately 5-7 billion tons of mining wastes are generated worldwide. This generation of residues is recently growing due to the increase of ores complexity and the decrease of ore grades (Edraki et al., 2014; Lébre et al., 2017). Usually, these wastes contain a low grade of non-ferrous metals and a considerable amount of sulphides. The generation of acid mine drainage (AMD), due to the dissolution of these sulphides and an inadequate tailings management, can cause soil and water contamination by the seepage or run-off (Lottermoser, 2010; Wills and Finch, 2015; Kefeny et al., 2017). AMD takes place when ores, such as pyrite (FeS_2), are (bio)-oxidised in an uncontrolled way (Kefeny et al., 2017).

Various available techniques for an appropriate tailings storage include the tailing dam storage, the cemented paste backfill (CPB), or the surface paste disposal (SPD), however these management approaches do not enable the recovery of target metals that remain after ore processing. Nowadays, other technologies for the reprocessing of these wastes are being studied to recover the metals content and to mitigate the hazardousness of these residues at a time. These alternatives processes are mainly focused in (bio)-hydrometallurgical techniques, such as bioleaching or oxygen pressure leaching. The valorisation of these tailings can be considered a win-win process due to the extractive process is improved while the environmental aspects are benefited (Mäkinen et al., 2020; Zhang et al., 2020; Muravyov and Fomchenko, 2018; Han et al., 2018; Hubau et al., 2020; Romero-García et al., 2019; Ye et al., 2017; Falagan et al., 2017).

In the case of bioleaching, this process has been applied in tailings reprocessing at laboratory (Hubau et al., 2020; Zhang et al., 2020; Makinen et al., 2020; Romero et al., 2019) and industrial scale (Neale et al., 2017; Cichy et al., 2017; Morin and Hugues, 2007), with a huge variety of mineral composition, from 2.5 to 90% of FeS_2 content. At laboratory scale, high performances regarding metal recoveries were obtained, between 50-60% Cu, 60-90% Co and 70-100% Zn, respectively (Hubau et al., 2020; Zhang et al., 2020; Makinen et al., 2020; Romero et al., 2019). Also, after bioleaching step, other metals, such as lead, silver and gold were extracted by brine leaching (Romero et al., 2019; Ye et al., 2019) or cyanidation (Muravyov and Fomchenko, 2018). At industrial scale, various mining companies (Cobre Las Cruces Mine, Kasese Mine or Vuonos Mine) have reprocessed, through hydrometallurgical techniques, their tailings to recover copper, nickel or cobalt. These tailings contained a relatively high richness in non-ferrous metals which makes the reprocessing an economically-viable option (e.g. 1.38% Co, 15.2% Ni

or about 1% Cu). Bioleaching was carried out in continuous stirred tank reactors (CSTRs), reaching metal extractions higher than 90% while sulphides were also oxidised in a controlled way (Neale et al., 2017; Cichy et al., 2017; Morin and Hugues, 2007).

In this work the bioleaching of tailings generated in a hydrometallurgical plant (Spain) is studied, aiming the increase of metals recovery from the ore body while the main environmental issues regarding AMD and hazardous metals release can be mitigated. This hydrometallurgical waste is generated after the ferric leaching of a secondary copper sulphide, where a low fraction of target metals remains in the solid fraction, like in flotation or other metallurgical processes these tailings contain an important fraction of hazardous compounds which can cause AMD. The in-situ bioleaching of these tailings in the mine site and the hydrometallurgical facilities could maximise the recovery of metals and transform the harmful wastes into more stable compounds. Through bioleaching, several metals, such as copper, zinc, or cobalt, can be dissolved according to the dissolution of different sulphides (r1 and r2), moreover, the jarosite precipitation, where $M^+ = K^+$, H^+, Ag^+ or NH_4^+, (r3) can also occur (Reyes et al., 2017; Carranza et al., 1997; Fomchenko et al., 2016). However, other metals, e.g., silver or lead, are not solubilised in this step and require additional steps to extract it, such as the use of brine leaching (r4 and r5) (Behnajady and Moghaddan, 2014).

$$2FeS_2 + \frac{15}{2}O_2 + H_2O \rightarrow 2Fe^{3+} + 4SO_4^{2-} + 2H^+ \qquad (r1)$$

$$MeS + 1/2\ O_2 + 2H^+ \rightarrow Me^{2+} + S^0 + H_2O \qquad (r2)$$

$$M^+ + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O \rightarrow MFe_3(SO_4)_2OH_6 + 6H^+ \qquad (r3)$$

$$PbSO_4 + 4Cl^- \rightarrow PbCl_4^{2-} + SO_4^{2-} \qquad (r4)$$

$$AgCl + 3Cl^- \rightarrow AgCl_4^{3-} \qquad (r5)$$

In this work, the bioleaching followed by brine leaching of the described tailings and the economic feasibility of this alternative management proposal was studied. For this, several bioleaching experiments were carried out, from flasks to different stirred tank reactors, after bioleaching the dissolution of silver and lead was tested by brine leaching. According to the results obtained in these assays and literature data, a preliminary feasibility assessment was performed.

2. Materials and methods

2.1. Tailings Characterisation

The used tailings were collected from a hydrometallurgical plant for the treatment of secondary copper sulphides (Spain). According to XRD and chemical analysis, the tailings were mainly composed of pyrite (50.4%) and quartz (42.6), and a low amount of elemental sulphur (0.89%). This elemental sulphur was generated in the hydrometallurgical step due to the dissolution of secondary copper sulphides. Iron and sulphur were the main measured elements: 23.5% and 27.5%, respectively, also 0.20% As was detected. In addition, a low concentration of target metals were detected: 0.29% Cu, 0.14% Zn, 0.58% Pb, 265.6 mg/kg Co, 24.7 mg/kg Ag and 0.6 mg/kg Au. This composition requires a polymetallic recovery from tailings to enable the maximum profit, some of these metals (Pb, Ag, and Au) are insoluble in bioleaching therefore additional leaching steps must be carried out to extract them. Brine leaching can dissolve lead and silver, while other processes, such as cyanidation, thiosulphate, or hypochlorite leaching, enable the gold dissolution (Behnajady and Moghaddan, 2014; Jeffrey et al., 2001).

2.2. Inoculum

Bioleaching tests were performed with an inoculum isolated from a drainage water from Rio Tinto Mine (Spain) and grown in 9K medium (9 g/L Fe^{2+}, 3 g/L $(NH_4)_2SO_4$, 0.5 g/L $MgSO_4 \cdot 7H_2O$, 0.5 g/L K_2HPO_4, 0.1 g/L KCl, 0.01 g/L $Ca(NO_3)_2$ and pH 2-2.3) (Silverman and Lundgren, 1959). The culture was characterised through DNA extraction, PCR amplification, sequencing and phylogenetic analysis, and also by isolation of single colonies in solid media (Segura, 1998; Mazuelos et al., 2012), being *Acidithiobacillus ferrooxidans, Leptospirillum ferrooxidans, Leptospirillum ferriphilum, Leptospirillum ferrodiazotrophum, Leptospirillum rubarum, Ferrimicrobium* and *Acidimicrobium ferrooxidans* the main found bacteria. Also, associated heterotrophs of *Acidiphilium* genus were isolated in solid media. This inoculum was progressively adapted to sulphide tailings and 9K basal salts (without ferrous ion) by a successive sub-culturing with a progressive increase of pulp density from 1 to 5%.

2.3. Abiotic tests

Before bioleaching experiments, various acid and ferric leaching tests were carried out to study the influence of bioleaching in metals dissolution. These assays were performed in similar conditions of temperature (30 ℃) and pulp density (20%) to bioleaching in 0.25L flasks tests (0.1L working volume) and orbital stirring (180 rpm). On the one hand, acid leaching was studied, in the concentration range of 0-100 g/L H_2SO_4, with the following

conditions: 30 ℃, 20% of pulp density, and 24h of leaching. On the other hand, ferric leaching experiments were carried out at different times (10-120 min) with a 0.22μm-filtered biogenic ferric solution (9 g/L ferric ion and pH 1.25), the other conditions were: 20% pulp density and 30 ℃. Once the tests finished, the pulp was filtered (0.45μm) and dried at 50 ℃. Fe, Cu, Zn, and Co were determined in both liquors and solids. In addition, redox potential and ferrous ion were measured in ferric leaching experiments.

2.4. Bioleaching Tests

Bioleaching was performed in flasks and, later, in stirred tank reactors. All tests were run in duplicates. Flasks tests were performed in 0.25 L flask reactors with orbital agitation, the fixed conditions were: 180 rpm, 30 °C, 20% inoculum, 80% of 9K basal salts, and a working volume of 0.1 L. A known mass of flotation tailings was mixed with 9K basal salts and the inoculum. Once inoculum was added, the assay started. Evaporation was daily corrected with distilled water, while pH and redox potential were also monitored. Pulp density, in the range of 5-20%, and bioleaching time were evaluated in these assays, therefore after a certain bioleaching time the pulp was filtered (Millipore, 0.45 μm) and washed with diluted sulphuric acid and, later, with distilled water. Prior to analysis, solid samples were dried at 50 ℃. Zn, Co, As, Cu, Pb, Ag, and Fe were determined in solids waste and liquors. The dissolution of pyrite was measured in solid residues through sequential digestion. This method consisted of a first digestion with HCl to dissolve jarosite and a later digestion with aqua regia to dissolve pyrite (Lorenzo-Tallafigo et al., 2019).

Bioleaching in stirred tank reactors followed a similar procedure, however, in these assays several liquid samples were withdrawn from bioreactors to determine Cu, Zn, Co, and Fe concentration along bioleaching time. Given the results obtained in flasks tests, where at high pulp densities iron dissolution was very similar to pyrite biooxidation, pyrite kinetics in stirred tank reactors (STR) was determined according to soluble iron determined in liquors. The sequential digestion to determine pyrite dissolution, above described, was performed to final solid residues to check it. Due to the higher volume of inoculum required for bioleaching test perfromed in 6L, the inoculum for this test was prepared in a stirred tank reactor at 20% pulp density. Experimental conditions for the two bioreactors volumes were the following: 0.1 L/min aeration, 500 rpm (mechanical stirring- axial rotors), 30 ℃, 20% inoculum, and 20% pulp density (0.8L working volume), and 2L/min aeration, 500 rpm (mechanical stirring- axial rotors), 30 ℃, 20% inoculum, and 20% pulp

density (6L working volume). The air inlet was set in the bottom of the bioreactor, below the agitator.

2.5. Brine Leaching Tests

Several brine leaching tests were performed with the bioleached tailings obtained in the 6L-STR. Temperature (30ºC and 60ºC), chloride concentration (50-150 g/L) and acidity (0-10 g/L H_2SO_4) were studied in these experiments. All tests were run for1h at 5% of pulp density in 0.25L flasks (0.1L of working volume with orbital stirring – 180 rpm). Leaching solutions were prepared and heated to the working temperature. Once test temperature was reached, the solid residue was added and brine leaching started. After 1h, the pulp was filtered and dried at 50 ºC. Weight loss, Fe, Pb, and Ag were determined in the solid fraction.

2.7. Analytical Methods

2.7.1. Elements Measurement

Metals content in liquors and solid were determined by atomic absorption spectrophotometry (AAS; Perkin Elmer 2380 Model, United States). Solid were previously dissolved in aqua regia (3HCl: 1HNO$_3$). Gold was only determined in solids by the fire assay method (Hoffman et al., 1998).

Sulphur content was determined by precipitation with barium chloride ($BaCl_2$) (Nydahl, 1954). Elemental sulphur was measured by extraction with carbon disulphide (CS_2) in a Soxhlet extractor and later distillation of CS_2 to weight the elemental sulphur fraction (Meyer et al., 1971).

2.7.2. X-ray diffraction Analysis

Mineral phases were determined by X-ray diffraction (XRD) using a powder diffractometer (Bruker D8 model advance A25, United States) and the DIFFRAC.EVA software /Bruker, United States). This technique was performed in CITIUS (Centro de Investigación, Tecnología e Innovación de la Universidad de Sevilla).

3. Results and discussions

3.1 Chemical leaching

Previous to biotic tests, several abiotic assays were performed to study the effect of acid and ferric ion on metals leaching. These abiotic tests were performed at 20% of pulp density and 30 ºC.

3.1.1 Acid leaching

Some acid leaching tests were performed at different sulphuric acid concentrations at 30 ºC and 24h (0-100 g/L H_2SO_4). Copper, zinc and cobalt extraction as a function of sulphuric acid concentration is shown in Fig. 1. Copper extraction was improved at a higher acid concentration reaching a maximum of 18.5%. Also, a fraction of copper was soluble in water (11.9%) that can be associated to impregnated pregnant liquor solution (PLS). When H_2SO_4 concentration rose over 20 g/L, copper extraction was slightly improved, this acid-soluble fraction could be associated with oxidised compounds or with a low fraction of sulphides that were dissolved by oxygen or ferric ion (released by acid addition). These results are in accordance with those observed by Antonijevic et al. (2008). Nonetheless, more than 80% of copper shown a recalcitrant behaviour, corresponding this fraction to the sulphide matrix. Unlike copper, zinc and cobalt were not solubilised in acid media, therefore these metals must be strongly associated to sulphide compounds.
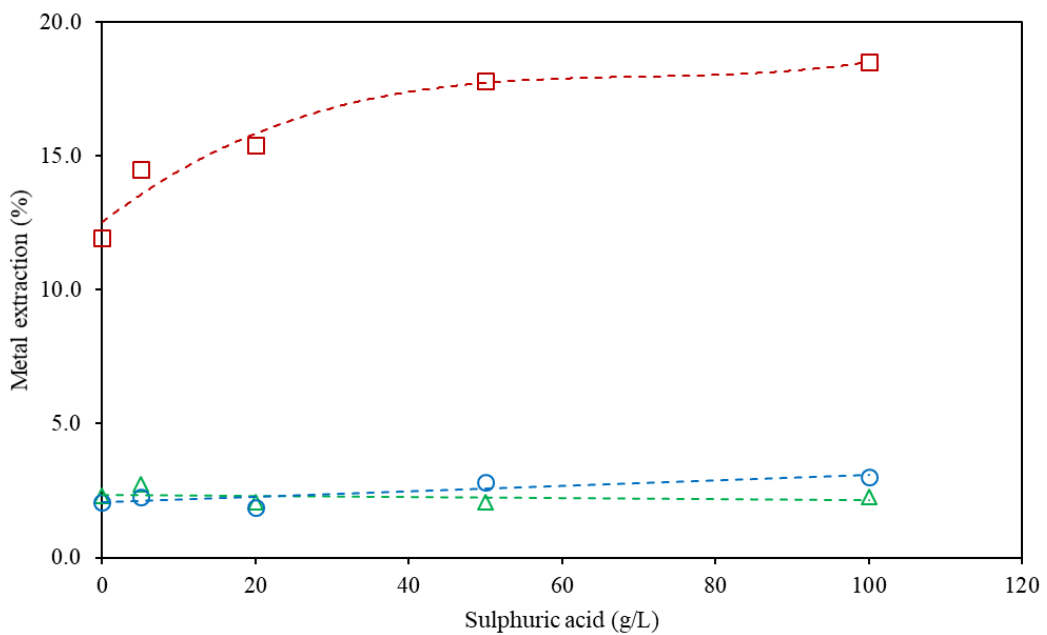
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Fig. 1. Metal extraction as a function of sulphuric acid concentration (g/L) in chemical assays (24h, 20% pulp density and 30 ℃) (red squares = copper; green triangles = zinc; blue circles = cobalt).

3.1.2. Ferric sulphate leaching

In order to examine the effect of ferric leaching, the kinetics of metals leaching for two hours in a biogenic ferric solution, filtered with 0.22µm, (9 g/L Fe^{3+} and pH 1.25) was studied. Metals extraction, ORP and ferrous ion concentration as a function of time is displayed in Fig. 2. Redox potential rapidly fell to 500 mV due to the ferrous ion generation which progressively rose to reach 1 g/L after 2h. Instead, metals dissolution remained constant along leaching time being the extraction level very similar to acid leaching results. This low metal extraction can be related to several phenomena according to tailings characteristics, on the one hand the remaining metals could belong to pyrite matrix and on the other hand non-ferrous metal sulphides could have been passivated in the hydrometallurgical step. In other works, where flotation tailings (non-oxidised) or sulphide ores were processed, the chemical leaching generated a rapid dissolution rate of copper and zinc followed by a deceleration phase due to the formation of a passivating film around sulphide particles (Souza et al., 2007; Mäkinen et al., 2020).
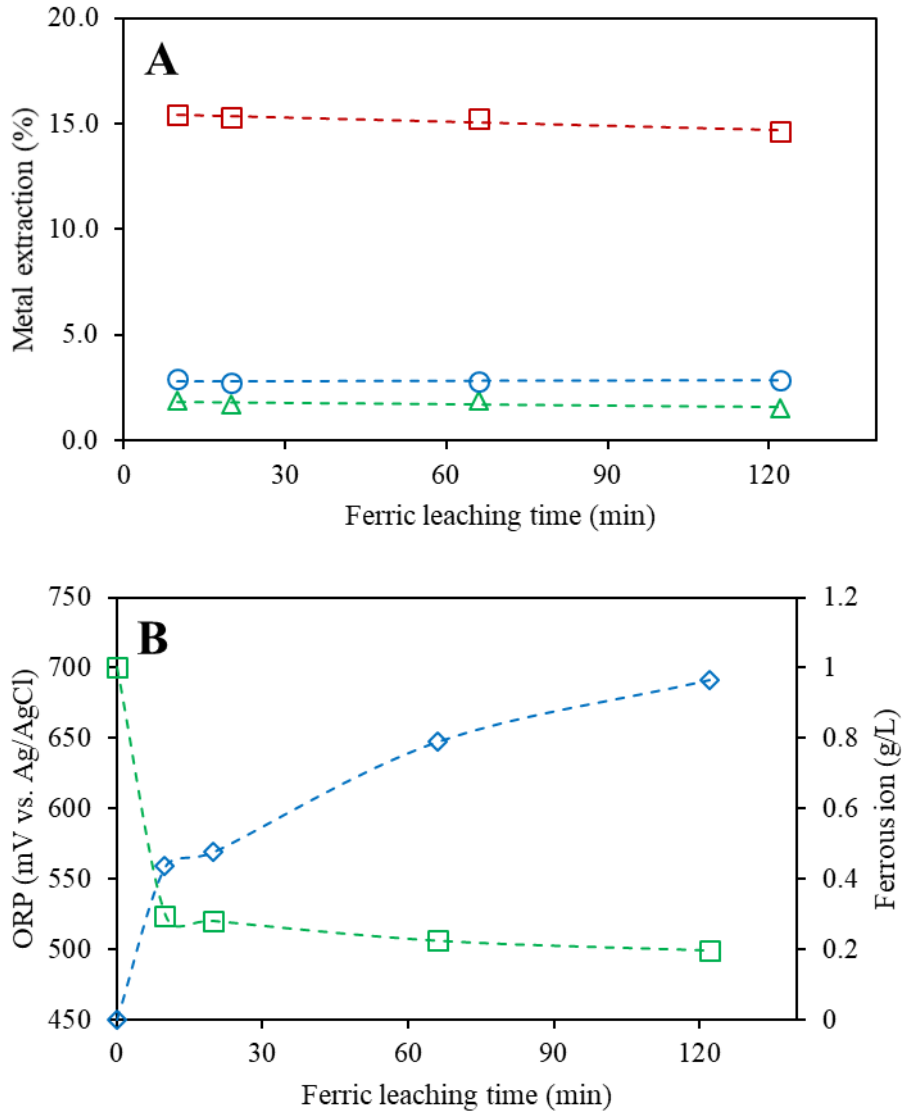
Fig. 2. Metal extraction (A) and ORP and ferrous ion concentration (B) over ferric leaching time (20% pulp density, 30 °C, 9 g/L ferric ion and pH 1.25) (red squares = copper; green triangles = zinc; blue circles = cobalt; blue diamond = ferrous ion concentration; green squares = ORP).

3.2. Bioleaching

To study the different phenomena above mentioned and the influence of bacteria in metals solubilisation several bioleaching experiments were performed. Bioleaching is a well-known technology for pyrite dissolution. In this work bioleaching was carried out from flasks to a stirred tank bioreactor with a working volume of 6L to study the influence of pulp density and the stirring system in the bioleaching efficiency. In this step, copper, zinc, cobalt, and pyrite dissolution were determined in each experiment. The figures of this section show the concentration of metals (Cu, Zn, Fe, and Co) to display the chemical

composition of bioleaching liquors, due to the bioleaching of tailings supposes a huge difference in liquors concentration regarding the beneficiation of sulphide concentrates or high-grade ores.

3.2.1 Bioleaching in flasks

Several biotic assays were performed in flasks at different pulp densities, from 5 to 20%, studying the metals and pyrite dissolution. Redox potential and pH were daily monitored. After certain time, cultures were filtered and liquids and solids (dried at 50 ºC) were analysed. pH and ORP changes in these assays at different pulp densities can be observed in Fig. 3, pH progressively dropped due to pyrite oxidation (r1), when pulp density rose over 10% a lag phase was observed (no changes in ORP and pH). The ORP dynamics shown a great difference regarding pulp density, at higher solids load redox potential decreased due to Fe^{3+}/Fe^{2+} was lower. This ratio can be affected by a decrease in microorganism activity, lower oxidant activity by an inhibitory effect, or by a lack of oxygen transfer rate (OTR) because high pulp densities could hinder it (Mahmoud et al., 2017; Derksen et al., 2000). The decrease of redox potential hugely affected pyrite oxidation (Fig. 4), decreasing the pyrite dissolution rate when pulp density was increased. While more than 80% of pyrite was oxidised at 5% p.d. in 10 days, only 70% of pyrite was dissolved after 38 days of bioleaching at 20% of pulp density. Nonetheless, in all cases similar pyrite dissolution curves were observed, starting with a linear dissolution rate, where the maximum rate was achieved, followed by a phase where oxidation rate was deaccelerated (approximately 70% of pyrite dissolution; curves are shown in Supplementary Material), probably caused by pyrite exhaustion.
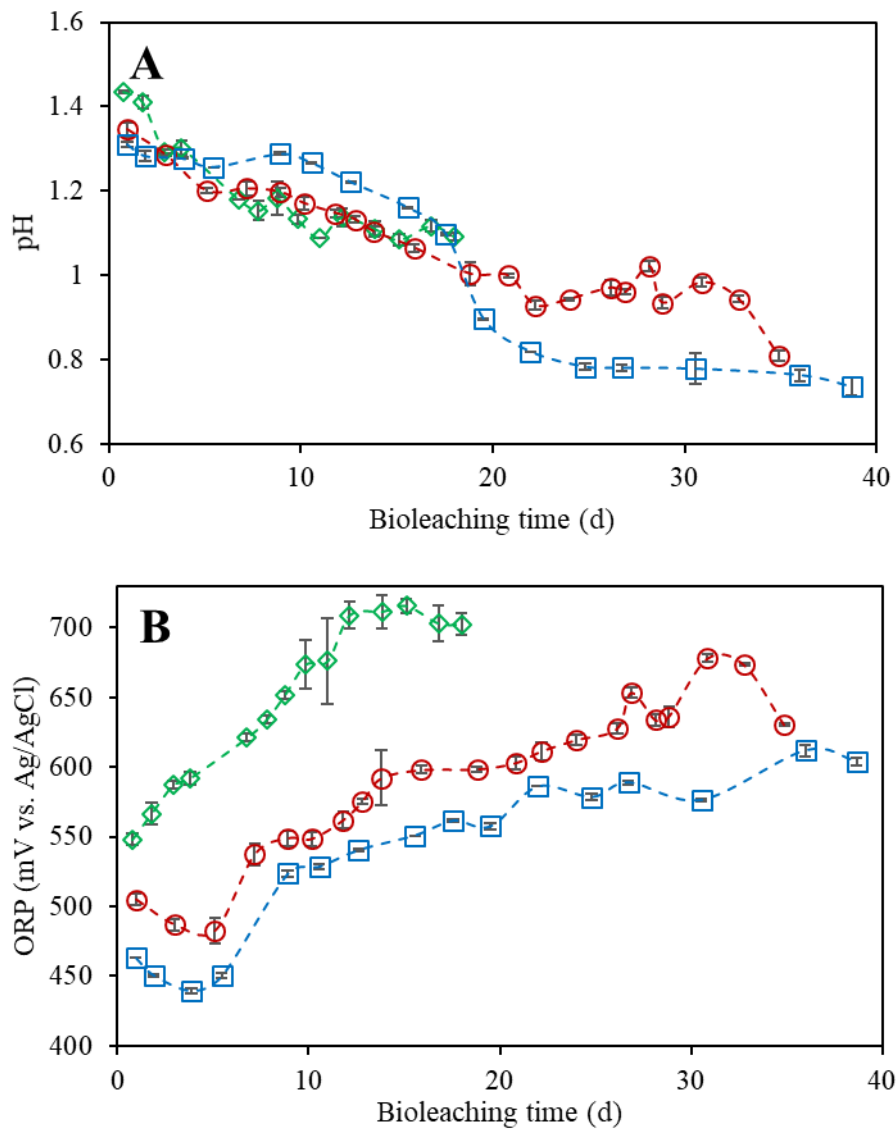
Fig. 3. pH (A) and ORP (B) as a function of time and pulp density in bioleaching tests carried out in flasks (30 ℃, 20% of inoculum and 0.1 L reaction volume) (green diamond = 5% p.d.; red circles = 10% p.d.; blue squares = 20% p.d.).
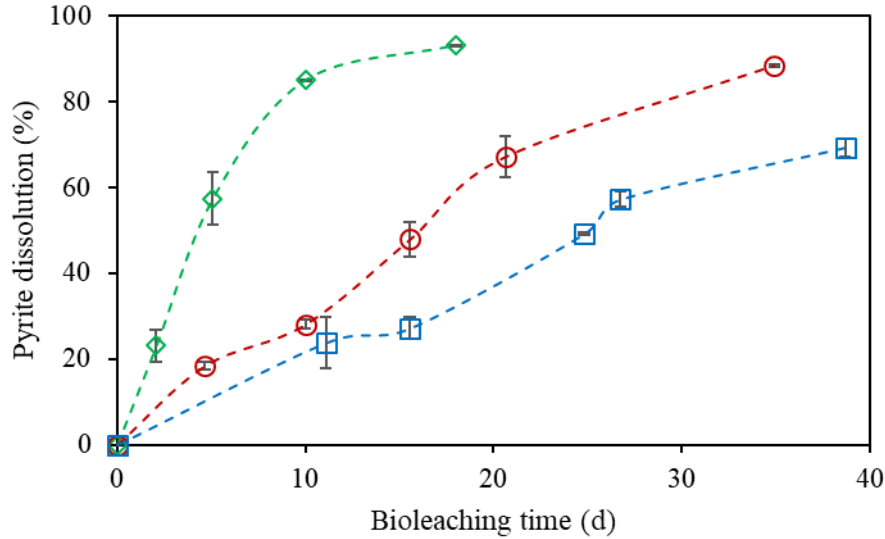
Fig. 4. Pyrite dissolution at different pulp densities for bioleaching tests performed in flasks (30 ℃, 20% of inoculum and 0.1 L reaction volume) (green diamond = 5% p.d.; red circles = 10% p.d.; blue squares = 20% p.d.).

In addition to iron, copper, zinc, and cobalt were also dissolved during bioleaching, showing a different behaviour than pyrite dissolution. Copper and zinc shown a similar trend, being linearly leached (Fig. 5A and 5B). After a certain time, zinc dissolution was decelerated, the leaching rate was negligible. These curves differed from bioleaching of flotation tailings, where bioleaching rate kinetics was parabolic because sulphides were fresh (non-leached) (Souza et al., 2007; Mäkinen et al., 2020). This linear kinetics could be associated to the mass transfer as the rate limiting step. Because of these tailings were generated after a leaching process, the remaining copper and zinc sulphides could be covered to a passivating film. In addition to the passive coat, mass transfer resistance in the liquid phase could also decrease the dissolution rate, due to the increase of pulp density in flasks did not proportionally improve (linear rate (mg $Cu^{2+} \cdot L^{-1} \cdot d^{-1}$): 1.52 at 5% p.d., and 2.36 at 20% p.d.). This increase of dissolution rate, when pulp density rose four times, supposed a great decrease of copper extraction rate from tailings. Similar results were observed with zinc, where the linear rate per unit of tailings mass decreased with a higher solid ratio. However, higher metal extractions were achieved at higher pulp densities because of these tests were run during longer times, from 18 (5% d.p.) to 39 days (20% d.p.). The results in abiotic tests and these low dissolution rates obtained in bioleaching assays supported the mass transfer rate as the rate limiting step.

Unlike copper and zinc, cobalt extraction decreased when pulp density rose over 10%, from 80.7% to 63.7% at 20% p.d. (Fig. 5C). this behaviour can be explained according to Fig. 5D, where the relationship between cobalt and iron concentration from different tests is shown. Cobalt concentration displayed a linear relationship regarding iron concentration, probably due to cobalt belonged to the pyrite matrix. This effect has been also reported in the bioleaching of other tailings, where the complete oxidation of pyrite was necessary to achieve high cobalt extraction levels (Morin and Hugues, 2007; Mäkinen et al., 2020). In addition, Hubau et al. (2020) observed an enhancement of cobalt dissolution when microbial activity rose.
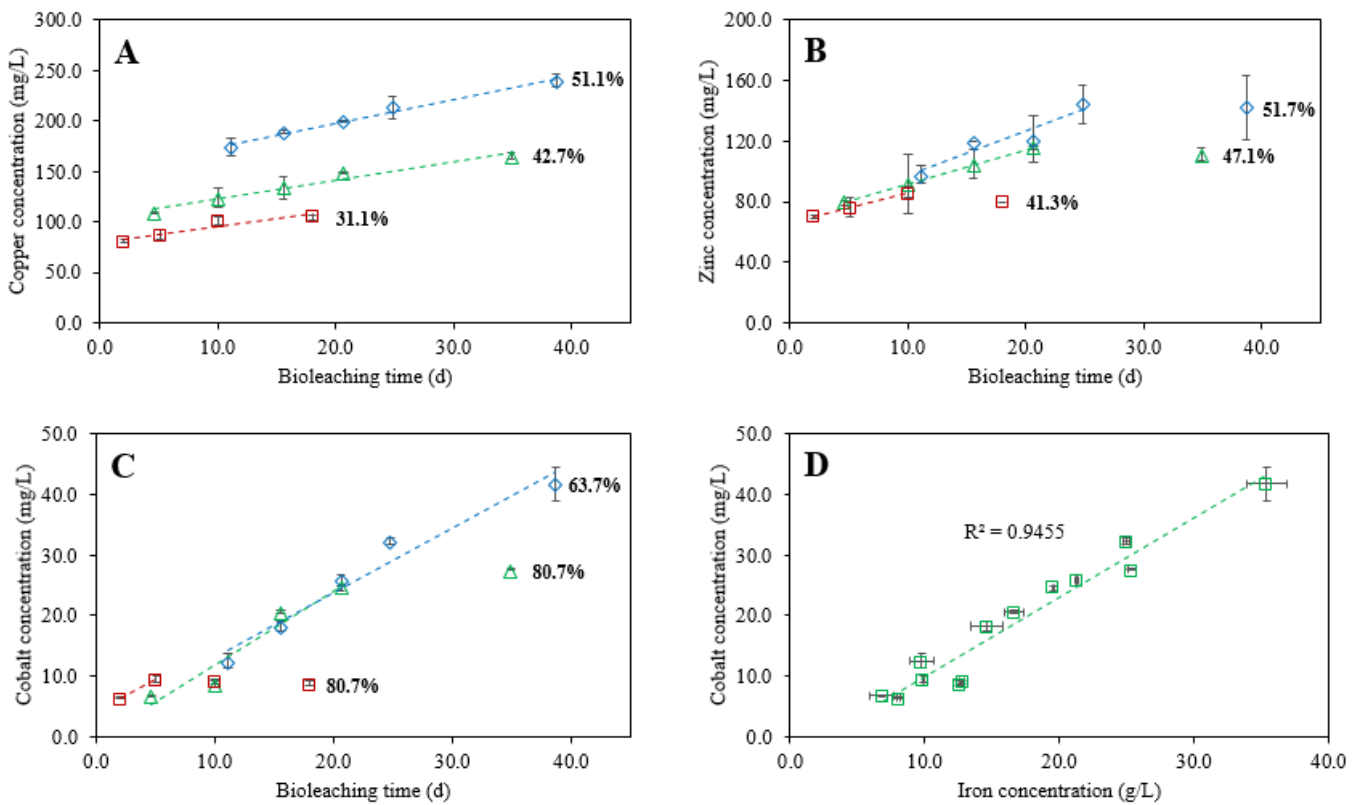

Fig. 5. Copper (A), zinc (B), cobalt (C) concentration over time, and relationship between cobalt and iron (D) in bioleaching tests performed in flasks. Final copper, zinc and cobalt extractions are indicated (red squares = 5% p.d.; green triangles = 10% p.d.; blue diamond = 20% p.d.).

The main results after bioleaching in flasks are shown in Table 1. The increase of pulp density generated greater acidic conditions, which supposed a decrease in jarosite precipitation. This fall in jarosite precipitation can be observed in the weight loss of bioleaching residue in HCl media, where jarosite is dissolved. While at 20% of pulp density only 4% of residue was soluble in hydrochloric acid, approximately 23% of

weight loss was reached at 5% of pulp density. According to chemical controls, where only 15% of copper was solubilised, bioleaching increased copper extraction by over 45% and enabled the extraction of 50% and 80% of zinc and cobalt, respectively.

Table 1. Main results obtained in bioleaching (tests duration, pH, ORP, metal extraction and chemical composition after bioleaching) (All tests were run in duplicate, errors are expressed as standard deviation; *weight loss obtained in the bioleaching residue treated with HCl) (30 ºC, 20% of inoculum and 0.1L reaction volume).

Pulp density (%)	Bioleaching time (d)	Final pH	Final ORP (mV)	Cu extr. (%)	Zn Extr. (%)	Co Extr. (%)	Fe extr. (%)	FeS$_2$ extr. (%)
5	18.0	1.09 ± 0.01	702.5 ± 7.8	31.1 ± 6.3	41.3 ± 2.0	80.7 ± 2.0	73.0 ± 0.9	92.98 ± 0.12
10	34.9	0.81 ± 0.01	630.5 ± 0.7	42.7 ± 1.2	47.1 ± 0.2	80.7 ± 1.3	80.2 ± 0.3	88.38 ± 0.20
20	38.7	0.74 ± 0.02	604.0 ± 2.8	51.1 ± 4.4	51.7 ± 0.2	63.7 ± 3.1	69.30 ± 1.7	71.50 ± 2.13

			Residue composition					
Pulp density (%)	Weight loss bioleaching (%)	Weight loss HCl (%)*	Fe (%)	Cu (%)	Zn (%)	Co (%)	Pb (%)	Ag (mg/kg)
5	24.18 ± 1.51	22.97 ± 2.92	8.24 ± 0.11	0.27 ± 0.03	0.10 ± 0.01	66.4 ± 8.4	1.07 ± 0.03	49.1 ± 0.9
10	31.57 ± 0.14	12.04 ± 2.89	6.70 ± 0.12	0.24 ± 0.01	0.10 ± 0.00	73.4 ± 4.9	0.94 ± 0.04	47.9 ± 2.6
20	27.92 ± 2.13	4.05 ± 4.05	9.15 ± 0.27	0.22 ± 0.02	0.09 ± 0.00	131.4 ± 7.4	0.76 ± 0.21	37.1 ± 5.6

3.2.2 Bioleaching in STR

Bioleaching in different stirring systems could explain the reason for the deceleration of pyrite dissolution when pulp density is increased, which can discern between biological (inhibition) or physical (oxygen transfer rate) limitations. Given the results obtained in flask assays, several bioleaching tests were performed in two stirred tank reactors (0.8L and 6L) to study the bioleaching at high pulp density (20%). Like previous experiments, pH and ORP were monitored along bioleaching time. In addition, several liquor samples were withdrawn to determine the metal content over time (Cu, Zn, Co, and Fe).

3.2.2.1 Bioleaching in 0.8L-STR

The bioleaching in this stirring system was run in duplicate. Like flask tests, a lag phase was observed, where pH (Fig. 6A) and ORP (Fig. 6B) did not vary. In both tests, pH dropped to approximately 0.7 after 20 days. After the lag phase, a fast increase of redox

potential was observed, reaching a maximum of 700 mV; these tests shown higher redox potentials than flask tests at 20% of pulp density probably due to a higher oxygen transfer rate. This improvement produced a huge increase in the pyrite dissolution rate (Fig. 7), reaching a pyrite extraction of approximately 86% after 20 days. The linear pyrite dissolution rate increased more than 4 times regarding flasks, from 1.82 to 7.56 g $FeS_2 \cdot L^{-1} \cdot d^{-1}$, this improvement enabled a reduction of bioleaching time to 20 days. Like flasks assays, this linear rate decreased about 70% of pyrite oxidation. Although different lag times were observed in these tests, when ORP rose over 500 mV (vs. Ag/AgCl), pyrite dissolution rate was very similar (7.51 and 7.58 g $FeS_2 \cdot L^{-1} \cdot d^{-1}$). This pyrite dissolution enhancement could be associated with an improvement of mass transfer rate; this would clarify that a low oxygen transfer rate caused a deterioration of bioleaching efficiency when solid load rose.
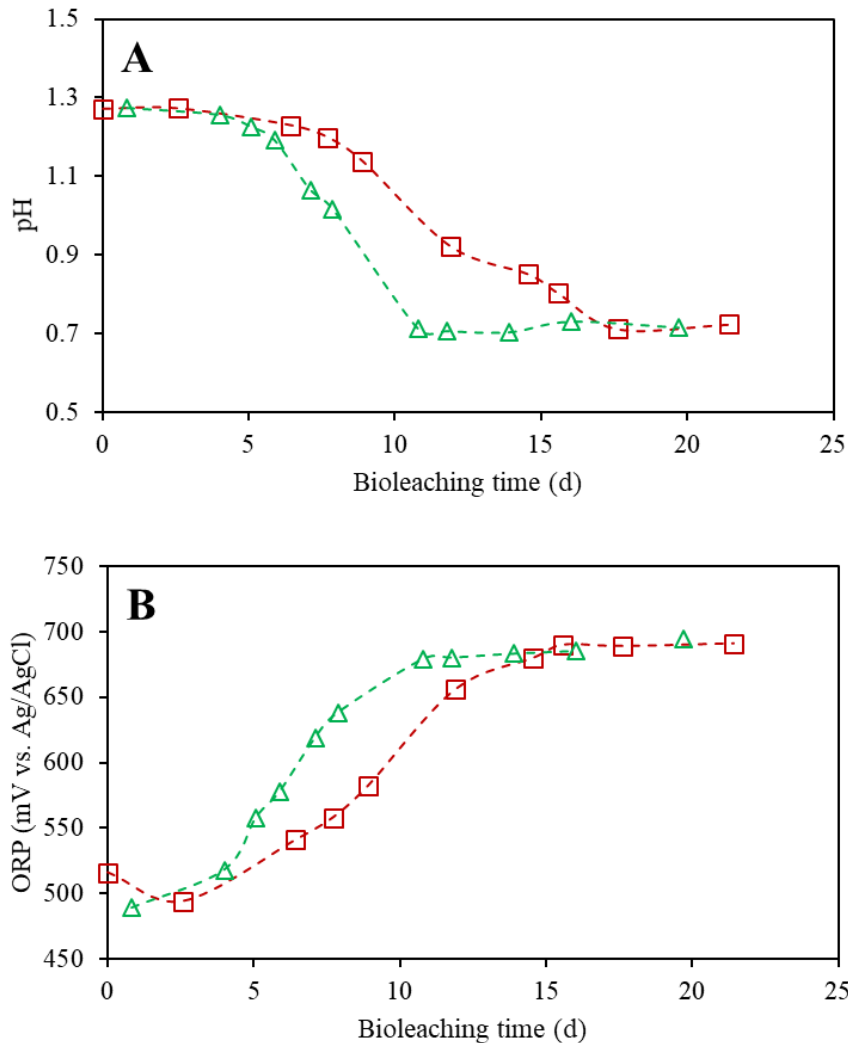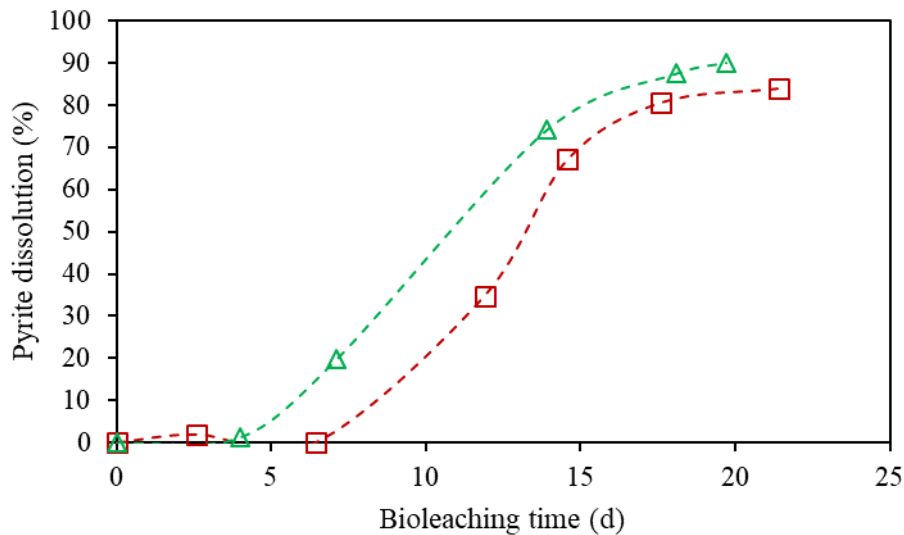
Fig. 7. Pyrite dissolution with respect time for two bioleaching tests in 0.8L-STR (20% p.d., 30 ℃, 500 rpm, 0.1L/min and 20% inoculum) (red squares = STR-1; green triangles = STR-2).

Copper, zinc and cobalt dissolution (Fig. 8 A-C) slightly varied in these tests, reaching similar recoveries than in flasks. Copper and zinc dissolution curves were identical to previous assays, the improvement of stirring conditions barely affected the dissolution of these metals. Thus, the main limitations for the extraction of these elements were intrinsic limits of the studied waste, such as zinc passivation about 50% of its dissolution. Nonetheless, the linear rate of zinc dissolution was improved in the 0.8L-STR experiments, reaching the passivation regime after 13-14 days, while in flask tests at 20% p.d. were required more than 20 days to achieve this regime. In the case of copper extraction, this decreased from 51.1 to 42.8% due to bioleaching time was shortened, the linear dissolution rate was similar to the rate achieved in the flask assays at 20% of pulp density.

Cobalt association to pyrite matrix was confirmed, showing a linear relationship between cobalt concentration and iron concentration in both 0.8L-STR assays (Fig. 8D). In addition, cobalt dissolution started when the lag phase finished (Fig. 7 and Fig. 8D), like

pyrite bio-oxidation. In these tests, cobalt extraction increased to 80.7% due to the higher pyrite removal, similar to flasks tests at low pulp density.
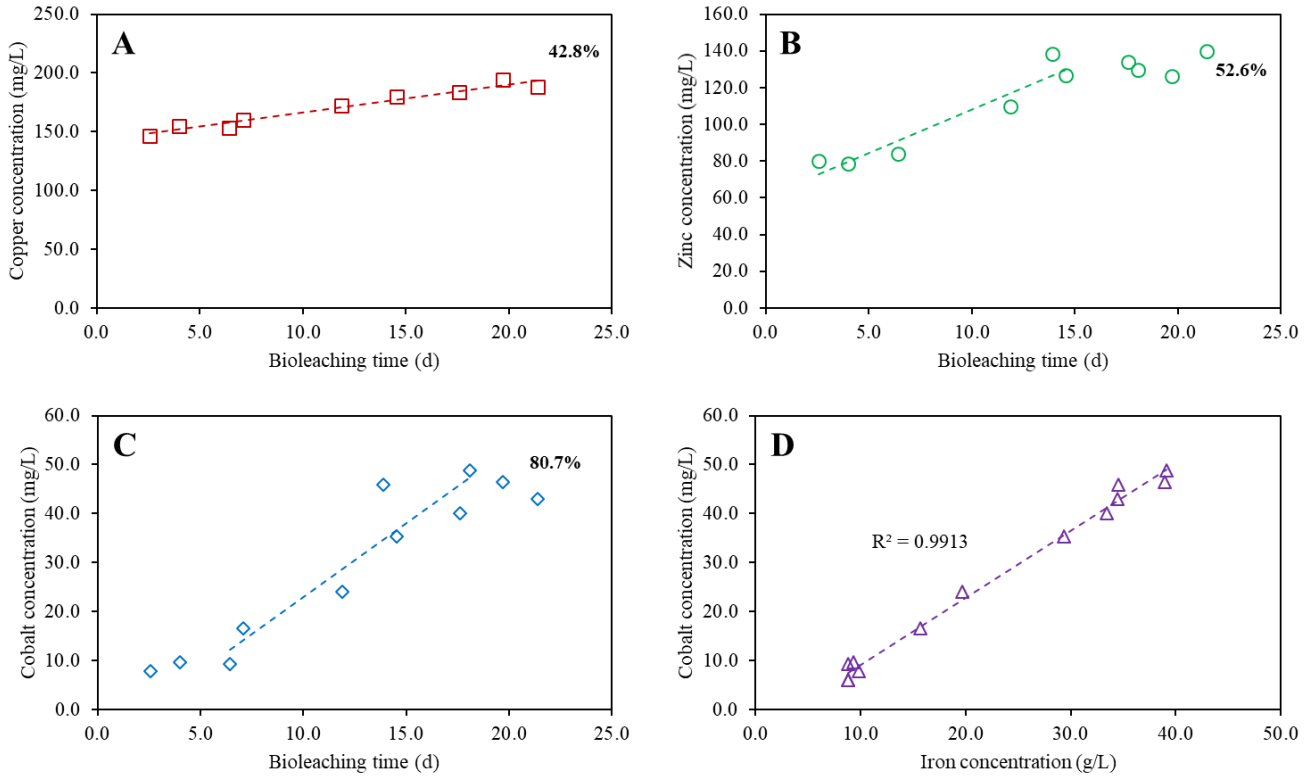

Fig. 8. Copper (A), zinc (B), cobalt (C) concentration and relationship between cobalt and iron concentration (D) in bioleaching. Final extractions of copper, zinc and cobalt are indicated (20% p.d., 30 ℃, 500 rpm, 0.1L/min of aeration and 20% inoculum).

After 20 days of bioleaching, the main achieved results are shown in Table 2. The use of a stirred tank reactor enabled the achievement of similar metal extractions than best results at low pulp density in flasks. Nevertheless, jarosite precipitation (associated to weight loss in HCl solution) was lower than in these tests due to a higher acidity.

Table 2. Main results (test duration, pH, ORP, metals extraction and residue composition) obtained in bioleaching (All tests were run in duplicate, errors are expressed as standard deviations, *weight loss obtained in the bioleaching residue treated with HCl) (30 ℃, 20% of inoculum, 20% of pulp density, 500 rpm, 0.1L/min of aeration and 0.8L reaction volume).

Test	Bioleaching time (d)	Final pH	Final ORP (mV)	Cu extr. (%)	Zn Extr. (%)	Co Extr. (%)	Fe extr. (%)	FeS$_2$ extr. (%)
STR–0.8L	20.5 ± 1.2	0.72 ± 0.00	692.5 ± 2.1	42.8 ± 0.1	52.6 ± 13.1	80.7 ± 5.2	82.6 ± 4.6	85.8 ± 5.6

			Residue composition					
Test	Weight loss bioleaching (%)	Weight loss HCl (%)*	Fe (%)	Cu (%)	Zn (%)	Co (%)	Pb (%)	Ag (mg/kg)
STR–0.8L	35.9 ± 2.2	5.4 ± 1.8	6.24 ± 1.43	0.26 ± 0.01	0.10 ± 0.01	78.4 ± 18.3	0.76 ± 0.05	40.5 ± 3.4

3.2.2.3 Bioleaching in 6L STR

A bioleaching test in a 6L-STR was carried out, with a double objective, the collection of an enough amount of bioleached tailings to study silver and lead dissolution and the study of bioleaching in larger reactors. As it is shown in Fig. 9A, in this test pH dropped since the beginning. Equally, redox potential rapidly increased over 600 mV, being the lag phase negligible. The improvement of aeration and the increase of pulp density in the inoculum preparation could promote this negligible lag phase, the increase of substrate in the inoculum could generate a higher microbial population at early bioleaching times. Similar pH and ORP values were obtained after bioleaching, about 0.7 and 700 mV (vs. Ag/AgCl), respectively. This fast increase of redox potential enabled the pyrite dissolution since the beginning (Fig. 10), reaching pyrite oxidation levels greater than 90% in 8 days (96% after 10 days). In addition, the scale-up in bioreactor size increased, again, the linear oxidation rate to 12.3 g FeS$_2 \cdot$L$^{-1} \cdot$d^{-1}. According to bioleaching results obtained in the different stirring systems, the rate limiting step must be directly related to mass transfer rate, probably oxygen transfer rate, due to pyrite dissolution rate varied as a function of the reactor (size, stirring, or airflow) under identical conditions of temperature, solid/liquid ratio, particle size and inoculum.
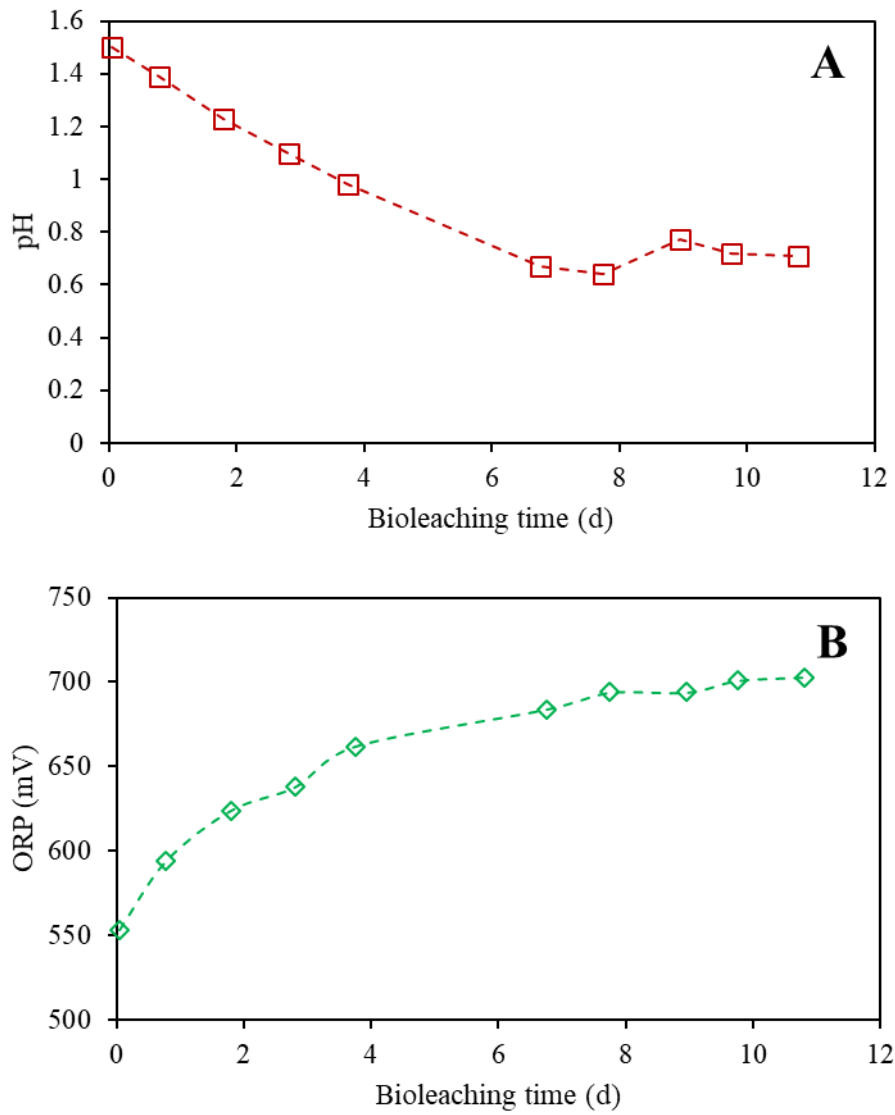
Fig. 9. pH (A) and ORP (B) as a function of time in 6L-STR bioleaching (20% p.d., 500 rpm, 30 ºC, 2 L/min of aeration rate and 20% inoculum).
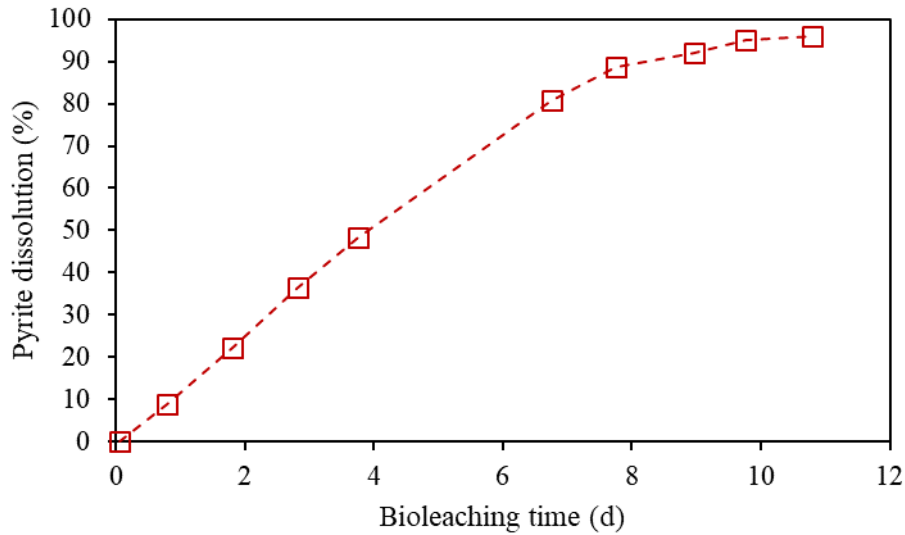
Fig. 10. Pyrite dissolution kinetics in bioleaching performed in 6L-STR (20% p.d., 500 rpm, 30 °C, 2 L/min of aeration rate and 20% inoculum).

Copper, zinc and cobalt dissolution followed identical curves to previous tests (Fig. 11A-C). Nonetheless, the linear rate of zinc and copper dissolution was increased reaching similar values obtained at low pulp density in flasks. Specifically, the linear rates in 6L-STR were 7.93 mg $Zn^{2+} \cdot L^{-1} \cdot d^{-1}$ and 7.40 mg $Cu^{2+} \cdot L^{-1} \cdot d^{-1}$, while in flasks at 20% of pulp density were 2.97 mg $Zn^{2+} \cdot L^{-1} \cdot d^{-1}$ and 2.36 mg $Cu^{2+} \cdot L^{-1} \cdot d^{-1}$. This enhancement enabled similar recoveries of copper and zinc in only 10 days. Cobalt was extracted jointly pyrite dissolution (Fig. 11C), reaching the maximum cobalt extraction (87%) due to pyrite dissolution (96%) was greater than previous assays. In this bioreactor test, a linear relationship between cobalt concentration and iron concentration was also observed (Fig. 11D), confirming that cobalt belonged to the pyrite matrix.
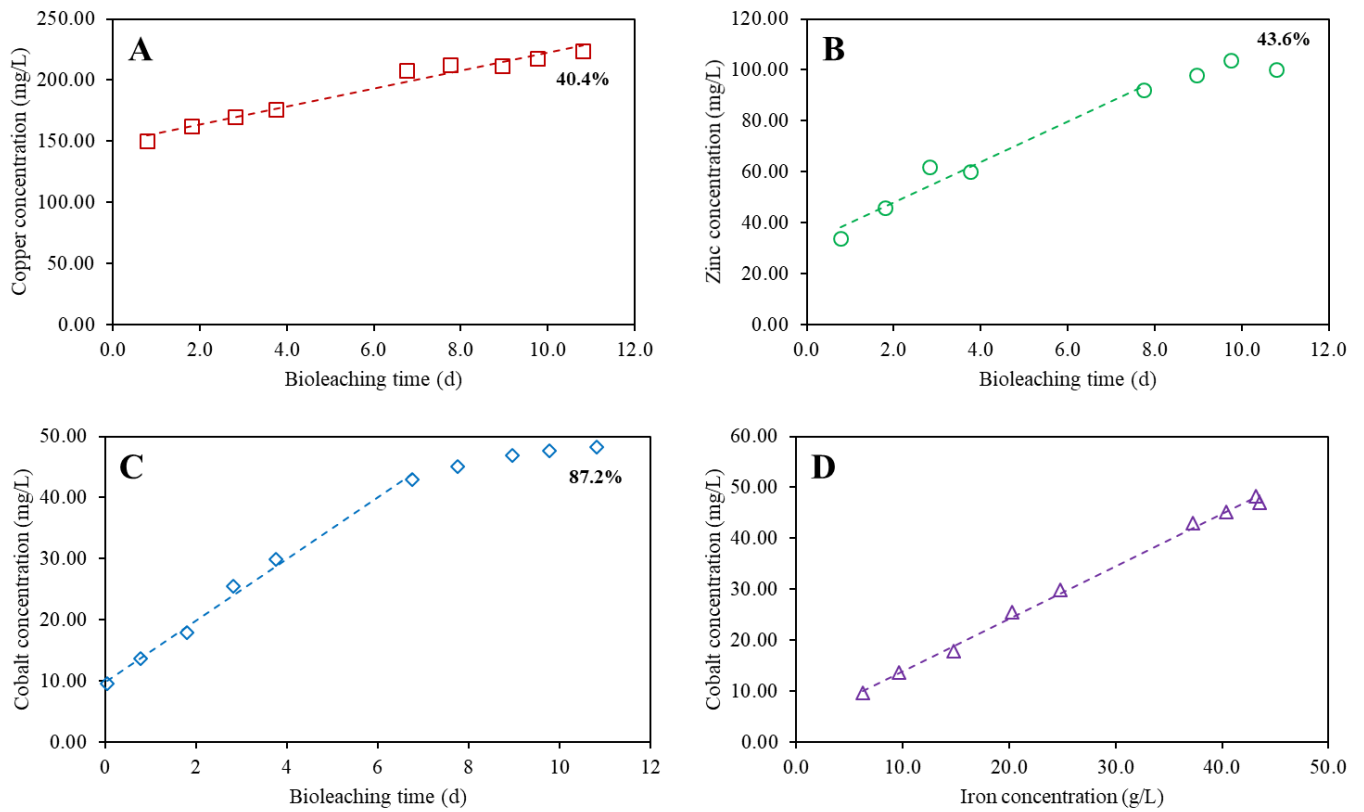
Fig. 11. Copper (A), zinc (B), cobalt (C) concentration and relationship between cobalt and iron concentration (D) in bioleaching in 6L-STR. Final extractions of copper, zinc and cobalt are shown (20% p.d., 500 rpm, 30 ºC, 2 L/min of aeration rate and 20% inoculum).

Main results of bioleaching test performed in 6L-STR are shown in Table 3. Like other tests at high pulp density, the great part of iron remained in solution due to the low pH. The bioleaching in the stirred tank reactor enabled the most dissolution of pyrite, which avoids the main environmental issues concerning AMD. After bioleaching, lead and silver, which remained in the solid residue, could be dissolved by brine leaching.

Table 3. Main results (test duration, pH, ORP, metals extraction and residue composition) obtained in bioleaching. *weight loss obtained in the bioleaching residue treated with HCl (30 ºC, 20% of inoculum, 20% of pulp density, 2L/min aeration, 500 rpm and 6L reaction volume).

Test	Bioleaching time (d)	Final pH	Final ORP (mV)	Cu extr. (%)	Zn Extr. (%)	Co Extr. (%)	Fe extr. (%)	FeS$_2$ extr. (%)
STR–6L	10.8	0.71	703.0	40.4	43.6	87.2	86.4	96.0

						Residue composition		
Test	Weight loss bioleaching (%)	Weight loss HCl (%)*	Fe (%)	Cu (%)	Zn (%)	Co (%)	Pb (%)	Ag (mg/kg)
STR–6L	39.6	8.72	5.19	0.29	0.12	55.2	0.75	37.1

3.3. Brine leaching

After bioleaching lead and silver remained in the solid residue (Table 4). Brine leaching enables the dissolution of these metals due to the formation of chloride complexes (Behnajady and Moghaddan, 2014). The dissolution of silver and lead was tested with the solid residue generated in the 6L-STR tests, the chemical composition of this solid was 0.75% Pb and 37.1 mg/kg Ag. The mineralogical composition of lead and silver compounds was not identified by XRD due to its low grade. Optimal conditions of brine leaching varied regarding raw material because lead and silver can belong to different compounds, such as lead sulphate, jarosite (Ag and Pb), sulphides (Ag and Pb), or silver chloride (Yang et al., 2019; Calla-Choque and Lapidus, 2020). Some of these compounds showed a refractory behaviour in chloride media, requiring the addition of acid or oxidising reagents to solubilise it. When brine leaching is applied in sulphidic tailings, which usually present very low-grade, softer conditions and low reagents consumption must be sought. Keeping in mind this, sodium chloride concentration, sulphuric acid concentration and temperature were studied in brine leaching. Specifically, the studied range was 30-60 ºC, 0-10 g/L H$_2$SO$_4$, and 50-150 g/L NaCl. The changes of ORP and pH before and after brine leaching are displayed in Table 4, as well as weight loss. pH did not vary in brine leaching that indicates an insignificant acid consumption. When acid was not added a pH decrease was observed due to a low part of bioleaching solution can

remain in the solid fraction. Redox potential increased with higher acid concentrations that could increase the dissolution of some silver compounds, such as silver sulphide or elemental silver. Iron extraction, like weight loss, was low in all cases, between 0.0 and 13.2%, due to the slight jarosite content.

Table 4. Brine leaching conditions and changes on pH and ORP in brine leaching (5% pulp density, 1h and 6L-STR residue).

Temperature (ºC)	H_2SO_4 (g/L)	NaCl (g/L)	pH_i	pH_f	ORP_i (mV)	ORP_f (mV)	w.l. (%)
30	0	100	7.20	3.53	280	379	2.7
30	5	100	0.75	0.75	559	503	2.8
30	10	100	0.52	0.52	563	506	2.8
30	5	50	0.95	0.95	558	499	1.6
30	5	150	0.56	0.57	560	507	3.5
60	0	100	6.50	3.18	280	366	2.6
60	5	100	0.80	0.80	561	520	1.0
60	10	100	0.56	0.55	570	530	2.4
60	5	50	0.93	1.02	574	522	3.3
60	5	150	0.68	0.73	572	525	3.1

The effect of different variables on lead extraction is shown in Fig. 12. An increase of temperature only improved lead dissolution at the higher acid concentration or at the lower chloride concentration. The enhancement at 10 g/L H_2SO_4 and 60 ºC can be associated with the dissolution of a jarosite structures (Fig. 12A). The temperature increase also enabled the decrease of sodium chloride concentration (Fig. 12B). The best result was achieved with 10 g/L of sulphuric acid and 60 ºC with a lead dissolution level of 55.9% (214 mg/L Pb^{2+}).
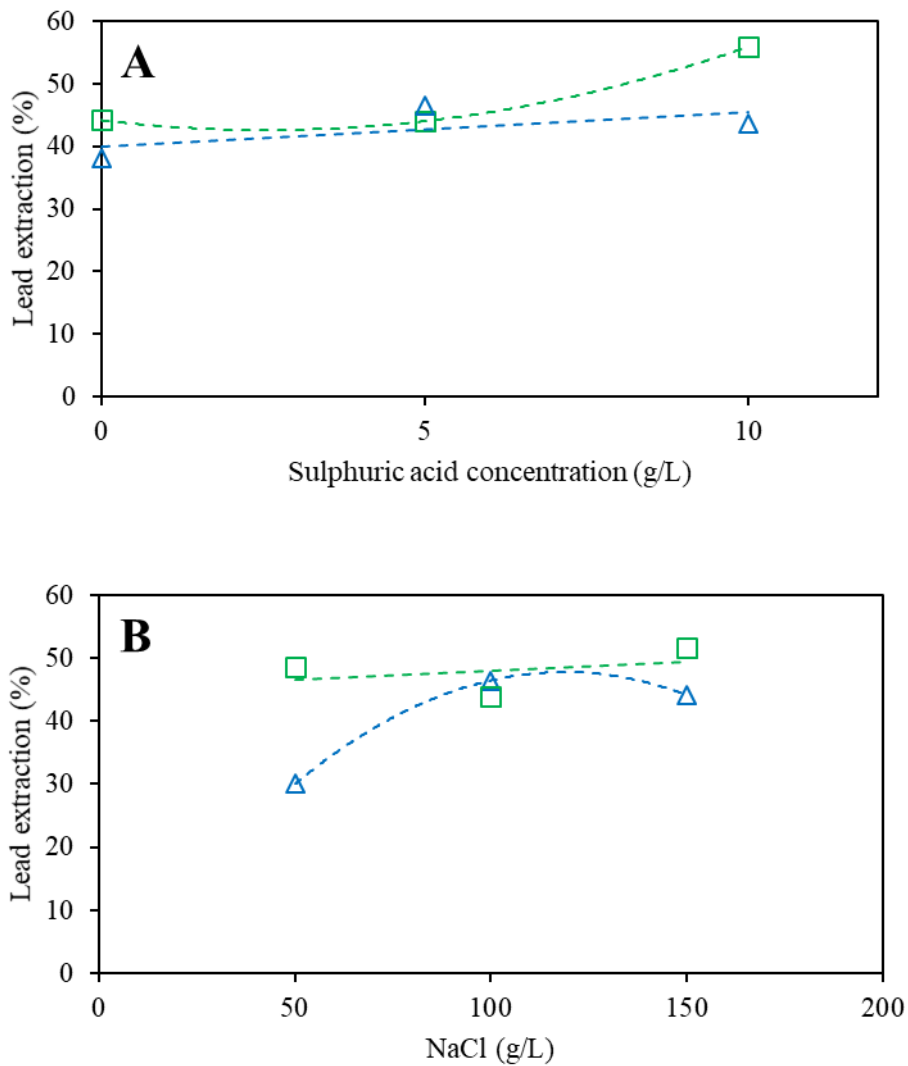
Fig. 12. Lead extraction on brine leaching as a function of sulphuric acid (100 g/L NaCl) (A) and sodium chloride (5 g/L H_2SO_4) (B) (5% p.d., STR-3 waste and 1h) (blue triangles = 30 ℃; green squares = 60 ℃).

Silver extraction as a function of brine leaching variables is shown in Fig. 13, like lead the increase of acid concentration to 10 ℃ at 60 ℃ obtained the best dissolution level (37.9%). The increase of leaching temperature had not a significant improvement on silver extraction in the other assays, only when sodium concentration was decreased below 100 g/L a decrease of silver leaching was observed at 30 ℃, from 28.3% (60 ℃) to 12.1%.
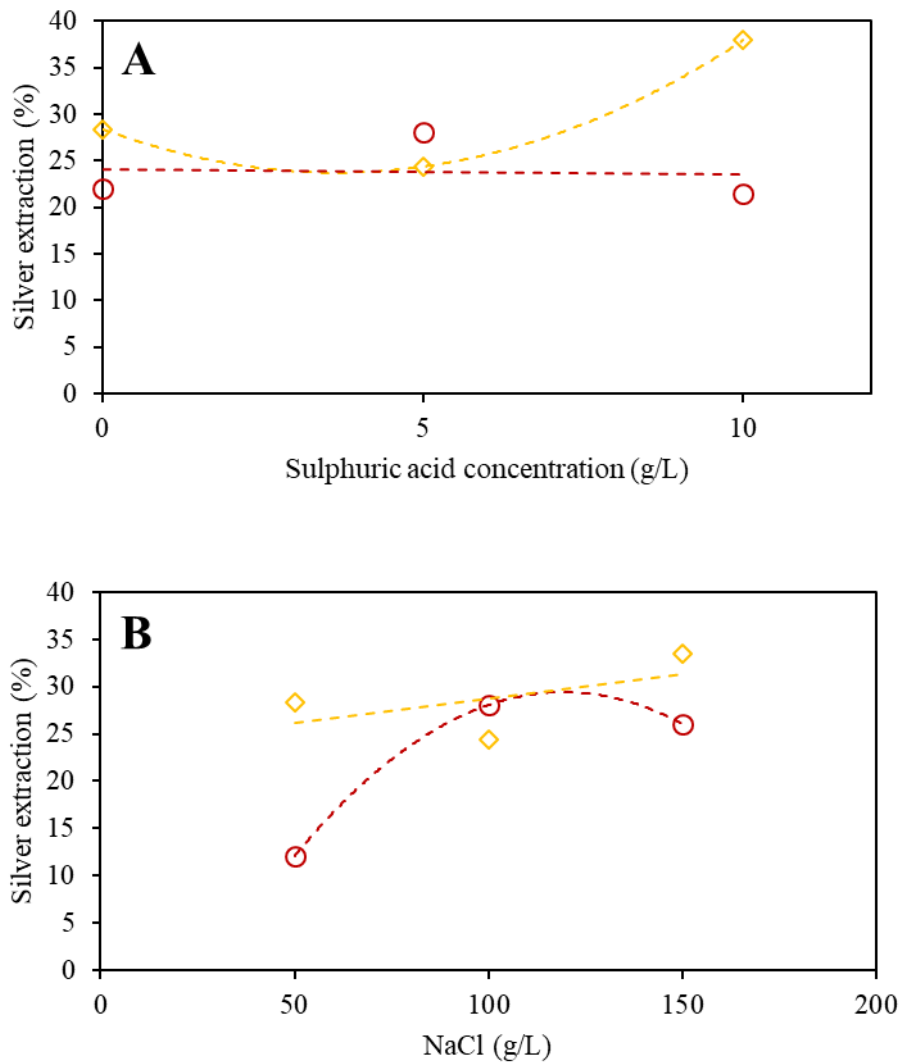
Fig. 13. Silver extraction on brine leaching as a function of sulphuric acid (100 g/L NaCl) (A) and sodium chloride (5 g/L H_2SO_4) (B) (5% p.d., STR-3 waste and 1h) (red circles = 30 ℃; yellow diamonds = 60 ℃).

According to these results, 55.9% Pb and 37.9% Ag can be extracted with moderate leaching conditions (100 g/L NaCl, 10 g/L H_2SO_4, 60 ℃ and 1h). The behaviour of both metals was very similar, coinciding with the best conditions. These dissolution levels were relatively low regarding results observed in literature where extractions above 90% were achieved (Norris et al., 2017; Romero et al., 2019), this can be attributed to the low grade of tailings that hinders higher extractions and the chosen experimental conditions. After brine leaching, the solution composition was 214 mg/L Pb^{2+} and 0.7 mg/L Ag^+, a very low concentration that could hinder the purification of these metals. Nonetheless,

the recirculation of this liquor would enable the increase of lead and silver concentration before downstream processes (metals purification).

3.4 Preliminary economic assessment

A preliminary economic analysis of the bioleaching step was performed according to experimental data and literature, the method used for this assessment is described in the Supplementary material. First, the metals dissolution in bioleaching and brine leaching and the savings in management costs associated to tailings storage were considered as the overall sales for a feed rate of 100 t/d. The operating expenditures (OPEX) of the bioleaching step were only considered. Additional costs of subsequent steps to recover gold, silver, and lead and to purify different metals were not calculated in this first approach.

On the one hand, sales were determined considering metals prices (27th May 2021 LME – lme.com) and the maximum extraction rate obtained in the experiments. Gold extraction rate was estimated according to literature, where recoveries between 57.1 and 96.0% were achieved by cyanidation after bioleaching of sulphidic tailings with similar gold contents (0.58-0.67 mg Au/kg), in this case, the minimum gold recovery from the literature (50% extraction) was selected (Kondrateva et al., 2012; Muravyov and Fomchenko, 2018). The reprocessing of these tailings can also suppose a saving in management costs that must be considered, Bastecin et al. (2016) reported the costs of different tailings storage methods. The surface paste disposal with cement, with a cost of 2.5 €/t tailing, was chosen for this assessment. The estimated sales are shown in Table 6, with total revenue of 49.8 €/t tailing, where gold, copper and cobalt were the most important incomes.

On the other hand, OPEX were estimated according to BIOX reports (Van Aswegen et al., 2007) and the reagents consumption for pH control (Supplementary Material) in the studied tailings for a feed rate of 100 t/d. Van Aswegen et al. (2007) reported that pH control and power supposed the main operating costs, 29% and 27%, respectively. Power is mainly used for the air spread in bioreactors. While reagents for pH control include the addition of sulphuric acid or lime/limestone on the bioleaching step and the subsequent precipitation of bioleaching liquors. Nutrients include phosphorous, nitrogen and potassium salts and water treatment reagents comprise all reagents associated with the treatment of process water, such as bactericides, fungicides or descaling agents (Van Aswegen et al., 2007). In this study, only limestone was used with a consumption of 520

kg CaCO$_3$/ t tailing (Supplementary Material), which was used in the precipitation step, that has a cost of 19.6 €/t tailing (37.6 €/t CaCO$_3$) (Trio-Maseda and Guillermo-Ortuño, 2017). The other OPEX items (Table 5) were determined from reagents for pH control, reaching a OPEX of 54.0 €/t tailings. These operating costs were over total sales, therefore the bioleaching of these tailings was economically not feasible considering only the metals recovery and the saving in tailings management. The high reagent consumption, directly related to ferric ion precipitation and acid neutralisation, generated huge amounts of an economically worthless compound, composed of amorphous ferric hydroxide and gypsum.

Table 5. Sales and operation costs for a feed rate of 100 t tailings/d, OPEX were calculated according to Van Aswegen et al. (2007) and prices for pH control (Trio-Maseda and Guillermo-Ortuño, 2017) (saving in tailings management is calculated according to the cost of surface paste disposal for tailings storage)

Sales			OPEX		
Item	**Value (€/t)**	**Proportion (%)**	**Item**	**Value (€/t)**	**Proportion (%)**
Copper	8.8	17.7	pH control	19.6	36.2
Zinc	1.5	3.0	Nutrients	5.9	10.9
Cobalt	8.5	17.1	Water treatment	1.5	2.8
Lead	6.0	12.0	Total reagents	26.9	49.9
Silver	7.1	14.3	Power	18.2	33.7
Gold	15.4	30.9	Labours	3.3	6.1
Saving in tailings management*	2.5	5.0	Maintenance	5.5	10.2
Total	49.8	100.0	Total	54.0	100.0

An alternative use of ferric ion and sulphuric acid can suppose an increase in sales and a saving in OPEX due to the decrease of reagents consumption (limestone) and the revenues from ferric sulphate sales. These tailings are generated after a ferric leaching of secondary copper sulphides, this hydrometallurgical process works in a closed circuit where the ferric ion is regenerated by oxygen supply. However, a purge of leaching solution must be applied to remove impurities, such as arsenic, that are progressively accumulated. This

purged liquor is treated with lime to neutralise the stream, and to precipitate different metals, therefore sulphuric acid and ferric ion must be added to replace it. Annually, 12,899.2 t and 1,802.4 t of ferric sulphate and sulphuric acid, respectively, are gotten into the hydrometallurgical process. These reagents could be supplied from bioleaching solution, this liquor contains approximately 40 g/L Fe^{3+} and pH 0.7. The use of bioleaching solutions can decrease the limestone consumption in the precipitation step (ferric ion is not removed), assuming a huge saving both in bioleaching of tailings and in hydrometallurgical plant. The supply costs of ferric sulphate and sulphuric acid and the tailings volume that satisfies this ferric sulphate and acid demand can be observed in Table 6. This reagent demand can be satisfied with 18,024.0 t tailings/ year (50.1 t/d with 360 d of operation). This feed rate does not require the late addition of limestone for pH control, which is the main reagent expense. The sum of these reagents ($Fe_2(SO_4)_3$ and H_2SO_4) supposes 13.48 M€/ year, where ferric sulphate is the main expense. This saving can be considered for the economic analysis, increasing the economic feasibility of tailings reprocessing.

Table 6. Costs, consumption of ferric sulphate and sulphuric acid and the saving of these reagents through the use of bioleaching liquors in the hydrometallurgical plant (ferric sulphate cost was calculated from the price of *Ferriclar*, that is a commercial ferric sulphate solution- 46.5% $Fe_2(SO_4)_3$).

Ferric sulphate (€/t)	Sulphuric acid (€/t)	Ferric sulphate (t/year)	Sulphuric acid (t/year)
1,032.0	94.0	12,755.4	1,802.4
Ferric sulphate (M€/year)	Sulphuric acid (M€/y)	Tailings (t/year)	Tailings (t/d)
13.31	0.17	18,024.0	50.1

The net present value (NPV) and the internal rate of return (IRR) were calculated for different feed rates, from 50 t/d to 300 t/d, according to Supplementary Material. Feed rates over 50 t/d increase the reagent consumption (limestone), due to a part of bioleaching liquor must be neutralised, and do not imply an increase of revenues from ferric sulphate and sulphuric acid. The following data or assumptions were used to calculate the cash flow for different feed rates:

- BIOX plant flowsheet was considered for tailings reprocessing with an operation time of 360 days. According to the above proposal, several modifications of the BIOX flowsheet (Aswegen et al., 2007) were proposed (Fig. 14). Dashed lines in Fig. 14 cluster the process steps that were included in the economic assessment. First, a liquor neutralisation in two steps to recover copper, zinc and cobalt, after iron removal, as hydroxides which are introduced in the hydrometallurgical plant to its refining. Liquors that are used as leaching solution in the hydrometallurgical circuit is not treated by this sequential precipitation. Also, an additional brine leaching step after bioleaching to dissolve lead and silver. The bioleaching circuit consists of 6 equidimensional reactors configured as 3 primary reactors operating in parallel followed by 3 secondary reactors operating in series (Aswegen et al., 2007). Total reaction volume and bioreactor sizes were calculated according to the following assumptions: 6 equidimensional reactors, 5 days of retention time and pulp density of 20%.

- Sales were the sum of metal revenues, saving in management costs and saving in ferric ion and sulphuric acid in the hydrometallurgical circuit. Metal sales and management cost proportionally increase with feed rate while saving in leaching reagent is constant (13.48 M€/year).

- OPEX was determined according to Table 6 with several adjustments. Due to the bioleaching solution generated from 50t tailings/d is used as leaching solution the expense of pH control is void, for greater feed rates this OPEX item rises proportionally according to Table 6, e.g., 100 t/d = 50% costs, 200 t/d = 75% costs.

- Capital expenditure (CAPEX) was calculated for each plant according to Van Aswegen et al. (2007), where the distribution of capital cost is shown as a function of mechanical equipment supply (MES). BIOX reactors represent 51% of MES, while direct costs are double MES, and the whole CAPEX is broken down as 76% of direct costs and 24% of indirect costs.
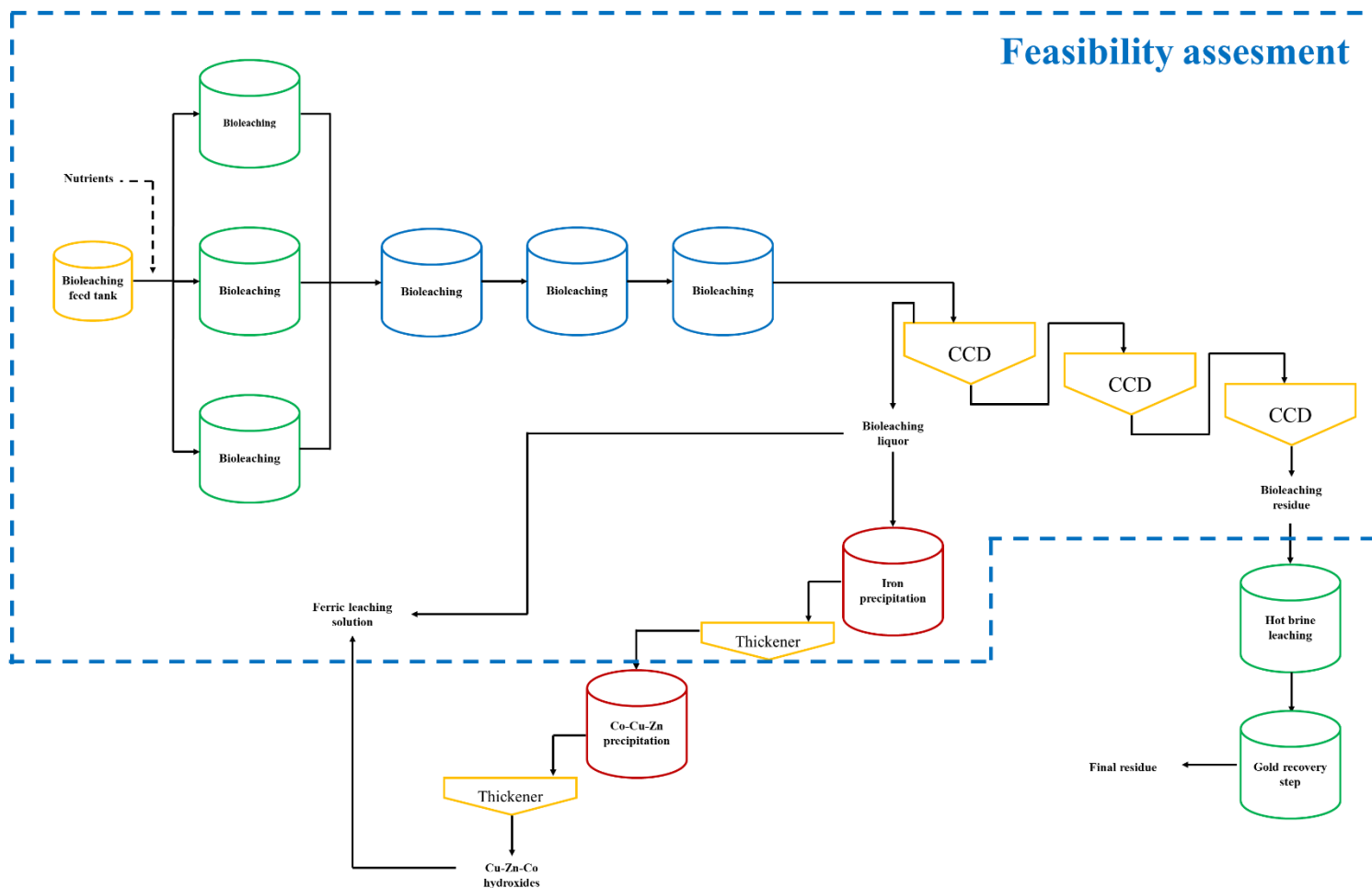
Fig. 14. Flowsheet for the bioleaching of tailings, adapted from BIOX process (Aswegen et al., 2007) including a hot brine leaching and a selective precipitation step for the recovery of Cu, Zn, Co, Pb and Ag (Dashed lines cluster the process steps that are included in the economic assessment).

The cash flows for each feed rate were shown in Table 7. In all cases a profitable project was obtained, dropping the profitability at greater feed rates because of a growing bioleaching liquor must be precipitated, and saving in leaching reagents in the hydrometallurgical plant is constant regarding feed rate. NPV and IRR for different feed rates (50-300 t tailings/d) are shown in Fig. 15, both decreased as a function of feed rate according to above mentioned reaching a maximum IRR of 30.2%. From 50 to 300 t/d a positive IRR was obtained, being the bioleaching of these tailings feasible in this range. Considering an interest rate of 10%, the maximum feed rate was 260 t/d, close to 100,000 tonnes per year. This feed is lower than the total tailings generation from the hydrometallurgical plant, but this proposal would enable the reprocessing of a part of tailings decreasing the wastes volume and the AMD potential, and at the same time increasing the metals recovery from raw materials.

Table 7. Cash flow (CAPEX, OPEX, working capital, amortization, taxes, net benefits and cash flow for each year) for different treatment feed rates with a project duration of 15 years.

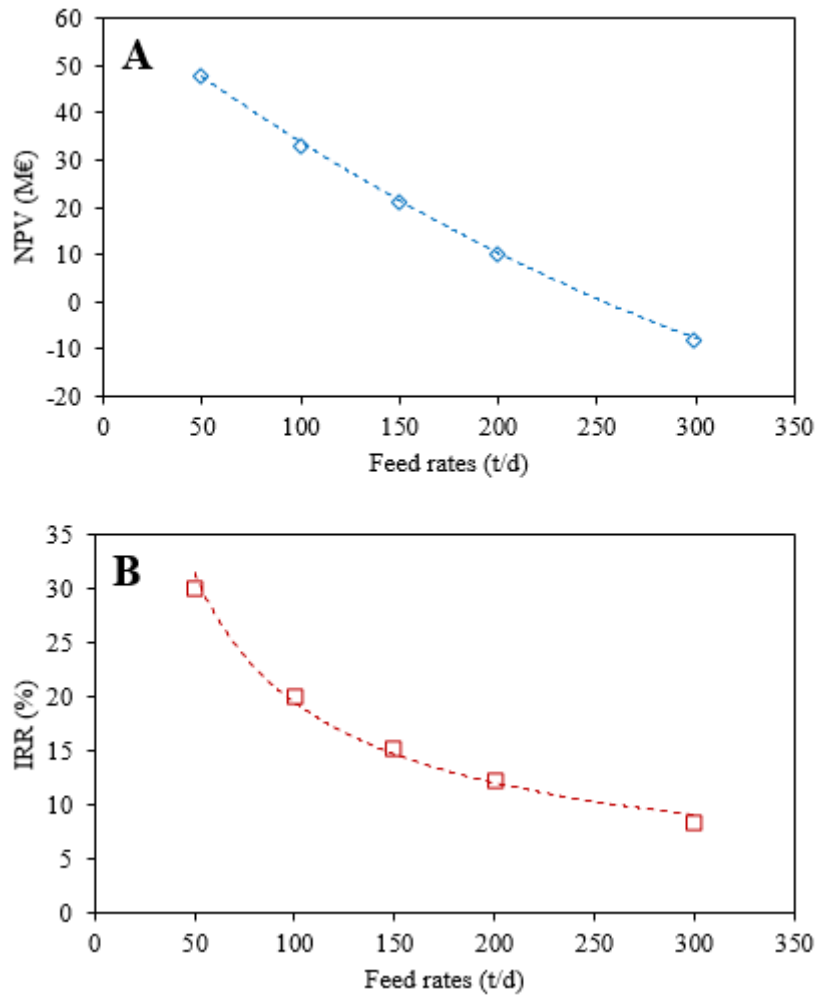|	Feed rates (t/d)				
Item	50	100	150	200	300
Reaction volume (m^3)	1250	2500	3750	5000	7500
Bioreactor size (m^3)	208.3	416.7	625.0	833.3	1250
Bioreactor price (M€)	1.1	1.6	2.1	2.5	3.1
CAPEX (M€)	-33.1	-50.1	-63.9	-76.0	-96.0
Working capital (M€)	-2.9	-3.1	-3.2	-3.4	-3.8
OPEX (M€/year)	-0.7	-1.6	-2.5	-3.4	-5.3
Revenues (M€/year)	14.4	15.3	16.2	17.0	18.8
Amortization 1-10 years (M€/year)	-3.31	-5.01	-6.39	-7.60	-9.66
Taxes 1-10 years (M€/year)	-2.6	-2.17	-1.83	-1.50	-0.96
Taxes 11-15 years (M€/year)	-3.43	-3.43	-3.43	-3.40	-3.38
Net benefits 1-10 years (M€/year)	7.79	6.52	5.48	4.50	2.88
Net benefits 11-15 years (M€/year)	10.28	10.28	10.28	10.20	10.13
Cash flow 0 year (M€/year)	-36.0	-53.2	-67.1	-79.4	-100.4
Cash flow 1-10 years (M€/year)	11.10	11.53	11.87	12.10	12.54
Cash flow 11-15 years (M€/year)	10.28	10.28	10.28	10.20	10.13

Fig. 15. NPV (A) and IRR (B) for the bioleaching of sulphidic tailings at different feed rates with a project duration of 15 years, the revenues include the sale of metals, the saving in ferric ion and sulphuric acid in the hydrometallurgical plant and in the storage of tailings.

5. Conclusions

The reprocessing of hydrometallurgical tailings, seeking the extraction of remaining metals and the decrease of environmental issues, has been studied. This reprocessing approach consists of several leaching steps, starting with the tailings bioleaching, that enables the dissolution of key metals and the controlled bio-oxidation of pyrite, followed by a brine leaching and a gold recovery step to dissolve the insoluble metals. In these leaching steps, low concentrations of metals were reached which supposes the modification of traditional purification processes. After 10 days of bioleaching in an STR at 30 °C, more than 80% of cobalt and 40% of zinc and copper were extracted. Also, after this time the 96% of pyrite was oxidised. After bioleaching, 56 and 38% of lead and silver, respectively, were leached in brine leaching with moderate conditions (100 g/L NaCl, 10

g/L H_2SO_4, 60 ºC, and 1h). Concerning the dissolution of metals, the bioleaching of hydrometallurgical tailings shown considerable differences regarding other tailings, such as flotation wastes. Copper, zinc and pyrite dissolution rates varied regarding stirring systems, improving when aeration and agitation were enhanced, this was in accordance with dissolution reactions controlled by mass transfer and with the origin of tailings. The bioleaching behaviour of different metals can be summarised as follows:

- The progressive scale-up in the stirring system, from flasks to 6L-STR, supposed a huge increase of pyrite dissolution rate, from 1.8 (flasks) to 12.3 (6L-STR) g $FeS_2 \cdot L^{-1} \cdot d^{-1}$.

- Cobalt extraction directly depends on the removal of pyrite matrix, in all stirring systems a linear relationship between cobalt dissolution and pyrite oxidation was observed.

- Copper and zinc dissolution shows a similar behaviour; in both cases, the dissolution was linear regarding bioleaching time. In the studied conditions, this linear rate only depended on stirring conditions. In the case of zinc, the maximum dissolution level was approximately 50% due to at this extraction level the dissolution rate slowed down until be negligible. Also, these low extractions can be related with the low metal grade of tailings, which hinder greater dissolution levels.

- The dissolution of lead and silver is favoured when temperature and acidity were increased in brine leaching. Harsher conditions in brine leaching can promote the dissolution of refractory compounds, such as jarosite or un-oxidised sulphides, therefore a part of silver and lead must belong to these compounds.

The bioleaching step generates a large amount of ferric ion and sulphuric acid which can be used in the hydrometallurgical circuit, this supposes a great saving in reagents costs and also decreases the alkali consumption in the bioleaching step. The use of biogenic ferric ion makes the implementation of this reprocessing approach economically feasible, reaching an IRR of 10% with a feed rate of 260 t/d.

6. Acknowledgements

7. References

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