



Depósito de Investigación  
Universidad de Sevilla

Depósito de investigación de la Universidad de Sevilla

<https://idus.us.es/>

“This is an Accepted Manuscript of an article published by Elsevier in Hydrometallurgy on July 2003, available at: [https://doi.org/10.1016/S0304-386X\(03\)00081-1](https://doi.org/10.1016/S0304-386X(03)00081-1) .”

# **Copper recovery from chalcopyrite concentrates by the BRISA process**

**R. Romero, A. Mazuelos, I. Palencia\*, F. Carranza**

Departamento de Ingeniería Química. Facultad de Química. Universidad de Sevilla.  
41071 Sevilla, Spain

\* Corresponding author. Tel.: +34-954-557182; fax: +34-954-557134  
E-mail address: palencia @us.es

R. Romero is professor of Computer System Dept., A. Mazuelos is associate professor of Chemical Engineering Dept., I. Palencia is professor of Chemical Engineering Dept., F. Carranza is professor of Chemical Engineering Dept.

# **Copper recovery from chalcopyrite concentrates by the BRISA process**

**R. Romero, A. Mazuelos, I. Palencia\*, F. Carranza**

## **Abstract**

The technical viability of the BRISA process (Biolixiviación Rápida Indirecta con Separación de Acciones: Fast Indirect Bioleaching with Actions Separation) for the copper recovery from chalcopyrite concentrates has been proved. Two copper concentrates (with a copper content of 8.9 and 9.9 wt%) with chalcopyrite as the dominant copper mineral have been leached with ferric sulphate at 12 g/L of ferric iron and pH 1.25 in agitated reactors using silver as a catalyst. Effects of temperature, amount of catalyst and catalyst addition time have been investigated. Small amounts of catalyst (from 0.5 to 2 mg Ag/g concentrate) were required to achieve high copper extractions (>95 %) from concentrates at 70°C and 8-10 h leaching. Liquors generated in the chemical leaching were biooxidized for ferrous iron oxidation and ferric regeneration with a mixed culture of ferrooxidant bacteria. No inhibition effect inherent in the liquor composition was detected. The silver added as a catalyst remained in the solid residue and it was never detected in solution. The recovery of silver may be achieved by leaching the leach residue in an acid-brine medium with 200 g/L of NaCl and either hydrochloric or sulphuric acid, provided elemental sulphur has been previously removed by steam hot filtration. The effect of variables such as temperature, NaCl concentration, type of acid and acidity-pulp density relationship on the silver extraction from an elemental sulphur-free residue has been examined. It is possible to obtain total recovery of the silver added as a catalyst plus 75% of the silver originally

present in concentrate B (44 mg/kg) by leaching a leach residue with a 200 g/L NaCl – 0.5M H<sub>2</sub>SO<sub>4</sub> medium at 90°C and 10 wt% of pulp density in two stages of 2 h each. The incorporation of silver catalysis to the BRISA process allows a technology based on bioleaching capable of processing chalcopyrite concentrates with a rapid kinetics.

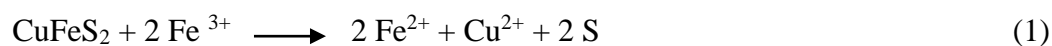
*Keywords:* Chalcopyrite, BRISA, silver catalysis

## **1. Introduction**

Copper has mainly been produced by smelting. Low-grade ore deposits of copper are not amenable to conventional pyrometallurgical processing; the pyrometallurgical treatment requires flotation concentrates with a minimum copper grade around 20%. In most low-grade deposits chalcopyrite is finely dispersed on pyrite and other sulphides and the pyrometallurgical treatment of these ores would require extensive grinding and flotation of the sulphides to produce finely divided concentrates. The production of these concentrates is not attractive from an economical point of view because of the intensive energy consumption in grinding and the low recovery. An alternative for the treatment of these deposits involves a coarser grind to produce a rougher concentrate yielding low copper concentrates (around 10% of copper) with an important energy saving and a higher metallic recovery. These concentrates, in which chalcopyrite is the majority copper-bearing mineral, have to be processed hydrometallurgically.

Among other hydrometallurgical processes, the BRISA process has been developed and successfully applied in recent years for the recovery of copper from

copper concentrates (Palencia et al., 2002). The BRISA process (Biolixiviación Rápida Indirecta con Separación de Acciones: Fast Indirect Bioleaching with Actions Separation), developed to improve the kinetics of bioleaching of metallic sulphides, is based on bioleaching by the indirect mechanism. In the BRISA process, the bioleaching process is performed in two separate stages: (a) a chemical stage based on Eq. (1) and (b) a biological stage based on Eq. (2) for the biooxidation of ferrous iron consumed in the chemical stage. Details of the BRISA process have previously been given (Carranza et al., 1997a; Palencia et al., 2002). The treatment of copper concentrates with chalcopyrite as the dominant copper mineral copes with the fact that chalcopyrite is, among the copper sulphides, the most refractory to leaching. The chemical leaching of chalcopyrite by an acidified solution of ferric sulphate (Eq. (1) ) proceeds at a very low rate.



The rate of this reaction in the range 50-110°C follows a parabolic law. Most authors agree that the decrease in rate is due to the formation of a film which builds up on the surface of the mineral and opposes the electron transfer from chalcopyrite to the ferric medium, necessary for the redox reaction. With regard to the nature of this passivating layer, there are two basic hypotheses: elemental sulfur (Miller and Portillo, 1979) and an intermediate sulphide resulting from the transformation of the original chalcopyrite, its reactivity being lower than that of the latter (Parker et al., 1981; Barriga et al. 1987). To improve chalcopyrite leaching rate much effort has been made and

several catalysts have been proposed, silver ion being the most effective one. It is well known that low concentrations of silver ion greatly accelerate the chalcopyrite leaching. Several mechanisms have been proposed to explain the catalytic action of the silver ion (Miller and Portillo, 1979, Hiroyoshi, N., 2002) their description and discussion being beyond the aim of this paper.

The use of silver as a catalyst in the chemical stage of the BRISA process is possible as the silver used for the activation of chalcopyrite remains in the leached residue as  $\text{Ag}_2\text{S}$  (the main proportion) and  $\text{Ag}^0$  (Miller and Portillo, 1979; Price and Warren, 1986; Barriga Mateos et al., 1993; Carranza, 1997b) and it could also be as argentojarosite in some conditions of temperature and acidity (Palencia et al., 1998). Silver ion inhibits the growth of ferroxidant bacteria used for ferric iron regeneration in the biological stage of the BRISA process; however, the separation of chemical and bacterial actions enables the use of this catalytic system because silver is always in the ferric leaching circuit and it will never reach the bioreactor. On the other hand, since practically the whole amount of silver added as a catalyst remains in the residue, its recovery at low cost is required in order to make this process commercially attractive.

Figure 1 shows the flowsheet of the BRISA process for the treatment of chalcopyrite concentrates. It consists of a stage of ferric leaching in which a silver salt is added. The solid residue contains elemental sulphur and all the silver added as a catalyst. The recovery of silver is accomplished after elemental sulphur removal.

The aim of this work is to establish the technical viability of the treatment of two copper concentrates with chalcopyrite as the dominant copper mineral via the BRISA process. In order to do this, the different stages of the process have been separately studied:

- Ferric sulphate leaching of concentrates with silver as a catalyst.

- Ferrous iron biooxidation of leach liquors.
- Silver extraction from the leach residue.

## **2. Materials and Methods**

### *2.1. Materials*

Two copper concentrates have been studied. Both were rougher concentrates:

A: Rougher concentrate from Compañía Minera del Pacífico (Chile)

B: Rougher concentrate from Industrial Minera Mejicana Sociedad Anónima (IMMSA) obtained from an ore from Compañía Minera Cananea (Mexico).

#### *2.1.1. Mineralogical and Chemical Composition*

Samples of the two materials were mounted in polished sections for mineralogical study using optical microscopy and scanning electron microscopy (SEM) equipped with an energy dispersive X-ray analyzer (EDX). The mineralogical data are summarised in Table 1. Quantitative mineralogical composition was determined by image analysis from optical microscopy images. Image analysis showed that the concentrate contained mainly chalcopyrite together with pyrite and gangue. In both concentrates gangue minerals were mainly silica, silicates, iron oxides and traces of titanium oxides, all of them liberated from sulphide minerals. Available granulometric data are shown in Table 2.

Samples were also analyzed by wet chemical methods using reagent grade chemicals and distilled water. The chemical analysis of concentrates is shown in Table 3

## 2.2. Procedure

### 2.2.1. Ferric sulphate leaching experiments

Leaching experiments were carried out in two different types of reactors under batch leaching conditions, shake flasks and stirred tanks. In all cases ferric sulphate solutions were first heated to the desired temperature and the reaction was initiated by adding a dried mineral sample.

Shake-flask tests.- Experiments were carried out in 250 mL Erlenmeyer flasks with 100 mL of ferric sulphate solution. The flasks were continuously agitated on an orbital shaker at  $280 \text{ min}^{-1}$  and thermostatted by forced air circulation.

Stirred tank leaching tests.- Experiments were carried out in a 7 L glass, baffled thermostatted vessel mechanically stirred with a six-bladed flat disk turbine. The solution volume was 4 L and the stirring speed  $800 \text{ min}^{-1}$ . During each experiment, samples of pulp were taken periodically and, after filtration, were analyzed for copper, total iron and ferrous iron.

In all tests, the water losses due to evaporation were determined by weight and were taken into account during copper recovery calculations. At the end of the experiment, the slurry was filtered using  $0.45 \mu\text{m}$  Millipore filters and the residue, after being washed with distilled water and dried, was stored in a desiccator for silver recovery. The leach liquor was analyzed for metals and was used for ferrous iron biooxidation tests. Copper extraction was calculated from mass balance and analysis of solids (concentrate and residue). In catalytic tests, the leaching medium consisted of ferric sulphate with silver as silver sulphate. An aliquot of a solution of silver sulphate in aqueous sulphuric acid at pH 1.25 containing 500 mg/L of silver was added to the ferric sulphate solution. The amount of catalyst is expressed as milligramme of  $\text{Ag}^+$ /gramme of concentrate. Unless otherwise stated, the experimental conditions were:



initial pH of solution 1.25, ferric iron concentration 12 g/L and duration of the test 8 h. A pH value of 1.25 was chosen as the more suitable for the process (Carranza et al., 1997b). Preliminary studies indicated that the copper extraction was almost independent of pulp density for both concentrates provided there remains sufficient ferric iron in solution. Because all the experiments were carried out at low ferric iron concentration (12 g/L) in batch systems, the studied pulp densities need to be low. As mentioned earlier (Carranza et al., 1997b) in a continuous operation the pulp density of leaching might be higher than the values considered in this study. The effect of the variables such as amount of catalyst, temperature and catalyst addition time was investigated.

#### 2.2.2. *Ferrous iron biooxidation*

The culture used for ferrous iron biooxidation was originally isolated from Rio Tinto mine drainage waters and it consists mainly of *Thiobacillus ferrooxidans*, *Leptospirillum ferrooxidans* and some heterotrophic bacteria mainly related to *Acidophilium*. Stock cultures were routinely maintained at 31°C on a modified Silverman and Lundgren 9k nutrient medium (Silverman and Lundgren, 1959) supplemented with copper sulphate (20 g/L) at pH 1.25; an aliquot of the culture was transferred into a fresh medium every 8 days. The ferrous iron biooxidation was carried out both in batch and continuous-flow reactors. Details of the experimental procedure have been given in a previous paper (Palencia et al., 1998).

#### 2.2.3. *Silver recovery*

The method followed for silver recovery consisted of two stages:

- 1) Elemental sulphur extraction. The dried sulphur-bearing residue from the ferric sulphate leach of the concentrate was placed on a fritted glass disk connected to a

vacuum water pump and to the outlet of a small boiler which produced steam that was reheated to 140 °C. As the steam passed through the filter (30 min) the sulphur content of the solid melted to form molten sulphur droplets which coalesced to form larger drops and finally to form a continuous liquid sulphur phase that flowed and passed through the filter. The residue was weighed before and after the extraction and the elemental sulphur was determined by difference.

2) Silver extraction. After separating the elemental sulphur the residue thus obtained was subjected to a wide range of NaCl-HCl or H<sub>2</sub>SO<sub>4</sub> leaching conditions. Silver dissolution experiments were conducted in 250-mL Erlenmeyer flasks with 100 mL of a solution containing NaCl and either hydrochloric acid or sulphuric acid. The flasks were agitated on an orbital shaker at 280 min<sup>-1</sup> and thermostatted by forced air circulation (for tests at 80°C and 90°C, the flasks were thermostatted on a hot plate and magnetically stirred). Solutions were first heated to the desired temperature, after which a dried elemental sulphur free-residue was introduced to start the leach experiment. At the end of the reaction period, the slurry was filtered while hot and the liquors were stored for analysis. The solid was washed with distilled water and dried at room temperature. Silver, copper and iron in solutions and in solid after digestion were determined. Metal extractions were calculated from analysis of solids and mass balance. Acid consumption during silver extraction was evaluated by difference between the acid in the leaching solution and the acid in the final leach liquor. The procedure consisted of determining the acid by titration with 1M NaOH solution to a pH of 1.5 in order to avoid alkali consumption by the precipitation of metallic hydroxides in the leach liquor. Silver extraction refers to the silver contained in the residue which included both the silver added as a catalyst and the silver originally present in the concentrate.

### 2.3. Analysis

Copper, iron and silver in leaching liquors were determined by Atomic Absorption Spectroscopy. Ferrous iron concentration was determined by standard potassium dichromate solution in an automatic titrator. The solids samples were analyzed by a wet chemical method using aqua regia at the boiling temperature of the mixture followed by Atomic Absorption Spectroscopy for metals (together with a Mercury/Hydride System for the determination of mercury and hydride-forming elements As, Sb, Bi using 3% NaBH<sub>4</sub> in 1% NaOH as reductant) and gravimetric analysis with barium chloride for sulphur.

## 3. Results

### 3.1. Ferric sulphate leaching of concentrates

The leaching of concentrates was initially studied at 25 °C and 70°C in shaken flasks. Table 4 shows the results of leaching tests. Pulp density was 2 (w/v %) for the concentrate A and 1.5 (w/v %) for the concentrate B. Ferric iron demand is expressed as gramme of ferrous iron generated per kg of concentrate. Copper extractions are low (lower than 25 % even at 70 °C) thus indicating slow kinetics of chalcopyrite with ferric sulphate. Therefore, it is necessary to employ a catalyst such as Ag (I) that kinetically activates the reaction between chalcopyrite and Fe (III).

### *3.1.1. Effect of the amount of catalyst*

For each concentrate, eight shake-flask tests were carried out with different amounts of silver over the range 0-4 mg silver/g of concentrate at 70 °C and 2 (w/v %) of pulp density.

The leaching results, shown in Figure 2, indicate a marked effect of the presence of catalyst on the copper extraction. There is a sharp increase in copper extraction up to 0.2 mg Ag/g concentrate for the concentrate A and up to 1 mg Ag/g concentrate for the concentrate B and this increase continues up to 0.5 and 3.0 mg Ag/g concentrate for concentrates A and B respectively; further increases in the amount of catalyst have little effect on the copper extraction.

### *3.1.2. Effect of temperature*

The effect of temperature on the copper extraction was studied in stirred tanks over the range 60-90 °C at 2 and 1.5 (w/v %) pulp density for concentrates A and B respectively. Concentrates were activated with 0.5 mg/g concentrate A and 2 mg Ag/g concentrate B. The leaching results, shown in Figures 3 and 4, indicate a marked effect of temperature on the copper extraction. From those figures it is evident that the initial rate of the catalytic reaction (slope of the curve) increased with increasing temperature, but the extent of passivation also increased leading to a final copper extraction which was maximum at 70 °C for both concentrates. The passivation effect became important at temperatures higher than 70 °C: at 80 °C the kinetic curve markedly flattens. This passivation is attributable to the extensive formation of jarosite compounds at high temperatures which precipitate on the elemental sulphur layer thus restricting the mass transfer of ions to solution ( $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$ ) and preventing iron (III) access to the mineral sulphide surface (Dutrizac and Jambor, 1984). The decrease in the weight loss

as temperature increases above 80°C (Tables 5 and 6) is consistent with such an explanation. Besides, the formation of argentojarosite  $[\text{AgFe}_3(\text{SO}_4)_2(\text{OH})_6]$  in this system which sequester silver ion from solution could also explain these results.

### *3.1.3. Effect of the catalyst addition time*

It has been demonstrated that the presence of sphalerite and secondary copper sulphides has a negative effect on the catalytic action of silver on chalcopyrite leaching; they act as sequestering agents for the silver solution, thus preventing its catalytic action on chalcopyrite (Barriga et al. 1987). Although secondary copper sulphides are present in concentrate B in small proportion they can partially sequester silver from solution and be responsible for the difficulty in reaching copper extractions higher than 95%. So the removal of these sulphides is necessary before silver catalytic leaching. In order to substantiate this fact the experiments were carried in which silver was not added at the beginning of the test but after 1 or 2 h from the start. Tests were run for 12 h at 70 °C, 1.5 w/v % pulp density and 2 mg Ag/g of concentrate in stirred tanks. Figure 5 shows that the final copper extraction was higher in those tests in which silver was added after 1 or 2 h of ferric sulphate leaching. The highest copper extraction (97.2%) was obtained with 1 h of non-catalytic followed with 11 h of catalytic leaching. The kinetic curves of tests in which silver was added after a given period of time from the start of leaching (1 and 2 hours) show an initial rate of the catalytic period faster than that of the test in which silver was added at the beginning of leaching; this feature will be advantageous in a continuous operation since the effect of short-circuiting flow (bypass) on the overall copper extraction will be reduced. Therefore the installation of a non-catalytic leaching stage before the catalytic one would have a beneficial effect on the copper extraction from concentrate B. The treatment of concentrate A would not require this non-catalytic

leaching stage since it does not contain appreciable amounts of secondary copper sulphides.

### *3.2. Ferrous iron biooxidation*

Liquors generated in the chemical leaching of concentrates were biooxidized in order to detect the presence of any inhibitory effect inherent in the liquor composition on the ferrous iron biooxidation and to establish the technical feasibility and effectiveness of this stage. Ferrous iron concentration in those liquors varied from 5 to 7 g/L, copper concentration ranged from 1.3 to 1.8 g/L and silver was never detected. Three media were firstly tested in static conditions: (i) liquor from the ferric sulphate leaching of concentrates, (ii) liquor from the ferric sulphate leaching of concentrates with 5 wt.% of salts of the 9k Silverman and Lundgren nutrient medium and (iii) 9k Silverman and Lundgren nutrient medium (with 9 g/L  $\text{Fe}^{2+}$  as ferrous sulphate) plus 5 g/L  $\text{Cu}^{2+}$  as copper sulphate. The three media were inoculated and incubated at 31 °C showing similar kinetic results; therefore, it can be concluded that the leaching liquors, with a composition very similar to that of an industrial treatment plant, can be effectively biooxidized by the mixed culture employed without the faintest sign of inhibition. On the other hand, an input of nutrient supplement is not necessary.

Afterwards, the continuous ferrous iron biooxidation of leach liquors on a supported biofilm reactor was undertaken. The packed-bed biooxidation reliability was evaluated by switching the inlet from maintenance liquors (tap water containing 9 g/L  $\text{Fe}^{2+}$  and 5 g/L  $\text{Cu}^{2+}$  at pH 1.25) to leach liquor while maintaining the same pH. Leach liquors, after pH adjustment to 1.25 with sulphuric acid, were continuously fed to this reactor. The results demonstrated that, after three days of biooxidation, the biofilm

retained its activity for ferrous iron oxidation. In all cases, ferrous iron oxidation ranged from 98% to 100% with mean residence times from 3 to 5 h.

### 3.3. *Silver recovery*

As mentioned earlier previous data indicated that virtually all of the silver added as catalyst remained in the leached residue. Also, the conditions of acidity, temperature and ferric sulphate concentration in the ferric sulphate catalyzed leaching are favorable for the precipitation of silver as argentojarosite [Dutrillac and Jambor, 1984]. The recovery of silver added as a catalyst to the ferric sulphate leaching may be achieved by leaching the leach residue in an acid-brine medium and either hydrochloric or sulfuric acid, provided elemental sulphur has been previously removed (Palencia et al., 1998). The recovery of elemental sulphur and silver as by-products makes the process more economically attractive

The effect of variables such as temperature, NaCl concentration, type of acid and acidity-pulp density relationship on the silver extraction from an elemental sulphur-free residue was examined. For concentrate A, the bulk of the testwork was performed with two S-free residues containing 1369 and 715 mg/kg of silver. For concentrate B, two S-free residues containing 3118 and 2536 mg/kg of silver were used. Tables 7-10 show the experimental conditions and results for concentrate A and Tables 11 and 12 show results for concentrate B.

An increase in silver extraction was observed as temperature increased (Tables 7 and 11). Table 7 shows that leaching at ambient temperature even at long times did not lead to high silver extractions. Above 50°C, the temperature improvement effect was small (Table 7). It is important to highlight that silver extraction was very fast for S-free residues of both concentrates: 98-99% of the silver was extracted after 1 h of leaching at

temperatures of 70-90°C, the leaching residues having a silver content of the order of that of the original concentrates (10-15 and 34-64 mg/kg Ag for concentrates A and B respectively).

Table 8 shows that the use of hydrochloric acid lead to silver extractions higher than those achieved with sulphuric acid of the same concentration no matter what the sodium chloride concentration of the leaching medium was. The effect of the sodium chloride concentration was negligible in hydrochloric medium but some positive effect was observed in sulphuric medium as it increased from 50 to 200 g/L. Taking into account that solid weight losses were higher in tests with hydrochloric acid, it is postulated that hydrochloric acid is more efficient than sulphuric acid for the dissolution of jarosites, which is required for high silver extraction.

Tables 9 and 10 show the effect of the acidity-pulp density relationship on the silver extraction of leached S-free concentrate A in sulphuric and hydrochloric media respectively. In both cases the acid demand for complete silver extraction increases with an increase in the pulp density. As already shown (Table 8), the substitution of hydrochloric acid by sulphuric acid of equal concentration leads to a noticeable decrease in silver extraction. Table 10 shows that for a pulp density of 1 (w/v %) the use of 0.25 M sulphuric acid leads to silver extractions of the order of those obtained with 0.1 M hydrochloric acid. Consequently, from a technical point of view hydrochloric acid can be substituted by sulphuric acid which represents both economic and handling advantages.

Results of the effect of the acidity-pulp density relationship on the silver extraction of leached S-free concentrate B, shown in Table 12, confirm the effect observed for concentrate A (Tables 9 and 10): the demand of acid for complete silver extraction increases with an increase in the pulp density. With 0.5 M sulphuric acid, the use of



pulp densities higher than 5 (w/v %) leads to an important decrease of the silver extraction, the residues having very high silver content. Tests with 5 and 10 (w/v %) pulp density were carried out again with intermediate acid addition, the silver extraction being similar to those obtained without acid addition. Therefore, the problem was supposed to be related to the equilibrium of the reaction and not only to the lack of acidity. With the purpose of confirming this hypothesis, and getting closer to the conditions of a continuous operation, two-stage leaching tests were performed. Results of one of these tests are summarized in Table 13. A mass balance for silver in the whole process (ferric sulphate leaching, elemental sulphur extraction and silver recovery) allows us to state that it is possible to obtain total recovery of the silver added as a catalyst plus 75% of the silver originally present in the concentrate (which is very interesting as this concentrate contains 44 mg/kg of silver). To calculate the average acid consumption, tests with 5 and 10 (w/v %) of pulp density were selected. The average acid consumption was 32 g of sulfuric acid per kg of concentrate.

#### **4. Conclusions**

The results obtained in this work show that chalcopyrite concentrates can be effectively leached by the BRISA process with fast kinetics and a high copper recovery. Two rougher copper concentrates having 8.9 and 9.9 wt% Cu with chalcopyrite as the dominant copper-bearing mineral and minor contents of others sulphides have been tested. The ferric sulphate leaching was carried out in agitated batch conditions with 12 g/L  $\text{Fe}^{3+}$  and pH 1.25 using silver as a catalyst. High copper extractions (>95 wt%) were obtained by activating concentrates A and B with 0.5 and 2 mg Ag/g of concentrate respectively at 70°C and 8/10 h leaching. Liquors generated in the ferric sulphate

leaching were silver-free and the ferrous iron was effectively biooxidized both in static and flow conditions at 31°C. The biooxidation stage regenerates the leaching agent (ferric iron) required in the chemical stage. Silver has been effectively recovered from residues by leaching them with an acid-brine medium with 200 g/L of NaCl and 0.5 M sulphuric acid provided elemental sulphur had been previously removed. High silver extractions (above 98 wt%) was obtained in 1h at 70°C for both concentrates. It is possible to obtain total recovery of the silver added as a catalyst plus some of the silver originally present in the concentrate by increasing temperature to 90°C provided that the acid was not limiting.

### **Acknowledgements**

The authors express their appreciation to Compañía Minera del Pacífico and Compañía Minera Cananea for making available the samples used in this study.

## References

Barriga Mateos, F., Pereda Marín, J., Palencia Pérez, I., 1993. Bacterial leaching of a bulk flotation concentrate of chalcopyrite-sphalerite. *Biorecovery* 2, 195-218

Barriga, F., Palencia, I., Carranza, F., 1987. The passivation of chalcopyrite subjected to ferric sulfate leaching and its reactivation with metal sulfides. *Hydrometallurgy* 19, 159-168.

Carranza, F., Palencia, I., Romero, R., Iglesias, N., 1997a. Application fields of the BRISA process. Influence of the ore mineralogy on the process flowsheet. In: Australian Mineral Foundation (Ed.), *Proceedings of the International Biohydrometallurgy Symposium IBS97-BIOMINE 97 "Biotechnology Comes of Age."*, Sydney, Australia, 4-6 August, 1997, M2.1.1 – M2.1.10.

Carranza, F., Palencia, I., Romero, R., 1997b. Silver catalyzed IBES process: application to a spanish copper-zinc sulphide concentrate. *Hydrometallurgy* 44, 29-42.

Dutrizac; J.E., Jambor, J.L., 1984. Formation and characterization of argentojarosite and plumbojarosite and their relevance to metallurgical processing. In: Park, W.C., Hausen, D.M., Hagni, R.D. (Eds.), *Applied mineralogy in the minerals industry. The Metallurgical Society of AIME, Los Angeles, California*, pp. 507-530.

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, 257-267.

Miller, J.D., Portillo, H.Q., 1979. Silver catalysis in ferric sulfate leaching of chalcopyrite. In: XIII Int. Mineral Process, Congr., Warsaw, Poland, pp. 691-742.

Palencia, I., Romero, R., Carranza, R., 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, 101-112.

Palencia, I., Romero, R., Carranza, F., Mazuelos, A., 2002. Treatment of secondary copper sulphides (chalcocite and covellite) by the BRISA process. *Hydrometallurgy* 66, 85-93.

Parker, A.J. Paul, R.L., Power, G.P., 1981. Electrochemical aspects of leaching copper from chalcopyrite in ferric and cupric salt solutions. *Aust. J. Chem.* 34, 13-34.

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, 303-324.

Silverman, M.P., Lundgren, D.G., 1959. Studies on the chemoautotrophic iron bacteria *Ferrobacillus ferrooxidans*. An improved medium and harvesting procedure for securing high yields. *J. Bacteriol.* 77, 642-64.

Table 1

## Mineralogical data for the materials

Concentrate	Major mineral phase			Minor mineral phase	Traces
	Chalcopyrite (wt. %)	Pyrite (wt. %)	Gangue (wt. %)		
A	27	44	29	Covellite, bornite, chalcocite	Molybdenite, tennantite
B	24	31	43	Bornite, chalcocite (1.5%), covellite (0.5%)	Sphalerite, tetrahedrite, tennantite, molybdenite

Table 2

## Granulometric data for the concentrates

Concentrate	Particle size ( $\mu\text{m}$ )					
	d <sub>10</sub>	d <sub>20</sub>	d <sub>50</sub>	d <sub>80</sub>	d <sub>90</sub>	d <sub>100</sub>
A	1.7	2.9	26.6	98.7	131.8	251.2
B	2.0	3.1	9.0	37.9	60.0	142.5

Table 3

## Analytical data for the materials

Element	Concentrate A	Concentrate B
Cu (wt. %)	8.9	9.9
Fe (wt. %)	31.4	21.4
S (wt. %)	32.0	25.3
Zn (wt. %)	0.02	0.1
Pb (mg/kg)	80	260
Ag (mg/kg)	12	44
Au (mg/kg)	1.9	0.5
As (mg/kg)	30	5000
Sb (mg/kg)	0.9	0.1
Bi (mg/kg)	3.4	n.d.
Hg (mg/kg)	3.3	n.d.
Cd (mg/kg)	3.0	-
Insolubles (wt. %)	24.0	34.9

n.d. not detected

Table 4

Leaching of concentrates A and B (shaken flasks, pH = 1.25, 8h, pulp density: 2 (w/v %) for A and 1.5 (w/v %) for B)

Concentrate	[Fe <sup>3+</sup> ] (g/L)	Temperature (°C)	Cu extraction (%)	Solid weight loss (wt. %)	Residue Cu content (wt. %)	Fe <sup>2+</sup> (g/kg of concentrate)
A	0 <sup>a</sup>	70	6.0	6.0	9.0	14
A	12	25	5.8	3.3	8.8	17
A	12	70	14.4	7.2	8.3	133
B	0 <sup>b</sup>	70	12.8	3.1	9.0	21
B	12	25	10.8	3.6	9.2	15
B	12	70	20.7	6.7	8.5	179

<sup>a</sup> Assay performed with a pulp density of 5 (w/v %) and 6 h

<sup>b</sup> Assay performed during 6 h

Table 5

Effect of temperature on the catalytic ferric sulphate leaching of concentrate A (stirred tanks, pH = 1.25, pulp density: 2 (w/v %), ferric iron concentration: 12 g/L, [Ag<sup>+</sup>] = 0.5 mg/g concentrate, 8 h)

Temperature (°C)	Cu extraction (%)	Solid weight loss (wt. %)	Residue Cu content (wt. %)	Fe <sup>2+</sup> (g/kg of concentrate)
60	90.3	16.4	1.04	379
70	97.5	20.6	0.28	379
80	94.5	16.2	0.61	384
90	86.5	8.9	1.36	350

Table 6

Effect of temperature on the catalytic ferric sulphate leaching of concentrate B (stirred tanks, pH = 1.25, pulp density: 1.5 (w/v %), ferric iron concentration: 12 g/L, [Ag<sup>+</sup>] = 2 mg/g concentrate, 10 h)

Temperature (°C)	Cu extraction (%)	Solid weight loss (wt. %)	Residue Cu content (wt. %)	Fe <sup>2+</sup> (g/kg of concentrate)
60	82.1	17.9	2.13	358
70	95.3	19.2	0.58	366
80	82.2	20.7	2.25	358
90	67.8	16.9	3.88	414

Table 7

Effect of temperature on the silver extraction of leached sulphur-free concentrate A (0.1 M HCl, 200 g/L NaCl, 1h, pulp density: 1 (w/v %), initial solid Ag content: 1369 mg/kg)

Temperature (°C)	Ag extraction (%)	Solid weight loss (wt. %)	Residue Ag content (mg/kg)
25	78.3	0.7	299
25*	88.0	3.5	248
50	97.1	3.7	42
70	98.9	5.5	15
90	99.3	6.5	10

\* Assay performed during 6 h

Table 8

Effect of the NaCl concentration in chloride and sulphuric media on the silver extraction of leached sulphur-free concentrate A (70°C, 1h, pulp density: 1 (w/v %), initial solid Ag content: 715 mg/kg)

[NaCl] (g/L)	[Acid] (M)	Ag extraction (%)	Solid weight loss (wt. %)	Residue Ag content (mg/kg)
50	0.05 (H <sub>2</sub> SO <sub>4</sub> )	79.4	3.6	153
100	0.05 (H <sub>2</sub> SO <sub>4</sub> )	80.2	3.0	146
150	0.05 (H <sub>2</sub> SO <sub>4</sub> )	80.2	3.8	147
200	0.05 (H <sub>2</sub> SO <sub>4</sub> )	86.0	3.3	103
50	0.1 (HCl)	97.7	5.5	17
100	0.1 (HCl)	98.6	5.6	11
150	0.1 (HCl)	98.6	5.1	11
200	0.1 (HCl)	98.4	5.8	12

Table 9

Effect of the acidity-pulp density relationship in chloride medium on the silver extraction of leached sulphur-free concentrate A (70°C, 200 g/L NaCl, 1 h, initial solid Ag content: 1369 mg/kg)

Pulp density (w/v %)	[HCl] (M)	Ag extraction (%)	Solid weight loss (wt. %)	Residue Ag content (mg/kg)
1	0.1	98.9	5.5	15
5	0.1	99.0	4.8	14
10	0.1	96.9	4.6	45
10	0.2	99.3	6.9	10

Table 10

Effect of the acidity-pulp density relationship in sulphuric medium on the silver extraction of leached sulphur-free concentrate A (70°C, 200 g/L NaCl, 1h)

Pulp density (w/v %)	[H <sub>2</sub> SO <sub>4</sub> ] (M)	Initial Ag content (mg/kg)	Ag extraction (%)	Solid weight loss (wt. %)	Residue Ag content (mg/kg)
1	0.05	715	86.0	3.3	103
1	0.25	715	96.0	5.5	31
1	0.5	715	98.6	6.3	11
1	1	715	98.8	5.7	9
5	0.5	582	98.6	9.8	9
10	0.5	649	98.4	7.5	11
20	0.5	649	95.4	7.5	32

Table 11

Effect of temperature on the silver extraction of leached sulphur-free concentrate B (200 g/L NaCl, 0.5 M H<sub>2</sub>SO<sub>4</sub>, pulp density: 1 (w/v %), 1 h, initial Ag content: 3118 mg/kg)

Temperature (°C)	Ag extraction (%)	Solid weight loss (wt. %)	Residue Ag content (mg/kg)
70	98.0	3.0	64
80	98.9	7.0	37
90	99.0	10.0	34

Table 12

Effect of acidity-pulp density relationship on the silver extraction of leached sulphur-free concentrate B (200g/L NaCl, 70 °C, 2 h, initial Ag content: 2536 mg/kg)

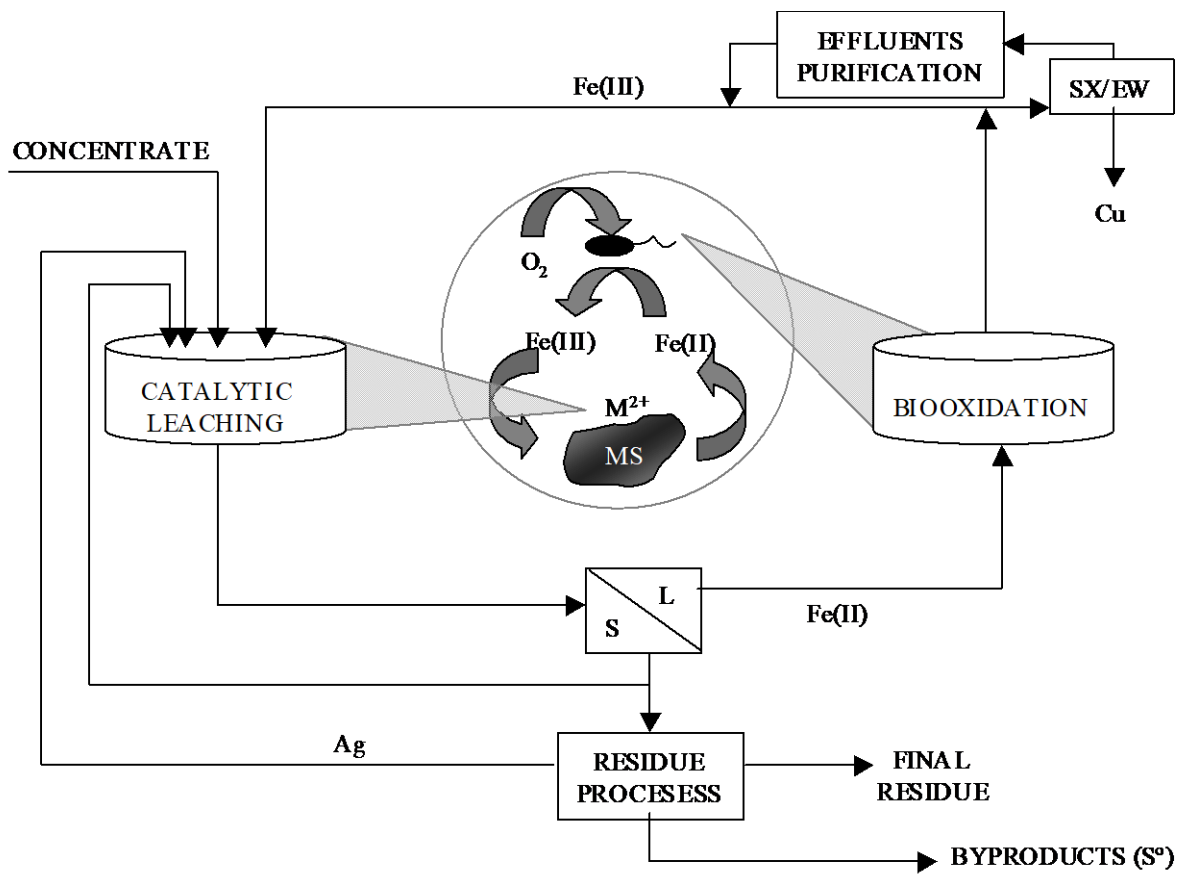
Pulp density (w/v %)	[H <sub>2</sub> SO <sub>4</sub> ] (M)	Ag extraction (wt. %)	Solid weight loss (wt. %)	Residue Ag content (mg/kg)
1	0.05	97.1	3.7	78
1	0.25	98.3	3.8	44
1	0.5	98.3	4.1	44
5	0.5	94.5	3.2	144
10	0.5	87.0	3.4	342

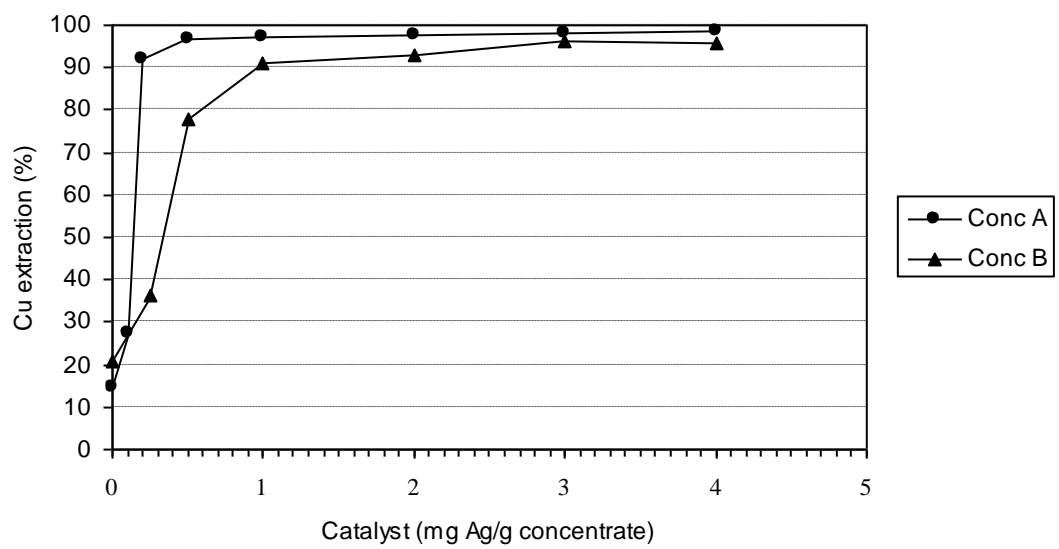


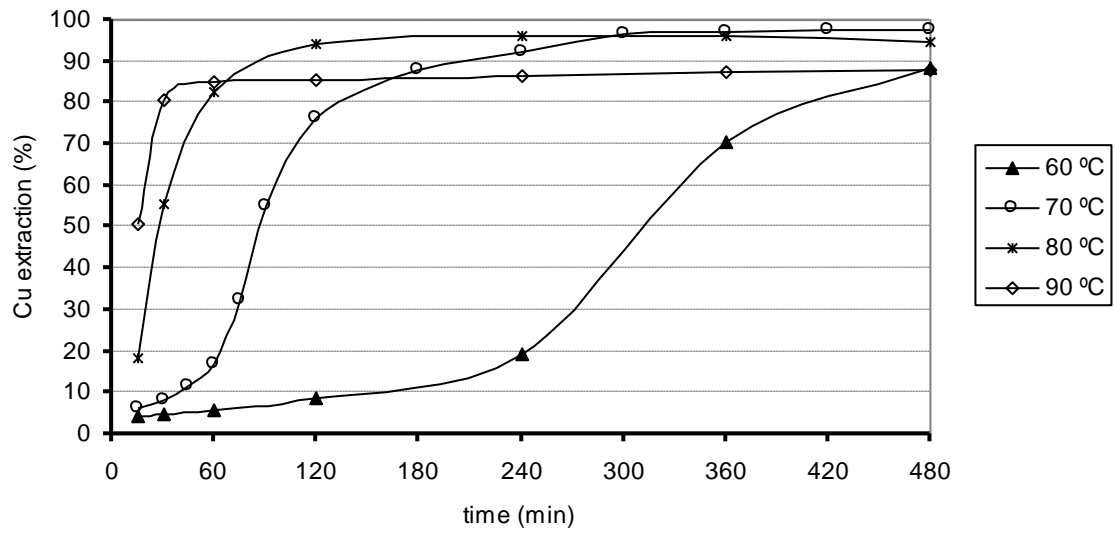
Table 13

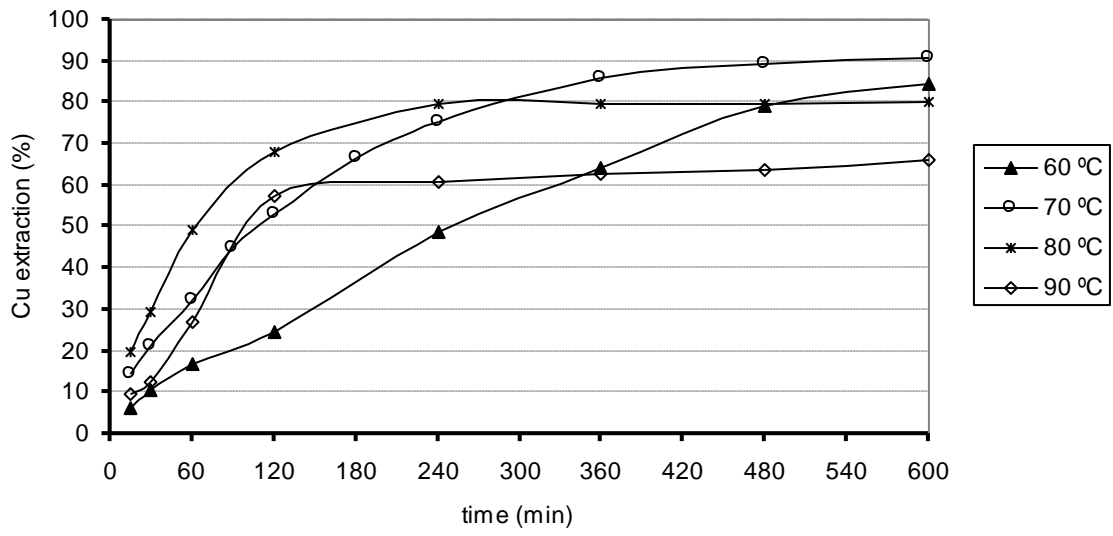
Two stages silver extraction of leached sulphur-free concentrate B (200g/L NaCl, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 90°C, pulp density: 10 (w/v %))

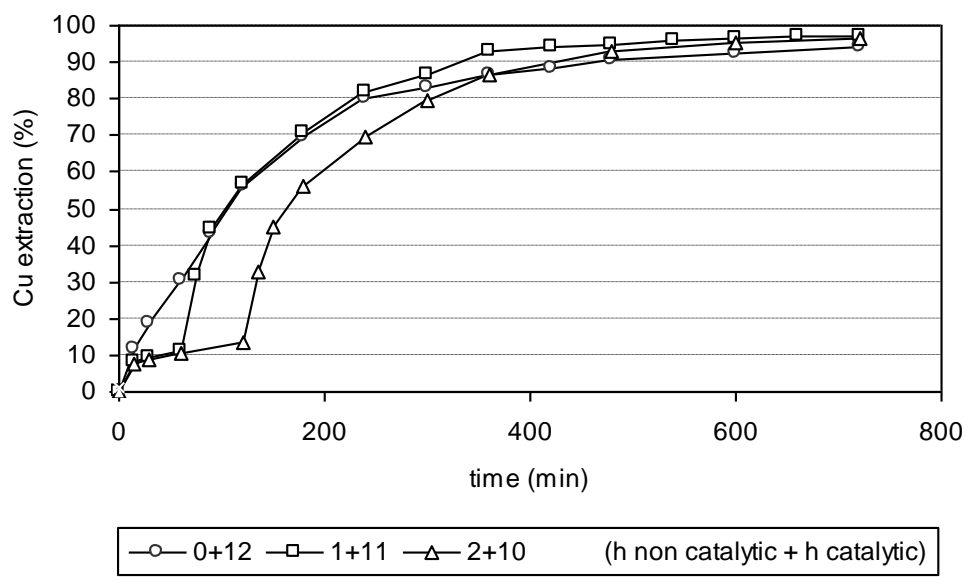
Time (h)	Initial Ag content (mg/kg)	Final Ag content (mg/kg)	Ag extraction (%)
2 (1 <sup>st</sup> stage)	2536	83	97.0
2 (2 <sup>nd</sup> stage)	83	14	99.5











## Figure captions

Figure 1. Flowsheet of the BRISA process for chalcopyrite concentrates.

Figure 2. Effect of the amount of catalyst on the ferric sulphate leaching of the concentrates (shaken flasks, pH = 1.25, pulp density: 2 (w/v %), 70 °C, ferric iron concentration: 12 g/L, 8 h).

Figure 3. Effect of temperature on the silver catalyzed ferric sulphate leaching of concentrate A. (stirred tanks, pH = 1.25, pulp density: 2 (w/v %), ferric iron concentration: 12 g/L,  $[Ag^+] = 0.5$  mg/g concentrate, 8 h).

Figure 4. Effect of temperature on the silver catalyzed ferric sulphate leaching of concentrate B (stirred tanks, pH = 1.25, pulp density: 1.5 (w/v %), ferric iron concentration: 12 g/L,  $[Ag^+] = 2$  mg/g concentrate, 10 h).

Figure 5. Effect of the catalyst addition time on the catalytic ferric sulphate leaching of concentrate B (stirred tanks, pH = 1.25, pulp density: 1.5 (w/v %), 70 °C, ferric iron concentration: 12 g/L,  $[Ag^+] = 2$  mg/g concentrate, 12 h).