# A novel hydrometallurgical treatment for the recovery of copper, zinc, lead and silver from bulk concentrates

Authors: Juan Lorenzo-Tallafigo*, Aurora Romero-García, Nieves Iglesias-González, Alfonso Mazuelos, Rafael Romero, Francisco Carranza

Chemical Engineering Department, Universidad de Sevilla
Calle Profesor García González s/n 41012 Sevilla (Spain)
Telephone; +34 954 557 182

*Corresponding Author: jltallafigo@us.es

## Keywords

Bulk sulphide concentrate

Ferric leaching

Catalysed leaching

Hot brine leaching

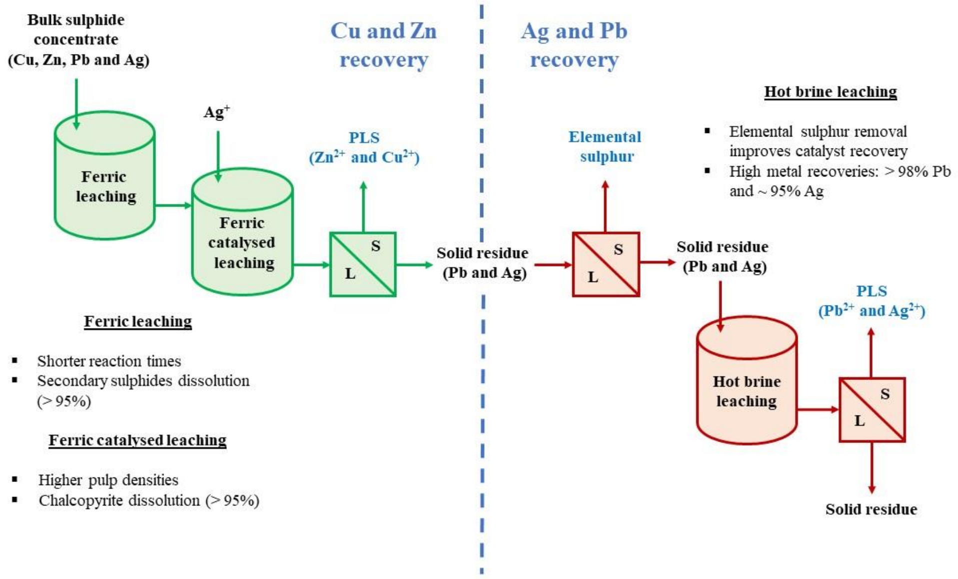
## Highlights

Copper, zinc, lead and silver can be benefited by a novel hydrometallurgical process

Direct catalytic leaching is not able to dissolve copper and zinc in a single step

Ferric leaching before catalytic leaching recovers more than 95% of copper and zinc

More than 95% of lead and 100% of catalyst are recovered by brine leaching



# Abstract

Nowadays sulphide ores exploitation is undergoing some troubles, which are hindering the treatment through traditional routes. Bulk flotation followed by a novel hydrometallurgical process can dodge these difficulties. In this work, an integral hydrometallurgical process consists of two ferric leaching steps, followed by a hot brine leaching stage, is proposed to recover target metals from a bulk sulphide concentrate (2.9% Cu, 7.4% Zn, 2.5% Pb, 67 ppm Ag and 37.2% Fe). In the first ferric leaching step, sphalerite, galena and copper secondary sulphides are dissolved and, in the second leaching step, a silver salt is added in order to catalyse chalcopyrite oxidation. If silver salt is added at the beginning of the process, sphalerite passivation is observed, and therefore zinc recovery is not possible. However, when catalytic leaching is performed after a previous ferric leaching, copper and zinc recoveries higher than 95% are achieved. The leached concentrate (0.3% Cu, 0.8% Zn, 3.3% Pb, 1438 ppm Ag, 38.0% Fe and 6.6% $S^0$), is treated by a hot brine leaching. When hot brine leaching is performed at high pulp density, elemental sulphur removal is necessary to recover all silver added as a catalyst. Extractions higher than 95% for Zn, Cu and Pb are achieved as well as the total recovery of catalyst. The proposed process is silver surplus; therefore, this agent can be recirculated.

# 1. Introduction

Currently, several changes are concerning to sulphide ores exploitation. Changes such as the exhaustion of current ore deposits, the discovery of ore deposits that are more complex to treat, the decrease in ore grade or more difficulties in environmental permits, which are driving to a technological innovation necessity (Brierley, 2008; Norgate and Jahanshahi, 2010; Fomchenko and Muravyov, 2019). In this situation, (bio)-hydrometallurgical technologies should play a key role to face these challenges and allow metals production from polymetallic and low-grade ores, as well as mining waste. In this field, several authors have studied different (bio)-hydrometallurgical processes to recover copper and zinc from polymetallic sulphide ores, paying special attention to ferric leaching and bioleaching (Lorenzo-Tallafigo et al., 2018; Fomchenko and Muravyov, 2019; Fomchenko et al., 2019; Fomchenko and Muravyov, 2018; Carranza et al., 1997; Tipre and Dave, 2004). Besides, other processes have been also proposed to recover target metals from polymetallic ores, such as pressure leaching (with oxygen or sulphur dioxide), roasting, chlorination, nitrate-sulphuric acid leaching, glycine leaching, sodium meta-bisulphate leaching, or hydrogen peroxide leaching (Xu et al., 2011, Akcil and Ciftci, 2003; Tarasov and Timoshenko, 2006; Cui et al., 2020; Sokic et al., 2017; Hara et al., 2020; Sokic et al., 2019; Shin et al., 2019).

Pyro- and hydrometallurgical processes usually require a froth flotation step to produce sulphide concentrates, which contain target metals. There are two flotation ways, differential and bulk flotation. On the one hand, differential flotation obtains concentrates of a single metal that later are usually processed by pyrometallurgical techniques (traditional route). On the other hand, bulk flotation produces a unique concentrate which contains all non-ferrous metals, being interesting new hydrometallurgical treatments to benefit it. Bulk flotation has several advantages such as higher target metals recovery, lower water and reagents consumption by far lower energetic supplies and minor particle size requirements. Moreover, hydrometallurgy in contrast to pyrometallurgy can benefit concentrates which contain impurities, such as arsenic or antimony (Carranza, 1985; Carranza et al., 1997; Tipre et al., 1999). Bulk flotation followed by a hydrometallurgical technology could be an attractive alternative compared to traditional routes, due to higher recovery yields and to a greater flexibility regarding raw material composition could be achieved (Frías et al., 2020).

Bulk sulphide concentrates are usually composed of pyrite ($FeS_2$), sphalerite (ZnS), galena (PbS) and chalcopyrite ($CuFeS_2$). Chalcopyrite shows a refractory behaviour in both bioleaching and leaching solutions, unlike sphalerite and galena (Lorenzo-Tallafigo et al., 2018; Fomchenko and Muravyov, 2019; Fomchenko et al., 2019; Fomchenko and Muravyov, 2018). Chalcopyrite is the most refractory of target sulphides in ferric sulphate media, this is due to the formation of a passivating layer that hinders the diffusion of ferric ion. For a time, the formation of a non-porous layer of elemental sulphur on chalcopyrite surface was considered responsible of this passivation. Nevertheless, recent electrochemical studies have observed that chalcopyrite passivation is because of the formation of a non-stoichiometric deficient in metal sulphide film as a consequence of the fact that iron is more reactive than copper, which remains on chalcopyrite surface without reacting. This passivation process can be described according to r1 (Miller and Portillo, 1979; Price and Warren, 1986; Hiroyoshi et al., 2002; Ghahreminezhad et al., 2015).

$$\mathrm{CuFeS_2} \rightarrow \mathrm{Cu_{1-x}Fe_{1-y}S_2} + \mathrm{xCu^{2+}} + \mathrm{yFe^{2+}} + 2(\mathrm{x}+\mathrm{y})\mathrm{e^-}; \mathrm{y} > \mathrm{x} \qquad \text{(r1)}$$

Silver salts greatly improve copper dissolution from chalcopyrite (Carranza et al., 1997; Cordoba et al., 2008; Hiroyoshi et al., 2002; Ghahreminezhad et al., 2015). The first proposed model explains this catalytic activity by the formation of $Ag_2S$ on chalcopyrite surface that avoids the refractoriness. Silver sulphide would be dissolved by ferric ions producing silver ions ($Ag^+$), starting the cycle again (r2-r3) (Miller and Portillo, 1979; Price and Warren, 1986; Hiroyoshi et al., 2002).

$$\mathrm{CuFeS_2} + 4\mathrm{Ag^+} \rightarrow \mathrm{Cu^{2+}} + \mathrm{Fe^{2+}} + 2\mathrm{Ag_2S} \qquad \text{(r2)}$$

$$2\mathrm{Ag_2S} + 4\mathrm{Fe^{3+}} \rightarrow 2\mathrm{S^0} + 4\mathrm{Ag^+} + 4\mathrm{Fe^{2+}} \qquad \text{(r3)}$$

According to Ghahreminezhad et al. (2015), silver ion is adsorbed onto chalcopyrite surface forming silver sulphide, which in turn produces a sulphur vacancy in mineral surface. The diffusion of silver and sulphur vacancies into passivated film improves the diffusion of copper through it. The generated changes in the passivating layer enhances the chalcopyrite dissolution kinetics.

The solid residue contains the silver, added as catalyst and contained in the concentrate, and anglesite ($PbSO_4$). As silver is an expensive metal, its recovery in a subsequent step is a pivotal factor in the viability of the proposed process. Brine leaching is the most widely recognised and extensively applied recovery method for silver and lead. In this type of leaching, NaCl, $MgCl_2$ or $CaCl_2$ are used as source of chloride; $FeCl_3$, $H_2O_2$, NaClO or $Ca(ClO)_2$ as oxidising agents; and HCl or $H_2SO_4$ to acidify leaching solutions (Guo et al., 2010; Behnajady and Moghaddam, 2011).

In previous studies, different ways of treating of sulphide concentrates have been postulated, paying special attention to ferric leaching and bioleaching (Carranza et al., 1993; Carranza et al., 1997; Fomchenko and Muravyov, 2018, Fomchenko and Muravyov, 2019; Fomchenko et al., 2019; Romero et al., 2019). Most of the works (Carranza et al., 1993; Fomchenko and Muravyov, 2018, Fomchenko and Muravyov, 2019; Fomchenko et al., 2019) propose a hydrometallurgical step, where zinc is dissolved, and an additional pyrometallurgical step to benefit copper. Otherwise, Carranza et al. (1997) proposed two ferric leaching steps, a ferric leaching followed by a silver-catalysed ferric leaching, where zinc and copper are extracted from zinc-copper concentrates. These ways could present several troubles, such as an inadequate extractive strategy due to the loss of other target metals (e.g., lead or silver) and to a part of chalcopyrite because of its dissolution under (bio)-leaching conditions (Dutrizac, 1981). On the other hand, the sale of copper concentrates obtained could have drawbacks such as very low grade, and dangerous transport to other facilities, thereby increasing the carbon footprint.

In view of above mentioned, an integral hydrometallurgical treatment is proposed in this work: two ferric leaching steps (ferric leaching followed by a silver catalysed leaching), where zinc and copper are extracted, and a hot brine leaching to recover lead and silver. In a continuous process, ferric ion can be regenerated in situ by oxygen supply or in a bioreactor where extremophilic bacteria would catalyse this reaction (Mazuelos et al., 2012; Carranza et al., 1997). Reactions (r2-r8) take place in ferric leaching steps (Carranza et al., 2004; Hiroyoshi et al., 2002; Da Silva, 2004). According to r2-r7, pyrite produces the greatest generation of ferrous ion in these solutions. The dissolution of silver and lead in chloride medium is due to the progressive formation of soluble chloro-complexes, according to r9-r10 (Behnajady and Moghaddam, 2014).

$$\mathrm{FeS_2} + 14\mathrm{Fe^{3+}} + 8\mathrm{H_2O} \rightarrow 15\mathrm{Fe^{2+}} + 16\mathrm{H^+} + 2\mathrm{SO_4^{2-}} \qquad \text{(r4)}$$

$$\mathrm{ZnS} + 2\mathrm{Fe^{3+}} \rightarrow \mathrm{Zn^{2+}} + 2\mathrm{Fe^{2+}} + \mathrm{S^0} \qquad \text{(r5)}$$

$$\mathrm{Cu_2S} + 4\mathrm{Fe^{3+}} \rightarrow 2\mathrm{Cu^{2+}} + 4\mathrm{Fe^{2+}} + \mathrm{S^0} \qquad \text{(r6)}$$

$$PbS + 2Fe^{3+} \rightarrow Pb^{2+} + 2Fe^{2+} + S^0 \qquad (r7)$$

$$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4 \qquad (r8)$$

$$Ag^{+} + 4Cl^{-} \rightarrow AgCl_4^{3-} \qquad (r9)$$

$$Pb^{2+} + 4Cl^{-} \rightarrow PbCl_4^{2-} \qquad (r10)$$

This proposed route can be located within the mining facilities, changing the production model: from trade in concentrate to the production and sale of metals ("from mine to metal"). Fig. 1 summarises the three different options, including our proposal, to recover non-ferrous metals from polymetallic sulphides.

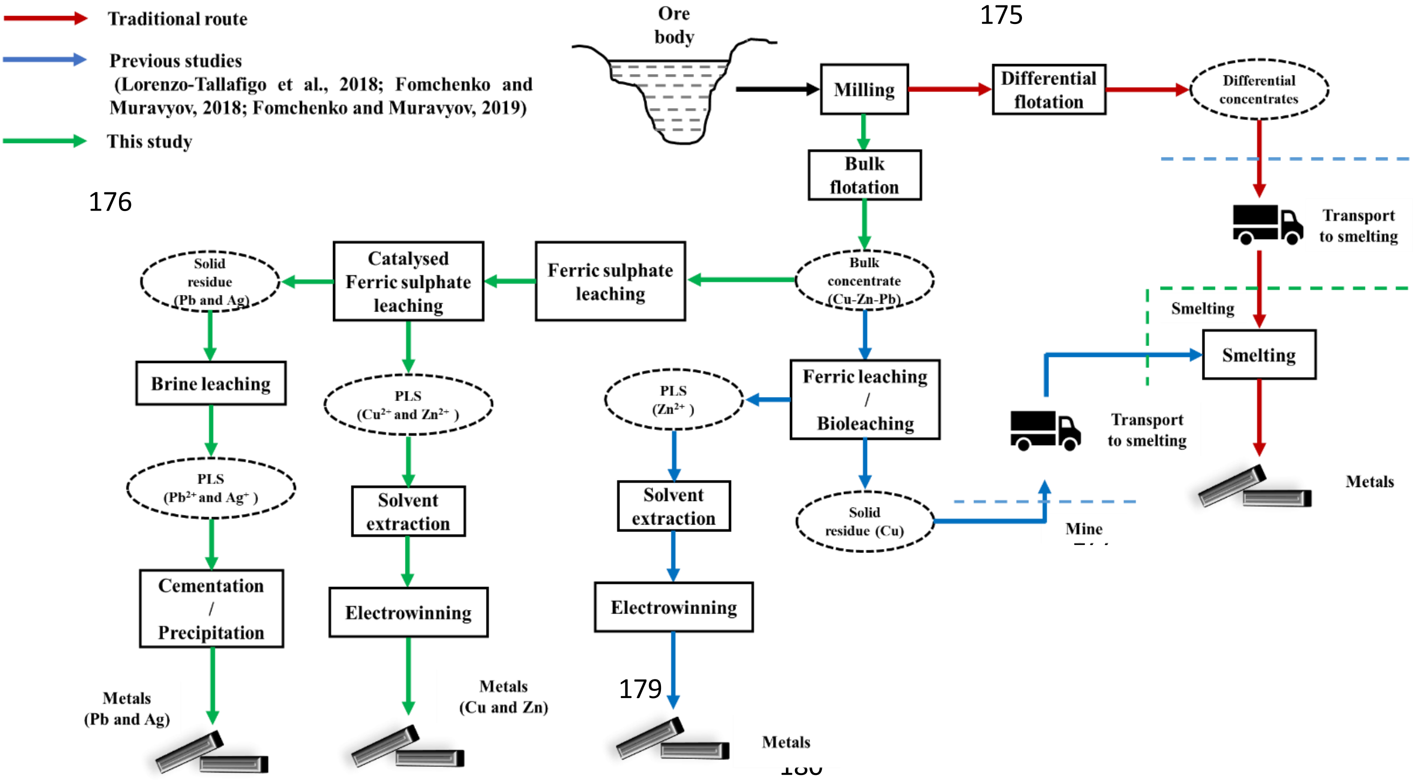


Fig. 1. Summary of different options to recover target metals from complex sulphide ores (red arrows = traditional route; blue arrows = previous studies; green arrows = proposal of this study).

The aim of this work is to demonstrate that the integral hydrometallurgical treatment of a bulk concentrate, by ferric leaching plus brine leaching, can result in high recoveries of Pb, Ag, Zn and Cu. This approach would avoid high costs and environmental risks associated to traditional routes for this natural resource.

## 2. Material and methods

### 2.1 Bulk concentrate

Table 1 shows the chemical and mineralogical composition of the bulk sulphide concentrate used in this work. This concentrate was obtained by bulk flotation of polymetallic sulphide ores (Las Cruces Mine, Spain). Non-ferrous metal contentis low regarding traditional differential concentrates (Cu + Zn + Pb = 12.8%). Low-grade concentrates are usual in bulk flotation to ensure metal recoveries higher than 90% from polymetallic sulphide ores (Frías et al., 2020). Soluble copper in cyanide solution can be associated with secondary copper sulphides, such as covellite or chalcocite (Fisher, 1994). In this case, 37% of copper was dissolved in cyanide solution (10% NaCN, 30 min, 0.5% p.d. and pH 11 at room temperature). From XRD analysis (Fig. 2) and microphotographs (Fig. 3), different sulphide phases were identified. The most abundant mineral phase was pyrite and the main non-ferrous sulphides found were sphalerite, galena, chalcopyrite and chalcocite. Granulometric analysis determined a D80 of 32.1 µm, D50 of 11.7 µm and D20 of 3.7 µm, being DX the maximum diameter for X% of particles.

Table 1: Chemical and mineralogical composition of bulk concentrate (Cu $CN^-$ corresponds to the copper percentage extracted in cyanide media; Secondary copper is estimated as chalcocite; Identified phases are marked with X; * mg/kg).

| Element | Cu | Cu $CN^-$ | Zn | Pb | Fe | S | Ag | Ca | As | Sb | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Content (%) | 2.9 | 1.07<br>(37%) | 7.4 | 2.5 | 37.2 | 44.2 | 67* | 0.6 | 0.67 | 0.14 | 95.61 |
| Ore | | $CuFeS_2$ | | ZnS | PbS | $FeS_2$ | Secondary copper | | $CaSO_4·2H_2O$ | | |
| XRD | | X | | X | X | X | | | | | |
| Microphotographs | | X | | X | X | X | X | | | | |
| Estimated (%) | | 5.6 | | 11.0 | 2.9 | 76.2 | 1.3 | | 2.6 | | 99.6 |

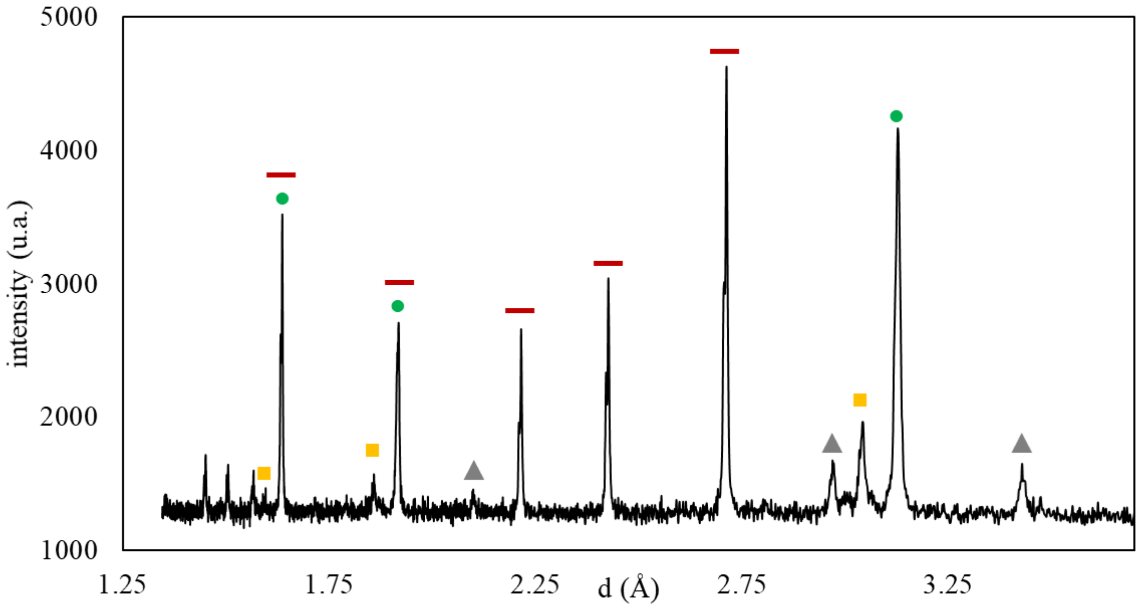


Fig. 2: XRD pattern of bulk concentrate (yellow squares = chalcopyrite; grey triangles = galena; green circles = sphalerite; red lines = pyrite).

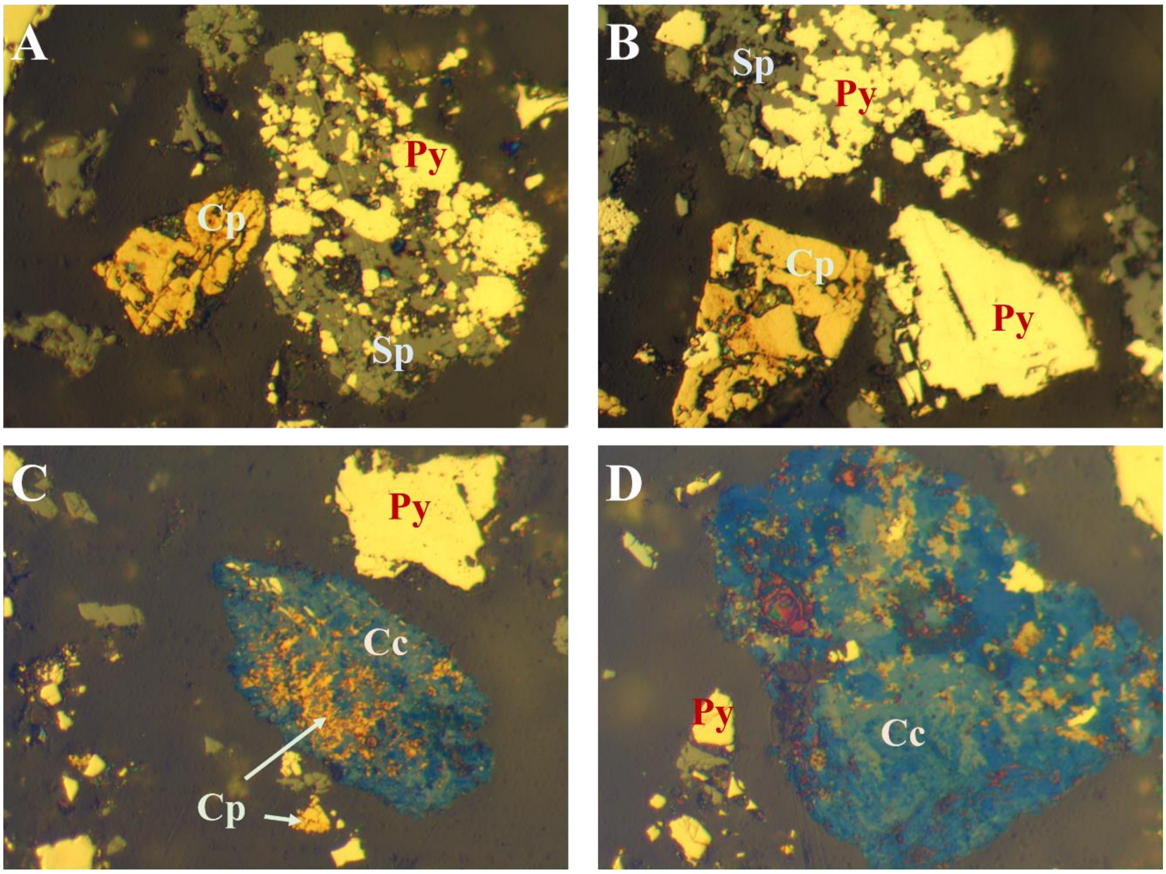


Fig. 3. Microphotographs (x500): sphalerite (Sp) occluded in pyrite (Py) particle and chalcopyrite (Cp) (A); particles of sphalerite, pyrite and chalcopyrite (B); chalcopyrite occluded in chalcocite (Cc) particle (C); chalcocite particle (D).

## 2.2 Analytical methods

### 2.2.1 Metal analysis

Iron, copper, zinc, lead and silver in liquors and solids were determined by atomic absorption spectrophotometry (Perkin Elmer 2380 Model, United States). In order to measure metals in solids, a previous acid digestion with aqua regia (3HCl: $1HNO_3$) of a known mass was performed.

Ferrous ion was determined in liquors by standard redox titration (Carranza et al., 2004) with potassium dichromate ($K_2Cr_2O_7$). These measurements were carried out with an automatic titrator (TTT80 model Radiometer Copenhagen, Denmark).

### 2.2.2 Sulphur analysis

Sulphur content in ore samples was determined by gravimetric analysis with barium chloride ($BaCl_2$). Sulphur content can be calculated according to eq. 1, where barium sulphate is the generated precipitated mass ($BaSO_4$) and sample mass the mass of concentrate.

$$\text{Sulphur content (\%)} = \frac{\text{barium sulphate (g)} \cdot 0.137}{\text{sample mass (g)}} \cdot 100 \qquad \text{(eq. 1)}$$

In order to determine elemental sulphur content in the leached concentrate, a known mass of leached sample was treated with carbon disulphide ($CS_2$) at 60 ºC in a Soxhlet extractor to dissolve the $S^0$ fraction. After 4 extraction steps, the carbon disulphide solution, rich in $S^0$, was distilled and the extracted elemental sulphur was weighted (Meyer et al., 1971).

### 2.2.3 Granulometric analysis

Particle size distribution was determined by laser diffraction (Beckman Coulter Ls 13-320-MW model, United States). The analyses were carried out with a disaggregant and an obscurance of 8-10%.

### 2.2.4 X-ray diffraction (XRD) analysis

XRD analyses were performed under the following conditions: $\text{Cu}k\alpha 1 = 1.5418$ Å and $2\theta$ from 3.0 to 70.0º. These analyses were carried out in CITIUS (Centro de Investigación, Tecnología e Innovación de la Universidad de Sevilla) with a powder diffractometer (Bruker D8 model advance A25, United States). The different compounds were determined with the DIFFRAC.EVA software (Bruker, United States).

## 2.3 Ferric leaching tests

Leaching time, pulp density (p.d.) and amount of catalyst were the variables studied in ferric leaching tests. These assays were carried out in an orbital shaker (Gallemkap) at 180 rpm to ease identical conditions of agitation and temperature in all tests.

Ferric leaching tests were performed in flask reactors (250 mL). In all tests, the initial work volume was 150 mL and the leaching solution was composed of 35 g/L of ferric ion (from a commercial solution of 210 g/L) and 20 g/L of sulphuric acid. Once leaching solution reached the work temperature (80 ºC), a known mass of concentrate was added and the test was then started. At the end of leaching assays, the pulp was filtered, and solid residue was dried at 60 ºC. Metals (Cu, Fe, Zn) were measured in solid and liquors, and ferrous ion was determined in liquors.

Ferrous ion concentration in liquors is useful to determine the ferrous ion generation. This value can be directly related with the required ferric ion amount that the bulk concentrate consumes in each leaching test. Ferrous ion generation is calculated according to eq. 2

$$\text{Ferrous ion generation (g Fe}^{2+}\text{/kg concentrate)} = \frac{\text{Fe}^{2+}\left(\frac{\text{g}}{\text{L}}\right)\cdot\text{work volume (L)}}{\text{concentrate mass (kg)}} \qquad \text{(eq. 2)}$$

Leaching procedure was analogous in catalysed ferric leaching tests, the only difference was the addition of silver. After sulphide concentrate addition, silver was added, from a500 mg/L silver solution prepared with silver nitrate. Several ferric leaching assays were performed in a 5L-stirred tank reactor (STR) to obtain an enough amount of leached concentrate to study the variables in the catalytic step.

### 2.4 Hot brine leaching tests

A set of chloride leaching tests were carried out in 250-mL stirred Erlenmeyer flasks, at 80°C and 180 rpm for 2 hours in an orbital shaker (Gallenkamp). In order to study the best conditions for chloride leaching, a $2^4$-factorial plan (4 variables, 2 levels) were performed at 1% of pulp density.

Table 2 shows the factors and level on the design of experiences (DOE). Sodium chloride was used as leaching agent, because it is the most promising according to several researchers (Ruşen et al., 2008; Behnajady and Moghaddam, 2011). In the presence of sodium chloride, silver and lead extraction is favoured given that provides enough chloride ions and produces soluble complexes. Even so, achieving high extractions of these metals requires the presence of acid. To promote the activity of $Cl^-$ ions and therefore the leaching, hydrochloric acid was used. This effect is especially significant in very acidic solutions. According to Chmielewski et al. (2007), a decrease in pH as well as an increase in temperature greatly improves the recovery of silver in chloride solutions, hence brine leaching is operated at low pH (0.1-0.5 M HCl) and at 80 °C. On the other hand, elemental sulphur generated by the oxidation of sulphides may cause low extraction yields. Carranza et al. (2004) found out that after the extraction of elemental sulphur, the chloride leaching enables silver extraction levels of 99%. Therefore, when is necessary, elemental sulphur was removed by extraction with carbon disulphide.

Table 2. Factors and levels on $2^4$ design of experiences at 1% pulp density.

| Factor | S° | [Fe(III)], g/L | HCl, M | [NaCl], g/L |
|---|---|---|---|---|
| Low Level | + | 0 | 0.1 | 50 |
| High Level | - | 5 | 0.5 | 250 |

In order to study the influence of solid/liquid ratio, tests were performed at 5, 10, 15 and 20% of pulp density. Finally, the influence of reaction time was studied in tests carried out under the best conditions found.

After each leaching, solid and liquid were separated by vacuum filtration (0.45 µm pore size) and Ag, Pb, Cu, Zn, and Fe were analysed in both phases.

## 3. Results and discussion

### 3.1 Silver impregnation

Silver solubility under leaching conditions was measured. Test was performed with the leaching solution (35 g/L $Fe^{3+}$ and 20 g/L $H_2SO_4$), 1% of pulp density and 2000 mg Ag/kg concentrate at room temperature. Test started when silver aliquot was added into reactor. Table 3 shows how silver precipitates rapidly when is added, remaining in solution less than 1% after leaching.

Table 3. Silver in solution and impregnated as a function of time (35 g/L ferric ion, 20 g/L sulphuric acid, 1% of pulp density, 2000 mg/kg concentrate, 180 rpm and room temperature).

| **Time (min)** | **0** | **0.1** | **1** | **2** | **5** | **10** |
|---|---|---|---|---|---|---|
| **Ag (mg/L)** | **20** | **0.25** | **0.2** | **0.18** | **0.18** | **0.16** |
| **Ag impregnated (%)** | **0** | **98.8** | **99.0** | **99.1** | **99.1** | **99.2** |

### 3.2 Copper and zinc recovery

#### 3.2.1 Direct catalysed ferric leaching

A direct catalysed ferric leaching was performed, where the studied variable was the catalyst/ bulk concentrate ratio (0-1000 mg $Ag^+$/ kg bulk concentrate). Experimental conditions, such as temperature or ferric ion concentration, were fixed in order to reach high metal recoveries according to the literature: 80 ºC, 1% of pulp density, 35 g/L ferric ion, 20 g/L sulphuric acid, 10 h and 180 rpm of orbital stirring (Romero-García et al., 2019; Fomchenko et al., 2019; Fomchenko and Muravyov, 2018; Lorenzo-Tallafigo et al., 2018). Fig. 4 shows copper and zinc extractions. When catalyst is not added, zinc extraction is higher than 90%, and copper recovery is about 50%, which can be attributed to chalcocite dissolution (Carranza et al., 2004) and a minor dissolution of chalcopyrite which shows a refractory behaviour (Cordoba et al., 2008; Mateos et al., 1987; Carranza et al., 1997).

The addition of silver has a negative effect on sphalerite dissolution. Sphalerite dissolution decreases from 94%, without catalyst to 55%, with 1000 mg Ag/ kg concentrate, which is in agreement with Palencia and Dutrizac (1991), Carranza et al. (1997) and Barriga et al. (1993). In contrast, copper extraction rises progressively due to chalcopyrite dissolution has been reactivated by silver ions (Romero et al., 2003). Iron dissolution and ferrous ion generation (g $Fe^{2+}$/ kg concentrate) are similar in all experiments, being about 52% and 1400 g $Fe^{2+}$/ kg concentrate respectively.

These results indicate that the joint recovery of copper and zinc in a single catalysed step is not feasible. Consequently, two leaching steps in series, a first non-catalysed leaching for zinc dissolution and a second catalysed leaching to recover copper from chalcopyrite, are proposed.

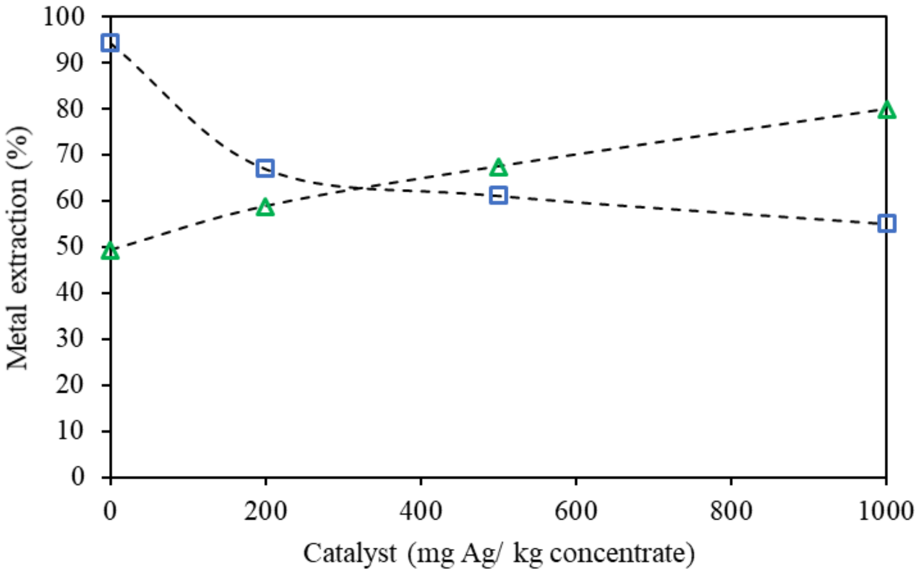


Fig. 4. Copper and zinc extractions as a function of catalyst amount in the direct catalytic ferric leaching tests (1% pulp density, 10h, 80 ºC, 35 g/L ferric ion, 20 g/L sulphuric acid and 180 rpm orbital shaking) (squares = zinc extraction; triangles = copper extraction).

### 3.2.2 Ferric leaching

In view of the above results, a ferric leaching as a previous step of catalytic leaching is proposed. A set of ferric leaching tests was performed; time, pulp density and $Fe^{2+}/Fe^{3+}$ ratio were the parameters tested.

Fig. 5 shows zinc and copper recoveries as a function of time. After 8h of ferric leaching, zinc and copper dissolution are 95.5 and 47.2%, respectively. According to Carranza et al. (2004), most of the dissolved copper must come from secondary sulphides, such as chalcocite. On other hand, under these conditions chalcopyrite shows refractory behaviour, reaching low dissolution levels (Mateos et al., 1987; Fomchenko and Muravyov, 2018; Dutrizac, 1981; Córdoba et al., 2008). These results are in accordance with copper mineralogical composition of the used concentrate (Table 1), where 37% of copper can be directly related with secondary sulphides (Fisher, 1994). High dissolution levels for zinc can be achieved in ferric sulphate media (Dutrizac, 2006; Souza et al., 2007b).

In both cases, at the beginning a fast leaching rate is observed followed by a decrease in it. Chalcopyrite (Dutrizac, 1981; Dutrizac et al., 1969) and copper secondary sulphides (Ruan et al., 2010; Chen and Lawson, 1991) leaching is controlled by diffusion phaenomena. Sphalerite can show two kinetics regimes: a first stage where the chemical reaction on the sphalerite surface is the rate limiting step and a second stage where diffusion through a sulphur layer is the rate controlling step (Lorenzo-Tallafigo et al. 2018; Karimi et al., 2017; Souza et al., 2007; Weisener et al., 2003).

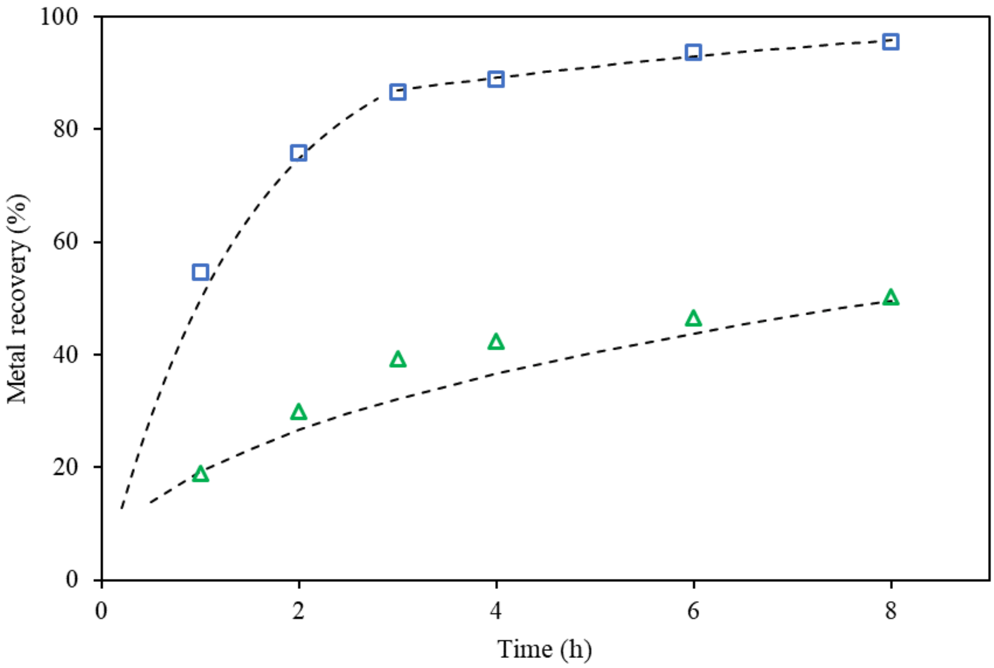


Fig. 5. Time effect on zinc and copper extraction (35 g/L ferric ion, 20 g/L sulphuric acid, 80 ºC, 1% pulp density) (squares = zinc recovery; triangles = copper recovery; dashed lines = kinetic models).

In order to study the effect of pulp density from 1 to 25%, several tests were carried out for 8 h. Fig. 6A presents the extraction of copper, zinc and iron as a function of pulp density. Unlike zinc, whose recovery decreases notoriously when pulp density increases above 10%, copper recovery does not show an important dependence with respect to pulp density. Carranza et al. (2004) also observed similar results in copper recovery when pulp density was increased in chalcopyrite and secondary copper sulphides concentrates.Carranza et al. (1997) reported an important dependence of sphalerite dissolution with respect pulp density (1-5% p.d.). However, in this work the last is only observed when pulp density is drastically increased. This behaviour can be explained by the low grade of non-ferrous metals in bulk concentrates. This low-grade allows working at higher pulp densities with similar yields because ferric ion consumption per unit of concentrate mass depends directly on the grade ofnon-ferrous sulphides.

Unlike zinc and copper sulphides, pyrite oxidation (iron dissolution) decreases drastically when pulp density increases. At high pulp densities, iron extraction remains constant around 15%. Since pyrite has a higher rest potential than the other sulphides, at higher ferrous ion concentrations pyrite is slightly oxidised.

When pulp density is increased, ferrous ion generation (g ferrous ion/ kg bulk concentration) is reduced due to the decrease of pyrite dissolution. Low generation of ferrous ion improves the process efficiency due to the increase of leaching selectivity (Fig. 6B). Fig. 6B shows ferrous ion generation data, both experimental and stoichiometric (considering the dissolution of sphalerite, galena and copper as chalcocite), finding 3% of pulp density the most appropriate to perform the following tests.

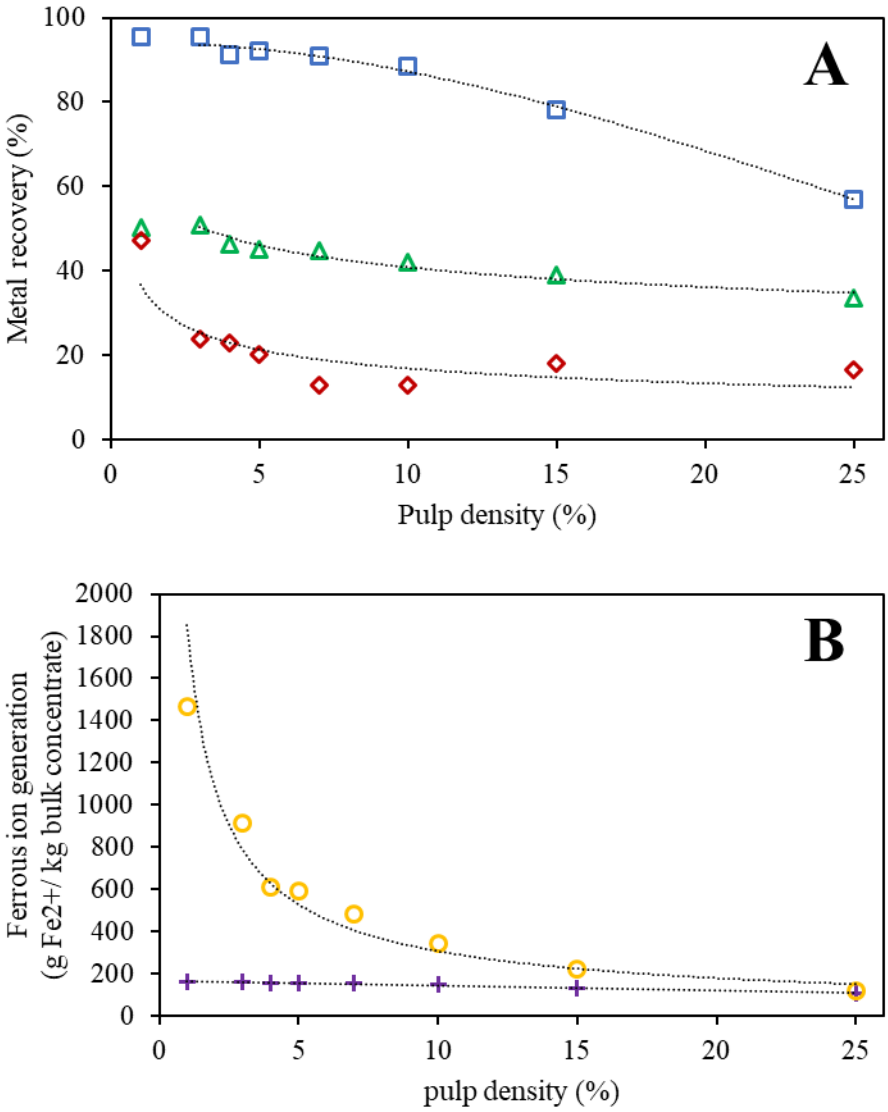


Fig. 6. Effect of pulp density on Cu, Zn and Fe extraction (A) and on ferrous ion generation (g ferrous ion/ kg of concentrate) (B) (80 ºC, 8h, 35 g/L $Fe^{3+}$ and 20 g/L $H_2SO_4$) (squares = Zn extraction; triangles = Cu extraction; diamonds = Fe extraction; circles = experimental data; crosses = stoichiometric data).

In commercial leaching processes, a considerable fraction of dissolved iron is ferrous ion (Dutrizac, 2006). The presence of ferrous ion could affect the leaching process decreasing the recovery of target metals. Ferrous sulphate effect on ferric leaching has not been extensively studied; while Dutrizac (2006) observed a negative effect on sphalerite dissolution, Lorenzo-Tallafigo et al. (2018) did not find any decrease of non-ferrous sulphide dissolution when ferrous ion concentration increased. In order to study this phenomenon, a set of ferric leaching tests with different $Fe^{2+}/Fe^{3+}$ ratio (total iron concentration = 35 g/L) was performed.

Fig. 7 shows the effect of $Fe^{2+}/Fe^{3+}$ ratio on zinc and copper extraction and on ferrous ion generation (g $Fe^{2+}$/ kg bulk concentrate). Zn and Cu extractions remain almost constant when the concentration of ferrous ion increases (Fig. 7A). However, ferrous ion generation decreases nearly three times when initial ferrous ion concentration was 20 g/L (Fig. 7B). In other words, the decrease of ferric ion concentration has an similar effect to increasing pulp density by increasing the leaching selectivity of target sulphides.

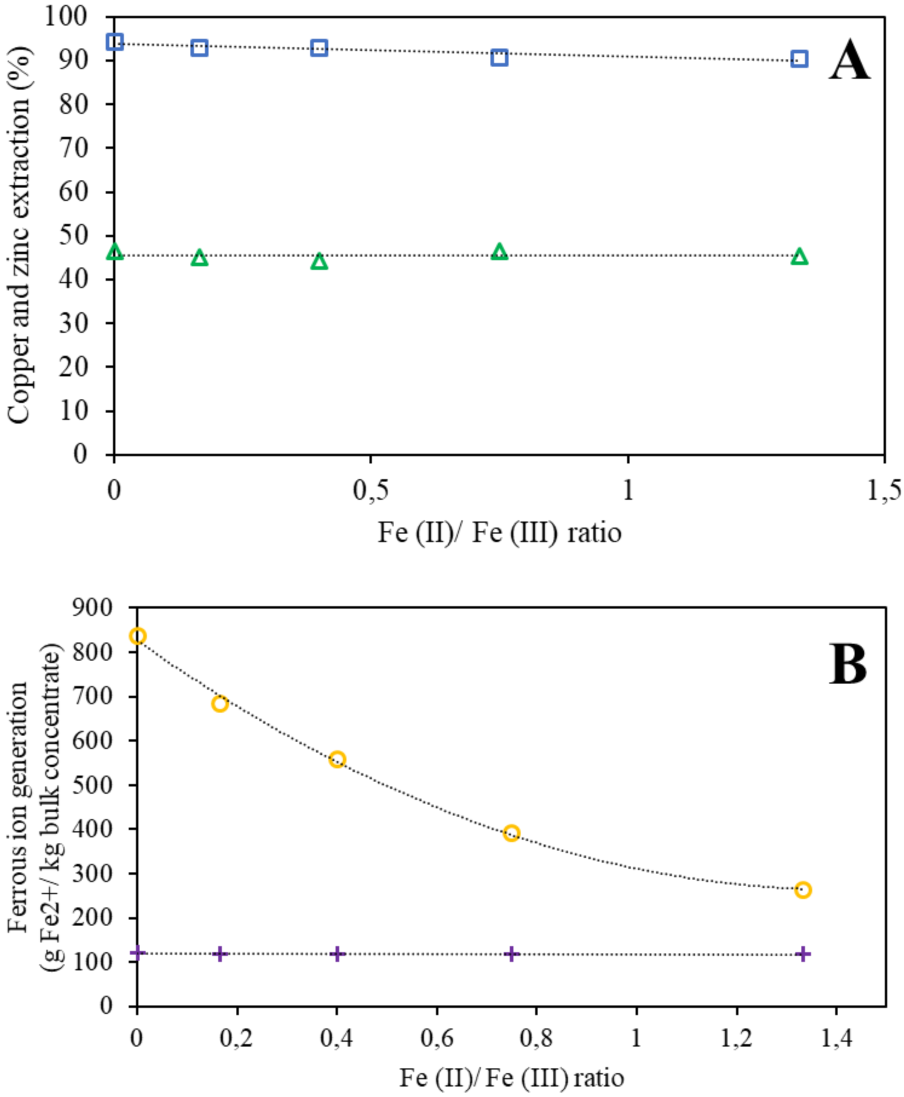


Fig.7. Zn and copper extraction (A) and experimental and stoichiometric ferrous ion generation (B) as a function of Fe (II)/ Fe (III) ratio (g $Fe^{2+}$/ kg bulk concentrate) (B) (80 ºC, 8h, 3% pulp density, 20 g/L $H_2SO_4$ and 35 g/L. $Fe_T$ = Fe (II) + Fe (III)) (triangles = Cu extraction; squares = Zn extraction; circles = experimental ferrous ion generation; crosses = stoichiometric ferrous ion generation).

### 3.2.3 Catalysed ferric leaching

Once direct catalysed leaching and ferric leaching have been tested separately, zinc and copper recovery in two leaching steps in series (ferric leaching followed by catalysed ferric leaching) was studied. After ferric leaching, sphalerite, galena and secondary copper sulphides are oxidised, and the leached concentrate is mainly composed of pyrite, anglesite, chalcopyrite and elemental sulphur.

First, in order to study the whole process, a set of leaching tests with different catalysts amount, from 0 to 4000 mg Ag/ kg concentrate were performed as follow: a previous ferric leaching followed by a catalysed ferric leaching with a filtration between both steps. Each leaching stage was carried out with fresh leaching liquor. Fig. 8 shows zinc and copper recoveries obtained with different catalyst amounts. An improvement in copper extraction can be observed when low silver amounts were added as a consequence of the catalytic dissolution of chalcopyrite. Copper and zinc recoveries higher than 95% can be reached when 1000 mg Ag/ kg concentrate is added. These results are in accordance with Carranza et al. (1997), Mateos et al. (1987) and Cordoba et al. (2008a), where chalcopyrite, contained in sphalerite-chalcopyrite and chalcopyrite concentrates, was dissolved using silver as a catalyst. The previous ferric leaching dissolves non-ferrous sulphides, except chalcopyrite, avoiding the passivation of them by catalyst addition.

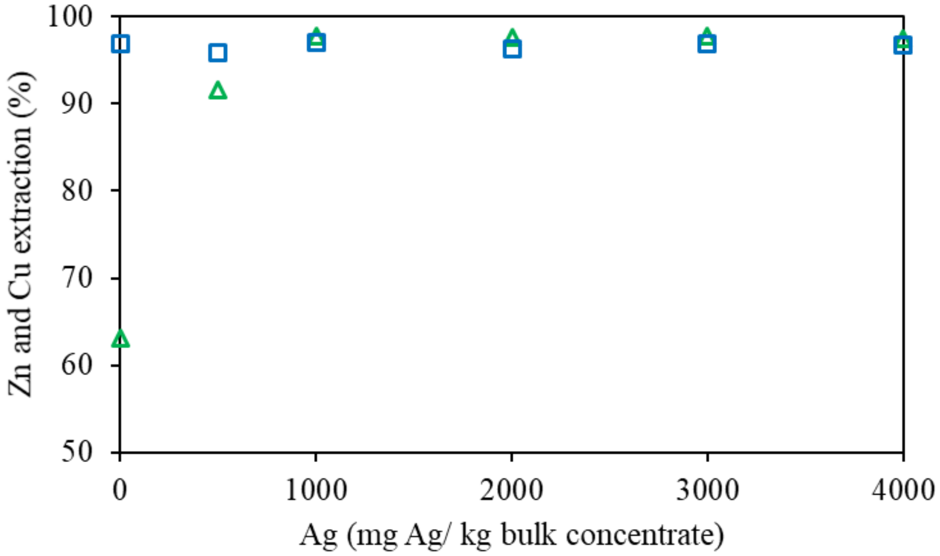


Fig. 8. Zn and Cu extraction in two leaching steps as a function of silver added (3% pulp density, 8h ferric leaching, 12h catalytic leaching, 35 g/L ferric ion, 20 g/L $H_2SO_4$ and 80 ºC) (triangles = copper extraction; squares = zinc extraction).

### 3.2.3.1 Ferric leaching time effect

In order to test the effect of ferric leaching time in catalytic step, a set of leaching tests, where the ferric leaching time was varied, was conducted. In these tests, both stages took place in the same flask, once ferric leaching was finished, silver was added, starting the catalysed leaching. Fig. 9 shows copper and zinc recovery achieved in these assays. Ferric leaching time does not modify copper recovery, and the mean copper extraction is 93%.

In contrast, Zn extraction progressively enhances with reaction time in the first step, from 84 to 96%. Four hours of ferric leaching are enough to leach more than 90% of copper and zinc. These results are in accordance with Carranza et al. (1997) and Carranza et al. (2004), where the time of ferric leaching previous to catalysed leaching was also studied in sphalerite-chalcopyrite and copper concentrates. Nevertheless, in the present study lower ferric leaching times were required to reach high metal recoveries, as this bulk concentrate contains a minor grade of target sulphides. In addition, Carranza et al. (1997) and Carranza et al. (2004) carried out these tests with low ferric ion concentrations.

In these assays, catalytic step starts with a part of ferric ion reduced to ferrous ion, from 5.4 to 13.5 g/L $Fe^{2+}$ (leaching liquor was not regenerated between both steps). This fact does not affect the process efficiency, allowing the copper and zinc recovery in a single stream.

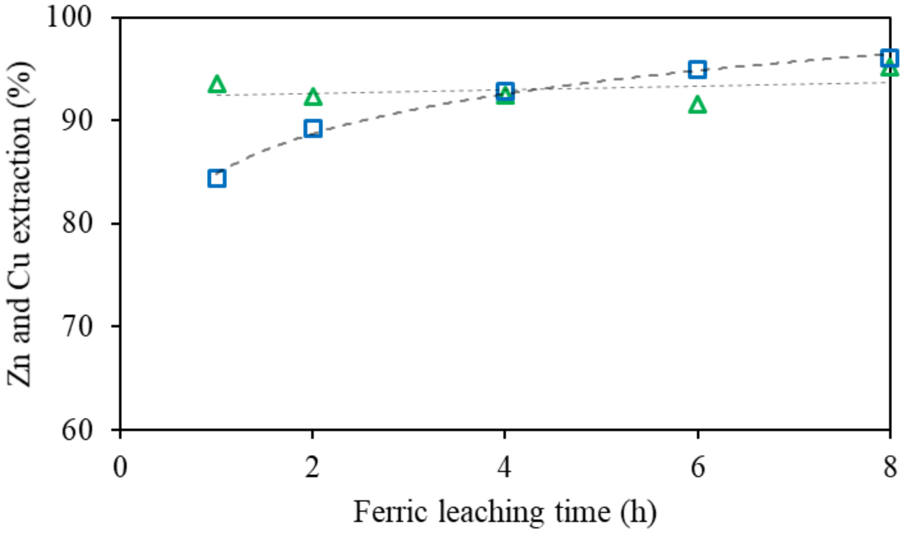


Fig 9. Zn and Cu recovery in two steps as a function of ferric leaching time (12h catalytic leaching, 35g/L ferric ion, 20 g/L $H_2SO_4$, 3% pulp density, 1000 mg Ag/ kg bulk concentrate, 80 ºC) (triangles = Cu recovery; squares = Zn recovery).

#### 3.2.3.2 Pulp density effect

A set of catalysed ferric leaching tests was conducted in order to study pulp density from 1 to 25 %. In order to observe a possible effect of pulp density, catalyst amount was decreased to 500 mg Ag/kg concentrate. Several ferric leaching tests were performed in a stirred tank reactor (STR) with a volume of 6L to generate enough amount of leached concentrate to study the catalytic stage, the results are shown in supplementary data (Fig. S1-3). In these tests (STR1-3), mean copper and zinc extractions of 44.4 and 92.2, respectively, were achieved.

Pulp density was studied from 3 to 25%. The tests for 3 to 12% were conducted with solid obtained in STR 1 and those between 12 and 25% were performed with the solid obtained in STR 2. Fig. 10 shows the results obtained after two ferric leaching steps (ferrous ion generation corresponds with the catalysed step). An increase in pulp density progressively enhances copper recovery (Fig. 10A), nonetheless, when pulp density exceeds 15% copper dissolution is reduced due to ferric ion exhaustion. The optimum pulp density to dissolve chalcopyrite from this concentrate is in the range of 9-15%. This improvement could be attributed to higher amounts of silver when pulp density increases, which could be mobilised between chalcopyrite and pyrite surfaces to dissolve copper faster. The increase of pulp density in catalytic leaching would allow decreasing the reactor volume or increasing the leaching productivity. In addition, higher copper concentrations in PLS would ease the subsequent concentration and purification steps. Zn recovery varies slightly, from 91 to 97%. Fig. 10B shows ferrous ion generation, which decreases rapidly as pulp density increases. At 15% of pulp density, the required ferric ion is reduced almost 3.5 times to reach better yields than with a pulp density of 3%. Like in ferric leaching, increasing the pulp density decreases the generation of ferrous ion, bringing experimental closer to stoichiometric ferrous ion generation (considering only the chalcopyrite dissolution).

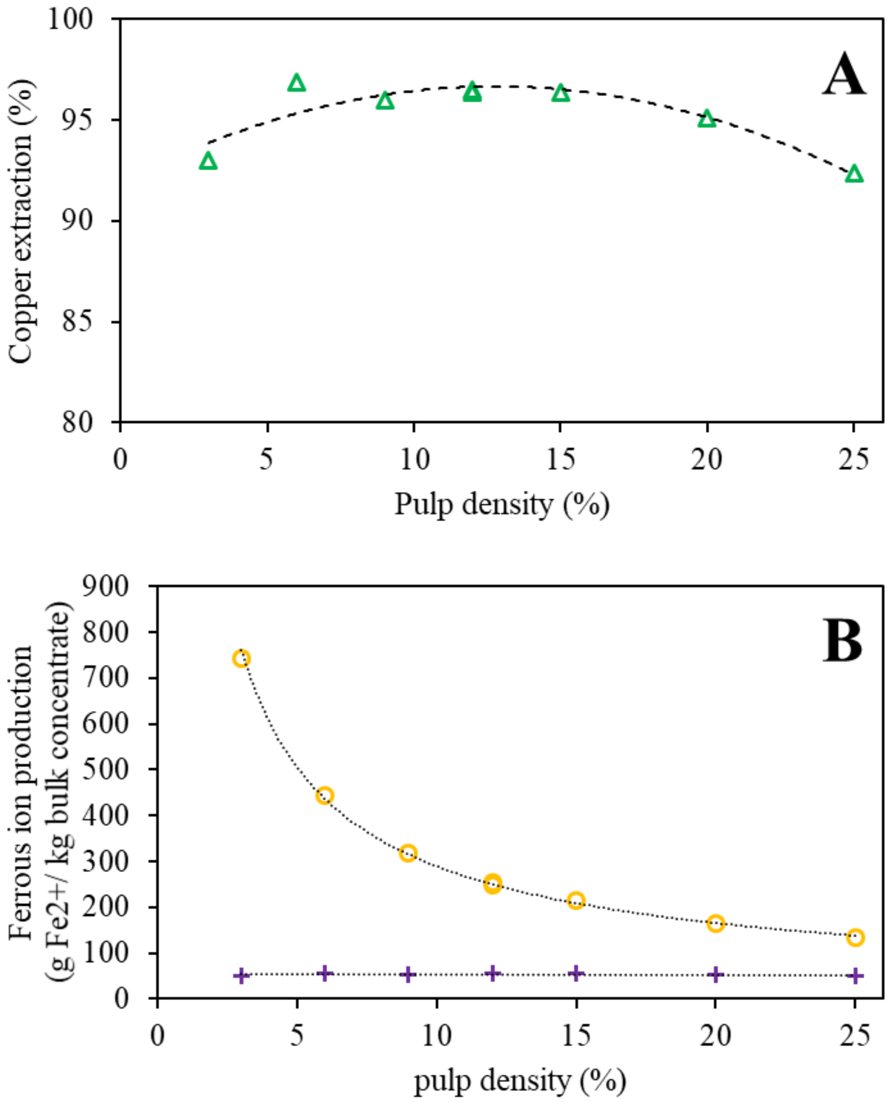


Fig. 10. Results obtained at different pulp densities in catalysed ferric leaching: Cu extraction (A) and ferrous ion generation (g $Fe^{2+}$/ kg bulk concentrate) (B) (500 mg Ag/ kg concentrate, 80 ºC, 35 g/L $Fe^{3+}$, 20 g/L $H_2SO_4$, 12h of catalytic leaching) (triangles = copper extraction; circles = experimental ferrous ion generation; crosses = stoichiometric ferrous ion generation).

### 3.2.3.3 Effect of catalyst amount

A third ferric leaching assay in a stirred tank reactor (test STR 3) was carried out to study the effect of catalyst amount; results are presented in Fig. S3 and Table S1. This leached concentrate was used to perform three catalysed ferric leaching tests in order to study the effect of catalyst amount, from 125 to 500 mg Ag/ kg concentrate. The other conditions were chosen according to the above results: 12% of pulp density, 80 ºC, 12h, 35 g/L ferric ion, 20 g/L sulphuric acid and 180 rpm of orbital shaking.

Fig. 11 shows copper and zinc extractions with different catalyst amounts. Copper extraction falls when silver amount is below 250 mg Ag/ kg concentrate, which decreases drastically to 70% when only 125 mg Ag/ kg concentrate is added. Nevertheless, zinc extraction remains almost constant.

Carranza et al. (1997) reported that 2000 mg Ag/ kg concentrate would be necessary to dissolve chalcopyrite from a copper-zinc concentrate (43.7% chalcopyrite). Carranza et al. (2004) studied the catalysed leaching in several copper concentrates, observing that the catalyst requirement decreased when the chalcopyrite content fell in the used concentrates; 1000 mg Ag/ kg concentrate was necessary to dissolve copper in a low-grade copper concentrate (1.40% chalcopyrite). In both studies, pulp density was low, between 1-3%. In this case, the chalcopyrite content in the leached concentrate is estimated at 6.94%, obtaining copper recoveries higher than 90% with 250 mg Ag/ kg concentrate and 12% of pulp density. This disagreement could be due to silver amount effect also depends on the leaching conditions (e.g. pulp density) and the mineral composition.

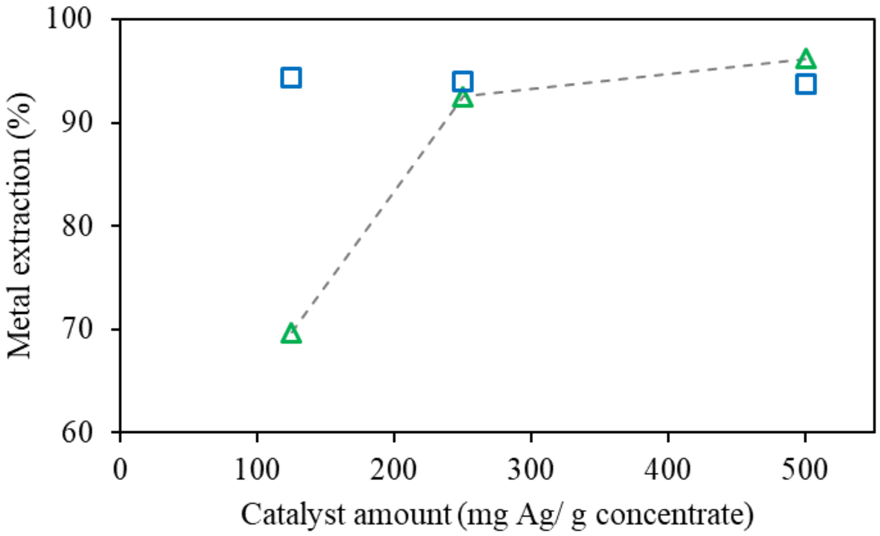


Fig. 11. Zn and Cu extraction as a function of catalyst amount (80 ºC, 12h catalysed leaching, 12% of pulp density, 20 g/L $H_2SO_4$ and 35 g/L $Fe^{3+}$) (triangles = Cu extraction; squares = Zn extraction).

### 3.2.3.4 Catalysed leaching time effect

A set of catalysed ferric leaching tests at different leaching times was performed in order to study chalcopyrite dissolution as a function of time. The leached concentrate obtained in test STR 3 was used to carry out these assays. Fig. 12 shows copper recovery and ferrous ion generation as a function of time. At early reaction times, copper recovery increases proportionally to time. But after two hours, chalcopyrite dissolution rate decreases, due to elemental sulphur film formation, when silver is added, which corresponds to diffusional control (Mateos et al., 1987; Carranza et al., 1997; Cordoba et al., 1998). After 8h of catalysed ferric leaching, copper extractions higher than 95% are reached. The generation of ferrous ion follows a similar curve to Cu recovery, due to the rest of the variables have already been optimised.

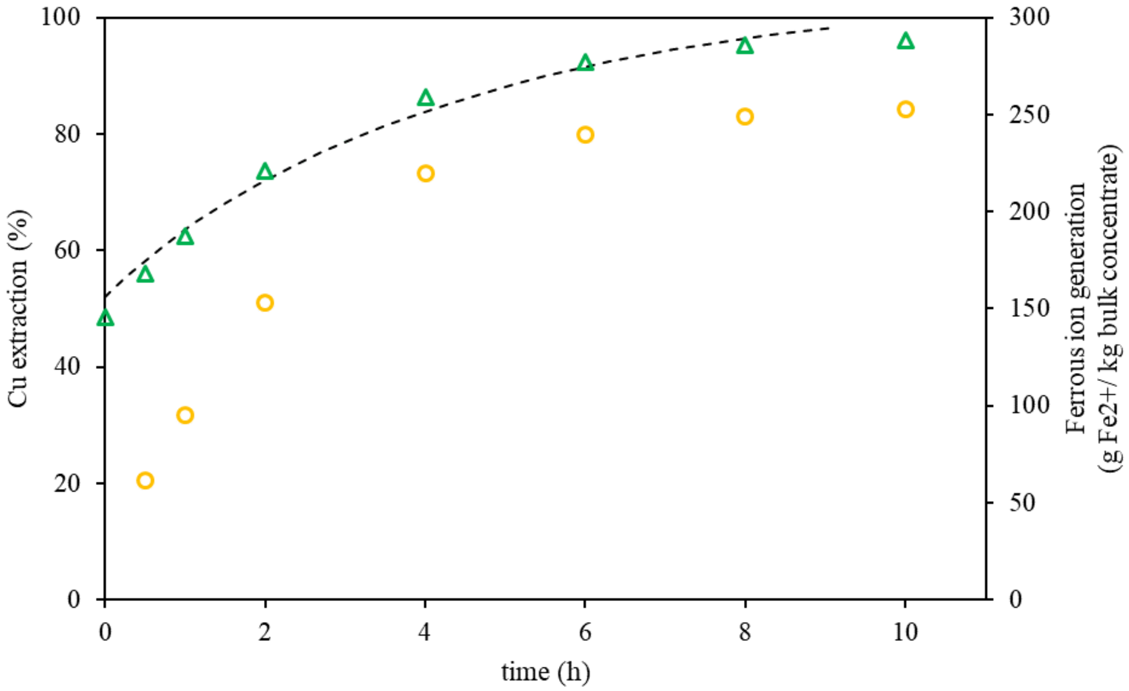


Fig. 12. Cu extraction and ferrous ion generation (g Fe$^{2+}$/ kg concentrate) with respect catalysed leaching time (triangles = Cu extraction; circles= ferrous ion generation; dashed lines = kinetic model – eq. 3) (solid = test STR 3; 12% of pulp density, 500 mg Ag$^{+}$/ kg bulk concentrate, 80 ºC, 35 g/L Fe$^{3+}$ and 20 g/L $H_2SO_4$).

### 3.3 Lead and silver recovery

In order to study lead and silver recovery in the last leaching stag,e a fourth leaching in the stirred tank reactor (STR-4) was performed. This leaching assay consisted of two steps, a first ferric leaching process under optimal conditions (3% pulp density, 80 ºC, 35 g/L ferric ion, 20 g/L sulphuric acid, 500 rpm and 8h) and a second catalysed ferric leaching with 1000 mg Ag/kg concentrate, in order to study silver recovery when a large catalyst amount is added (12% pulp density, 80 ºC, 35 g/L ferric ion, 20 g/L sulphuric acid, 500 rpm and 8h). After the two leaching steps, copper and zinc recoveries of 94.5 and 93.4, respectively, were achieved.

#### 3.3.1 Leached concentrate characterisation

Fig. 13 shows the XRD pattern of the leached concentrate, where pyrite, elemental sulphur, anglesite and quartz were the found species. Table 4 present the chemical and mineralogical compositions; a low amount of copper and zinc remains in the leached concentrate as unreacted chalcopyrite and sphalerite particles. During leaching, galena was converted to anglesite, which together with silver can be re-dissolved in chloride media. A 6.6% of elemental sulphur was determined, and according to granulometric analysis (Fig. S4), this elemental sulphur is forming a layer around the reacted sulphide particles.

Table 4. Chemical and mineralogical analysis of leached concentrate after two ferric leaching steps (Cu and Zn in leached concentrate are considered as chalcopyrite and sphalerite, respectively; * mg/kg).

| Element | Cu | Zn | Pb | Fe | S | Ag | | Total |
|---|---|---|---|---|---|---|---|---|
| Content (%) | 0.3 | 0.8 | 3.3 | 38 | 51.8 | 1438* | | 94.2 |
| Ore | $CuFeS_2$ | ZnS | | PbSO4 | $FeS_2$ | S0 | SiO2 | |
| XRD | | | | X | X | X | X | |
| Estimated (%) | 0.8 | 1.2 | | 4.8 | 81 | 6.6 | - | 94.5 |

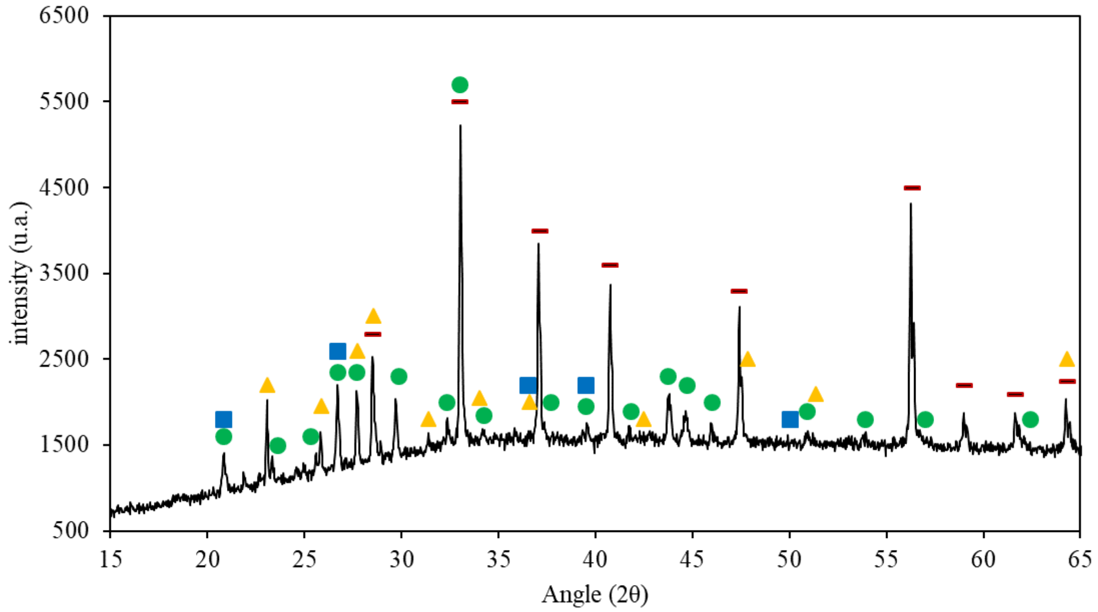


Fig. 13. XRD pattern of leached concentrate (red lines = pyrite; green circles = anglesite; blue squares = quartz; yellow triangles = elemental sulphur).

## 3.3.2 Hot brine leaching

### 3.3.2.1. Preliminary tests

In order to study the best conditions for chloride leaching, a $2^4$-factorial plan (4 variables, 2 levels) was performed. Table 5 shows the operation conditions studied, the extractions of silver and lead, and the final composition of these metals in the residues obtained in tests performed at 1% of pulp density. Regarding to Fe, Cu and Zn metals, the final composition of residues of all tests (A1-A16) is on the order of 41%, 0.25% and 0.5% respectively. Ag extractions are between 91 and 97% and Pb extractions between 95 and 99%, obtaining the best results in the absence of elemental sulphur, with a concentration of HCl of 0.5 M and a NaCl concentration of 50 g/L (test A15). Extractions equal to 92.75% (with elemental sulphur) and to 92.71% (without elemental sulphur) in brine leaching tests involve the total recovery of the catalyst. Extractions higher than these values entail the recovery of the silver contained in the bulk concentrate, therefore, according to Table 5, all the catalyst and part of the silver contained in the concentrate is recovered in all tests carried out in absence of elemental sulphur.

Table 5. Experimental conditions, Ag and Pb extractions for leaching tests A1-A16 performed at 1% of pulp density at 80 ºC and 180 rpm for 2 hours and final Ag and Pb composition (+ = presence Sº; - = absence Sº).

| Test | Sº | Fe(III), g/L | HCl, M | NaCl, g/L | Ext. Ag, % | Ext. Pb, % | Final grade Ag, ppm | Final grade Pb, % |
|---|---|---|---|---|---|---|---|---|
| **A1** | + | 0 | 0.10 | 50 | 91.23 | 97.63 | 138 | 0.08 |
| **A2** | + | 5 | 0.10 | 50 | 93.17 | 98.61 | 116 | 0.05 |
| **A3** | + | 5 | 0.50 | 50 | 92.86 | 98.42 | 120 | 0.06 |
| **A4** | + | 5 | 0.50 | 250 | 91.66 | 97.96 | 140 | 0.08 |
| **A5** | + | 0 | 0.10 | 250 | 92.57 | 95.85 | 118 | 0.15 |
| **A6** | + | 0 | 0.50 | 250 | 92.42 | 95.80 | 118 | 0.15 |
| **A7** | + | 0 | 0.50 | 50 | 92.80 | 95.84 | 115 | 0.15 |
| **A8** | + | 5 | 0.10 | 250 | 91.42 | 95.90 | 144 | 0.16 |
| **A9** | - | 0 | 0.10 | 50 | 93.28 | 97.74 | 131 | 0.08 |
| **A10** | - | 5 | 0.10 | 50 | 96.01 | 97.71 | 77 | 0.08 |
| **A11** | - | 5 | 0.50 | 50 | 95.77 | 97.85 | 83 | 0.05 |
| **A12** | - | 5 | 0.50 | 250 | 94.32 | 97.76 | 119 | 0.07 |
| **A13** | - | 0 | 0.10 | 250 | 93.57 | 97.53 | 120 | 0.08 |
| **A14** | - | 0 | 0.50 | 250 | 93.98 | 97.65 | 116 | 0.06 |
| **A15** | - | 0 | 0.50 | 50 | 96.62 | 97.92 | 63 | 0.06 |
| **A16** | - | 5 | 0.10 | 250 | 93.18 | 97.79 | 139 | 0.06 |

With the purpose of verify if the effect of the variables and the interactions between them are statistically significant or not, statistical analysis of variance (ANOVA) was performed. Pb extractions higher than 95% are obtained in all tests (A1-A16), for this reason, silver extraction is considered the response variable. Table 6 shows the results obtained, which includes the sum of squares (SS), degree of freedom (df), mean square (MS), F-value and P-value. Considering significant to be at the 95% confidence level (P-value < 0.05%), the significant variables are the elemental sulphur and the chloride concentration. It is noticeable that there are no interactions between the different factors, therefore a more complete study of some of them can be carried out without considering the others.

Table 6. ANOVA results for tests at 1% pulp density.

| | SS | df | MS | F | P |
|---|---|---|---|---|---|
| (1) S | 14.43604 | 1 | 14.43604 | **20.19843** | **0.006433** |
| (2) $Fe^{3+}$ (g/L) | 0.25162 | 1 | 0.25162 | 0.35206 | 0.578768 |
| (3) $H^+$ (M) | 2.42317 | 1 | 2.42317 | 3.39042 | 0.124937 |
| (4) $Cl^-$ (g/L) | 5.00965 | 1 | 5.00965 | **7.00933** | **0.045562** |
| 1 by 2 | 0.21296 | 1 | 0.21296 | 0.29797 | 0.608618 |
| 1 by 3 | 0.79063 | 1 | 0.79063 | 1.10622 | 0.341057 |
| 1 by 4 | 1.58167 | 1 | 1.58167 | 2.21302 | 0.197010 |
| 2 by 3 | 1.26152 | 1 | 1.26152 | 1.76507 | 0.241398 |
| 2 by 4 | 2.16779 | 1 | 2.16779 | 3.03310 | 0.142056 |
| 3 by 4 | 0.48667 | 1 | 0.48667 | 0.68093 | 0.446835 |
| Error | 3.57356 | 5 | 0.71471 | | |
| Total SS | 32.19527 | 15 | | | |

According to statistical results, elemental sulphur is significant with respect to silver extraction, which evidences a diffusional problem that prevents the access of chloride ions to silver due to the presence of the sulphur layer that was formed during the ferric leaching. On the other hand, chloride concentration is also significant, even though it affects slightly. However, it is convenient to use a high level of this complexing agent in order to maintain a high concentration of lead or silver in solution.

### 3.3.2.2. Pulp density effect

In order to study the effect of pulp density (pd), tests were carried out at 5, 10, 15 and 20%. Experimental conditions, the extractions of silver and lead, and the final composition of these metals in residues obtained in tests A17-A28 are shown in Table 7.

Table 7. Experimental conditions, Ag and Pb extractions for leaching tests A17-A28 performed at 80 ºC and 180 rpm for 2 hours and final Ag and Pb composition (+ = presence Sº; - = absence Sº).

| Test | Sulphur | Fe(III), g/L | pd, % | Ext. Ag, % | Ext. Pb, % | Final grade Ag, ppm | Final grade Pb, % |
|---|---|---|---|---|---|---|---|
| **A17** | - | 5 | 5 | 92.80 | 98.62 | 123 | 0.05 |
| **A18** | - | 5 | 10 | 93.22 | 99.19 | 115 | 0.03 |
| **A19** | - | 5 | 15 | 93.58 | 99.10 | 109 | 0.03 |
| **A20** | - | 5 | 20 | 94.33 | 99.21 | 96 | 0.03 |
| **A21** | + | 5 | 5 | 91.76 | 97.82 | 130 | 0.08 |
| **A22** | + | 5 | 10 | 92.17 | 98.96 | 121 | 0.04 |
| **A23** | + | 5 | 15 | 91.50 | 98.19 | 131 | 0.06 |
| **A24** | + | 5 | 20 | 91.24 | 98.26 | 135 | 0.06 |
| **A25** | - | 0 | 5 | 88.70 | 98.07 | 183 | 0.07 |
| **A26** | - | 0 | 10 | 85.50 | 97.93 | 237 | 0.08 |
| **A27** | - | 0 | 15 | 81.38 | 98.51 | 303 | 0.06 |
| **A28** | - | 0 | 20 | 77.62 | 98.61 | 366 | 0.05 |

An increase in pulp density could make uninteresting factors to become significant. In tests A17-A28, the concentration of NaCl is 250 g/L, at pulp densities higher than 1%, a sodium chloride concentration of 250 g/L is used, since lead and silver concentration is also higher as pulp density is increased. It is because at higher pulp densities, the amount of lead and silver that keep in solution is greater. Hydrochloric acid concentration is 0.5 M in all tests (A17-A28), which implies an enough concentration of acid to counteract the possible presence of acid consumers, due to the increase in pulp density. In this way, it is possible to maintain a minimum and adequate concentration of acid with the purpose of the precipitation of silver and lead jarosites does not occur (Madden et al., 2012). On the other hand, Fe(III) concentration may be a significant factor at high pulp densities, because residual non-ferrous sulphides that remain in residue can cause silver precipitation, and an oxidising attack may be necessary to eliminate them. Therefore, the need for an oxidising agent that remove these sulphides is investigated in tests with 5 g/L of Fe(III).

According to the results shown in Table 7, pulp density is not a relevant factor to recover silver and lead. Lead extractions is satisfactory for every studied condition. Nevertheless, the best results for both metals are obtained when Fe (III) is added. The effect of sulphur is relatively small considering that the average silver extractions are 93.48% in absence of elemental sulphur and 91.66% in its presence. However, in presence of Sº, the complete recovery of silver added as a catalyst does not occur (92.75% extraction is not reached).

In addition, since silver is a metal of great economic value, a 1.82% difference in its extraction can be economically significant. In spite of Fe(III) did not result a significant variable for silver extraction at 1% of pulp density, it becomes important at higher pulp densities, as the low silver extractions in tests A25-A28 indicate.

On the other hand, the effect of Fe(III) on the extraction of Cu and Zn is observed. Copper extractions for tests A17-A24 are on the order of 20% while Zn extractions of 50%. It could be postulated that in chloride medium, Fe(III) is more active than in sulphate medium, and pyrite is partially attacked resulting in the release of occluded copper and zinc sulphides that are oxidised in these conditions.

#### 3.3.2.3. Leaching time effect

The influence of time on chloride leaching was studied at 20% of pulp density under the best conditions, that is, elemental sulphur layer removed, 5 g/L of Fe(III), 0.5M HCl and 250 g/L of NaCl. Table 8 shows the extractions of silver and lead and residue composition at 15, 30, 60, 90, 120 and 150 minutes.

Table 8. Ag and Pb extractions at different times (20% dp, 5 g/L Fe(III), 0.5 M HCl and 250 g/L NaCl).

| | | Extractions | | Residue composition | |
|---|---|---|---|---|---|
| **Test** | Time (min) | Ag (%) | Pb (%) | Ag (ppm) | Pb (%) |
| **A29** | 15 | 70.2 | 98.8 | 509 | 0,04 |
| **A30** | 30 | 76.8 | 98.2 | 397 | 0.07 |
| **A31** | 60 | 82.6 | 98.8 | 302 | 0.05 |
| **A20** | 120 | 94.3 | 99.1 | 96 | 0.03 |
| **A32** | 150 | 94.3 | 98.7 | 98 | 0.05 |

In the studied sample, lead is found as anglesite as a result of the previous ferric leaching, which is soluble in chloride medium. Lead extractions higher than 98% are obtained in just 30 minutes. Lead remaining in solid must be occluded because lead extraction remains almost constant. On the other hand, 120 minutes of leaching are necessary to reach silver extraction of 94.3%; afterwards the extraction is not significantly increased. It is worthy to note that an Ag extraction of 94.3% means both the total extraction of added silver as a catalyst, and the 22% of silver contained initially in the bulk concentrate.

## 4. Conclusions

In order to recover copper and zinc, a leaching process consisting of a ferric leaching followed by a catalysed ferric leaching is proposed. High recoveries of both metals are not feasible in a single catalysed step. Sphalerite dissolution is passivated when silver is added, reaching recoveries lower than 60% with 1000 mg Ag/kg concentrate. When a previous ferric leaching is performed, higher zinc and copper recoveries can be achieved (>95%). A minimum time of 4h of ferric leaching is necessary to achieve recoveries higher than 90% of both metals. In the catalysed leaching, copper recoveries greater than 90% are achieved with low catalyst amounts (250 mg/kg concentrate) when pulp density is increased.

Chloride leaching is a successful method to recover Pb and Ag from the catalysed ferric leaching residue. In chloride leaching tests, lead extractions are between 95 and 99% in the studied experimental conditions. The best conditions for silver extraction in chloride medium at 1% of pulp density and 80°C are the absence of elemental sulphur, 0.5 M HCl and 50 g/L NaCl. In these conditions, silver extraction is 96.62%. Within the limits of the studied range, the best conditions for silver extraction at high pulp density and 80°C are 20% dp, 120 minutes as reaction time, removal of $S^o$, 5 g/L Fe (III), 0.5 M HCl and 250 g/L NaCl. Under these conditions, the extractions of Pb and Ag are 98.9% and 94.3% respectively, which means the total extraction of silver added as a catalyst and the 22% of silver contained in the bulk concentrate.

It can be concluded that silver-catalysed ferric leaching followed by brine leaching with prior removal of elemental sulphur is a viable hydrometallurgical alternative for the treatment of a Cu-Zn-Pb bulk concentrate. Extractions higher than 95% for Zn, Cu and Pb are achieved as well as the total recovery of catalyst. The proposed process is silver surplus, therefore this agent can be recirculated.

## 5. Acknowledgements

Thanks are given to CLC (project 2665/0124) and VI PPIT-US for funding this work.

## 6. References

Akcil, A., & Ciftci, H. (2003). Metals recovery from multimetal sulphide concentrates (CuFeS2–PbS–ZnS): combination of thermal process and pressure leaching. International Journal of Mineral Processing, 71(1-4), 233-246.

Bahram, B., & Javad, M. (2011). Chloride leaching of lead and silver from refractory zinc plant residue. Res. J. Chem. Environ, 15, 473-480.

Barriga Mateos, F., Pereda Marin, J., & Palencia Pérez, I. (1993). Bacterial leaching of a bulk flotation concentrate of chalcopyrite-sphalerite. Biorecovery (Berkhamsted), 2(3), 195-218.

Behnajady, B., & Moghaddam, J. (2011). Chloride leaching of lead and silver from refractory zinc plant residue. Res. J. Chem. Environ, 15, 473-480.

Behnajady, B., & Moghaddam, J. (2014). Optimization of lead and silver extraction from zinc plant residues in the presence of calcium hypochlorite using statistical design of experiments. Metallurgical and Materials Transactions B, 45(6), 2018-2026.

Brierley, C. L. (2008). How will biomining be applied in future?.future? Transactions of nonferrous metals society of China, 18(6), 1302-1310.

Carranza, F., 1985. Las piritas españolas: un recurso natural poco explotado. Quím. Sur. 13–15.

Carranza, F., Iglesias, N., Mazuelos, A., Palencia, I., & Romero, R. (2004). Treatment of copper concentrates containing chalcopyrite and non-ferrous sulphides by the BRISA process. Hydrometallurgy, 71(3-4), 413-420.

Carranza, F., Iglesias, N., Romero, R., & Palencia, I. (1993). Kinetics improvement of high-grade sulphides bioleaching by effects separation. FEMS microbiology reviews, 11(1-3), 129-138.

Carranza, F., Palencia, I., & Romero, R. (1997). Silver catalyzed IBES process: application to a Spanish copper-zinc sulphide concentrate. Hydrometallurgy, 44(1-2), 29-42.

Cheng, C. Y., & Lawson, F. (1991). The kinetics of leaching chalcocite in acidic oxygenated sulphate-chloride solutions. Hydrometallurgy, 27(3), 249-268.

Chmielewski, T., Gibas, K., Borowski, K., Adamski, Z., Wozniak, B., & Muszer, A. (2017). Chloride leaching of silver and lead from a solid residue after atmospheric leaching of flotation copper concentrates. Physicochemical Problems of Mineral Processing, 53.

Córdoba, E. M., Muñoz, J. A., Blázquez, M. L., González, F., & Ballester, A. (2008a). Leaching of chalcopyrite with ferric ion. Part I: General aspects. Hydrometallurgy, 93(3-4), 81-87.

Córdoba, E. M., Muñoz, J. A., Blázquez, M. L., González, F., & Ballester, A. (2008b). Leaching of chalcopyrite with ferric ion. Part III: Effect of redox potential on the silver-catalyzed process. Hydrometallurgy, 93(3-4), 97-105.

Cui, F., Mu, W., Zhai, Y., & Guo, X. (2020). The selective chlorination of nickel and copper from low-grade nickel-copper sulfide-oxide ore: Mechanism and kinetics. Separation and Purification Technology, 239, 116577.

Da Silva, G. (2004). Kinetics and mechanism of the bacterial and ferric sulphate oxidation of galena. Hydrometallurgy, 75(1-4), 99-110.

Dutizac, J. E., MAC, D., & Ingraham, T. R. (1969). The kinetics of dissolution of synthetic chalcopyrite in aqueous acidic ferric sulfate solutions. TRANS MET SOC AIME, 245(5), 955-959.

Dutrizac, J. E. (1981). The dissolution of chalcopyrite in ferric sulfate and ferric chloride media. Metallurgical Transactions B, 12(2), 371-378.

Dutrizac, J. E. (2006). The dissolution of sphalerite in ferric sulfate media. Metallurgical and Materials Transactions B, 37(2), 161-171.

Fisher, W. W. (1994). Comparison of chalcocite dissolution in the sulfate, perchlorate, nitrate, chloride, ammonia, and cyanide systems. Minerals engineering, 7(1), 99-103.

Fomchenko, N. V., & Muravyov, M. I. (2018). Two-step biohydrometallurgical technology of copper-zinc concentrate processing as an opportunity to reduce negative impacts on the environment. Journal of environmental management, 226, 270-277.

Fomchenko, N., Uvarova, T., & Muravyov, M. (2019). Effect of mineral composition of sulfidic polymetallic concentrates on non-ferrous metals bioleaching. Minerals Engineering, 138, 1-6.

Frias, C., Gotor, J., Sanchez, F., Blanco, J., Moreno, N., & Vera, E. (2020). Advanced Concept “Poly Metallurgical Refinery” Developed by Cobre Las Cruces. In PbZn 2020: 9th International Symposium on Lead and Zinc Processing (pp. 913-922). Springer, Cham.

Ghahremaninezhad, A., Radzinski, R., Gheorghiu, T., Dixon, D. G., & Asselin, E. (2015). A model for silver ion catalysis of chalcopyrite (CuFeS2) dissolution. Hydrometallurgy, 155, 95-104.

Guo, Z. H., Pan, F. K., Xiao, X. Y., Zhang, L., & Jiang, K. Q. (2010). Optimization of brine leaching of metals from hydrometallurgical residue. Transactions of Nonferrous Metals Society of China, 20(10), 2000-2005.

Hara, Y. R., Kaluba, G., Musowoya, D., Chikontwe, K., Muchindu, C., Simfukwe, H., & Parirenyatwa, S. (2020). Leaching of Copper, Cobalt, and Nickel from Complex Ore. In Characterization of Minerals, Metals, and Materials 2020 (pp. 227-236). Springer, Cham.

Hiroyoshi, N., Arai, M., Miki, H., Tsunekawa, M., & Hirajima, T. (2002). A new reaction model for the catalytic effect of silver ions on chalcopyrite leaching in sulfuric acid solutions. Hydrometallurgy, 63(3), 257-267.

Karimi, S., Rashchi, F., & Moghaddam, J. (2017). Parameters optimization and kinetics of direct atmospheric leaching of Angouran sphalerite. International Journal of Mineral Processing, 162, 58-68.

Lorenzo-Tallafigo, J., Iglesias-Gonzalez, N., Romero, R., Mazuelos, A., & Carranza, F. (2018). Ferric leaching of the sphalerite contained in a bulk concentrate: Kinetic study. Minerals Engineering, 125, 50-59.

Madden, M. E., Madden, A. S., Rimstidt, J. D., Zahrai, S., Kendall, M. R., & Miller, M. A. (2012). Jarosite dissolution rates and nanoscale mineralogy. Geochimica et Cosmochimica Acta, 91, 306-321.

Mateos, F. B., Pérez, I. P., & Mora, F. C. (1987). The passivation of chalcopyrite subjected to ferric sulfate leaching and its reactivation with metal sulfides. Hydrometallurgy, 19(2), 159-167.

Mazuelos, A., Moreno, J. M., Carranza, F., Palomino, C., Torres, A., & Villalobo, E. (2012). Biotic factor does not limit operational pH in packed-bed bioreactor for ferrous iron biooxidation. Journal of industrial microbiology & biotechnology, 39(12), 1851-1858.

Meyer, B., Austin, J. M., & Jensen, D. (1971). Solubility of sulfur in liquid sulfur dioxide, carbon disulfide, and carbon tetrachloride. Journal of Chemical & Engineering Data, 16(3), 364-366.

Miller, J.D., Portillo, H.Q. (1979). Silver catalysis in ferric sulphate leaching of chalcopyrite.In: Lawskosky, A.J. (Ed.), 13th International Mineral Processing Congress. Part A.Elsevier, Amsterdam, pp. 851–901.

Norgate, T., & Jahanshahi, S. (2010). Low grade ores–smelt, leach or concentrate?. Minerals Engineering, 23(2), 65-73.

Palencia, I. P., & Dutrizac, J. E. (1991). The effect of the iron content of sphalerite on its rate of dissolution in ferric sulphate and ferric chloride media. Hydrometallurgy, 26(2), 211-232.

Palencia, I., Romero, R., & Carranza, F. (1998). Silver catalyzed IBES process: application to a Spanish copper–zinc sulphide concentrate. Part 2. Biooxidation of the ferrous iron and catalyst recovery. Hydrometallurgy, 48(1), 101-112.

Price, D. W., & Warren, G. W. (1986). The influence of silver ion on the electrochemical response of chalcopyrite and other mineral sulfide electrodes in sulfuric acid. Hydrometallurgy, 15(3), 303-324.

Romero, R., Mazuelos, A., Palencia, I., & Carranza, F. (2003). Copper recovery from chalcopyrite concentrates by the BRISA process. Hydrometallurgy, 70(1-3), 205-215.

Romero-García, A., Iglesias-González, N., Romero, R., Lorenzo-Tallafigo, J., Mazuelos, A., & Carranza, F. (2019). Valorisation of a flotation tailing by bioleaching and brine leaching, fostering environmental protection and sustainable development. Journal of cleaner production, 233, 573-581.

Ruan, R., Zhou, E., Liu, X., Wu, B., Zhou, G., & Wen, J. (2010). Comparison on the leaching kinetics of chalcocite and pyrite with or without bacteria. Rare Metals, 29(6), 552-556.

Ruşen, A., Sunkar, A. S., & Topkaya, Y. A. (2008). Zinc and lead extraction from Çinkur leach residues by using hydrometallurgical method. Hydrometallurgy, 93(1-2), 45-50.

Shin, D., Ahn, J., & Lee, J. (2019). Kinetic study of copper leaching from chalcopyrite concentrate in alkaline glycine solution. Hydrometallurgy, 183, 71-78.

Sokić, M. D., Stojanović, J. N., Marković, B. R., Bugarčić, M., Štrbac, N. D., Kamberović, Ž. J., & Manojlović, V. D. (2017). Effects of structural and textural grain characteristics on leaching of sulphide minerals from a polymetallic concentrate by sodium nitrate and sulphuric acid solution. Hemijska industrija, 71(6), 461-469.

Sokić, M., Marković, B., Stanković, S., Kamberović, Ž., Štrbac, N., Manojlović, V., & Petronijević, N. (2019). Kinetics of chalcopyrite leaching by hydrogen peroxide in sulfuric acid. Metals, 9(11), 1173.

Souza, A. D. D., Pina, P. D. S., Leão, V. A., Silva, C. A. D., & Siqueira, P. D. F. (2007). The leaching kinetics of a zinc sulphide concentrate in acid ferric sulphate. Hydrometallurgy, 89(1-2), 72-81.

Souza, A. D., Pina, P. S., & Leão, V. A. (2007b). Bioleaching and chemical leaching as an integrated process in the zinc industry. Minerals Engineering, 20(6), 591-599.

Tarasov, A. V., & Timoshenko, E. M. (2006). Sulfur dioxide in hydrometallurgical technologies for integrated processing of polymetallic concentrates. In 2006 TMS Fall Extraction and Processing Division: Sohn International Symposium (pp. 443-448).

Tipre, D. R., & Dave, S. R. (2004). Bioleaching process for Cu–Pb–Zn bulk concentrate at high pulp density. Hydrometallurgy, 75(1-4), 37-43.

Tipre, D.R., Vora, S.B., Dave, S.R. (1999). Comparative copper and zinc bioextraction at various stages of scale up using Thiobacillus ferrooxidans consortium. In: Amils, R., Ballester, A. (Eds.), International Biohydrometallurgy Symposium on Biohydrometallurgy and the Environment towards the Mining of the 21st Century, Part A. Elsevier, Amsterdam, pp. 219–229.

Weisener, C. G., Smart, R. S. T. C., & Gerson, A. R. (2003). Kinetics and mechanisms of the leaching of low Fe sphalerite. Geochimica et Cosmochimica Acta, 67(5), 823-830.

Xu, B., Zhong, H., Wang, K. T., & Jiang, T. (2011). Two stage adverse current oxygen pressure acid leaching of complex Cu-Pb-Zn-Ag bulk concentrate. The Chinese Journal of Nonferrous Metals, (4), 29.