

COPPER SOLVENT EXTRACTION FROM CHALCOPYRITE CONCENTRATE ACID LEACH SOLUTIONS BY LIX 984

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Abstract

Copper production from ores or sulphide concentrates is classically realized by pyrometallurgical route. In this study, hydrometallurgical treatment of a copper sulphide concentrate, provided by Hajar Mine (ONA-Group, Morocco), was tested by using a mixture of nitric and hexafluorosilicic acids. Copper is present in the solid product as chalcopryrite and its amount is 28.1 % by weight. Leaching stage allows to dissolve more than 90% of copper with is accompanied, in the same averages, by Zn and Fe. The leach solution obtained has pH = 0.6 and Eh = 580 mV/ENH and contains 19.3 g/L Cu, 18.1 g/L Fe, 4.5 g/L Zn and 0.03 g/L Pb. The recovery of copper from this leach solution was carried out by solvent extraction using Lix 984, diluted in Escald 110.

McCabe - Thiele distribution isotherms showed that at pH 1.7 total and selective copper extraction can be realized with $O_o:O_a = 1.5:1$ in 3 extraction stages. Stripping of the loaded copper by treating the organic phases was easily obtained by a sulphuric acid solution.

Keywords: Chalcopryrite, Solvent extraction, Nitric acid, Hexafluorosilic acid, Lix 984.

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1. Introduction

Hydrometallurgy of chalcopyrite knew a leap in the latter decades to remediate the problems linked to the environmental pollution and the cost of pyrometallurgical process. This is even the copper production is realized classically by pyrometallurgic way. Numerous media for leaching chalcopyrite were investigated, but no one of them reached the industrial stage [1-6].

Copper recovery from leach solutions is also well known. Solvent extraction is the most studied technique. It was applied for copper recovery from sulphuric solutions, using Lix reagents [7,8], from chloride solutions, in Cuprex process [4] and ammoniacal solution by using some Lix reagents as Lix 54, 26, 34 [8-10].

A singular leaching medium, H_2SiF_6 – HNO_3 mixture which was tested on copper refining anodic slimes [11] was also tested on the leaching of chalcopyrite concentrate provided by Hajar Mine (Morocco) [12]. The concentrate contains 28.1% Cu, 5.8% Zn, 1.9% Pb, 33.7% S. In the leaching stage dissolution of copper is effective but not selective. Leach solution obtained is so rich in copper, lead and zinc.

The aim of this work was to test the solvent extraction of copper from a nitro-fluorosilicic acid leach solution, rich in copper associated to various other metals such as Zn, Pb and Fe. This solution (Hajar Mine Copper Concentrate Leach Solution (HMCCLS)) is obtained by the treatment in HNO_3 - H_2SiF_6 mixture of a sample of Copper Concentrate coming from Hajar Mine (Morocco). The leach solution being concentrated in various metals, the study had also concerned the selectivity of copper from these elements.

A similar solution containing copper, As, Se, Te and Sb was treated by an oxime reagent (Lix 63 -70) and a dithiophosphonic acid (Cyanex 301). Results showed that copper extraction is more efficient by Cyanex 301 [13].

The study consisted on the appliance of one kind of oxime reagents (Lix 984) which are classically used for the selective recovery of copper from sulphuric solutions. The copper loaded organic phases are then subjected to a stripping stage using the sulphuric acid solution.

2. Experimental procedure

A stock of Hajar Mine Copper Concentrate Leach Solution (HMCCLS) was prepared by treating the solid sample of copper concentrate in a mixture of H_2SiF_6 – HNO_3 . Solution obtained is characterized by : pH = 0.6, Eh = 580 mV/ENH, 19.3 g/L Cu, 18.1 g/L Fe, 4.5 g/L Zn and 0.03 g/L Pb.

Lix 984 used here is provided by Henkel Corporation. The solvent of dilution, which was useful in this study was Escaid 110.

Lix 984 being a mixture of two extractants (5 dodecylsalicylaldoxime (Lix 860) and the 2-hydroxy-5-nonyl-acetophenone oxime (Lix 84)) with a volume ratio of 1. These extractants are chelating agents belonging to the oximes family.

The equilibrium distributions of copper between the organic and aqueous phase were determined by mixing equal volumes (50 ml) of the two phases by rapid magnetic stirring. After each test, the phases were separated and contents of the elements concerned are determined in the aqueous phase before and after extraction, to determine their rate of recovery by Inductive Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). Organic phase metal contents were determined by mass balance.

3. Results and Discussion

To determine the effect of the most significant parameters governing the solvent extraction, namely: the effect of the pH of the solution, the kinetics of the extraction, and extractant concentration in the solvent % (v/v), the experiments were carried out at ambient temperature and atmospheric pressure, with organic phase (O_o) to aqueous phase (O_a) volume ratio of 1:1 ($\text{O}_o/\text{O}_a = 1:1$). The distribution isotherms of copper were established according to McCabe - Thiele diagrams', that permit to determine the number of theoretical counter-current stages of extraction.

The copper re-extraction from the loaded organic phases was carried out by a sulphuric acid solution. The studied parameters are the acid concentration of the stripping solution, the re-extraction kinetics and the O_o/O_a volume ratio.

3.1. Copper extraction from HMCCLS

By varying the concentrations of the extractants in Escaid, between 5 and 20% by volume, and keeping constant the other operational parameters : 15 minutes of contacting time, $\text{O}_o/\text{O}_a = 1:1$ and ambient temperature, the results obtained are presented in the Fig. 1 which shows that the recovery of copper increases with the reagent concentration. The distribution coefficient ($E = \text{Cu concentration in organic phase} / \text{Copper concentration in aqueous phase}$) at 20% is 0.39. It is also very selective toward copper. For the continuation of the study, one will retain a concentration of 20% in volume.

While operating with a concentration of the extractant of 20% v/v, an ambient temperature and a O_o/O_a of 1:1, one obtains the results presented in Fig. 2, when the contact time varies from 2 to 15 minutes. The kinetic of extraction reaches the equilibrium in 10 minutes. The rate of extraction of copper is then about 28%.

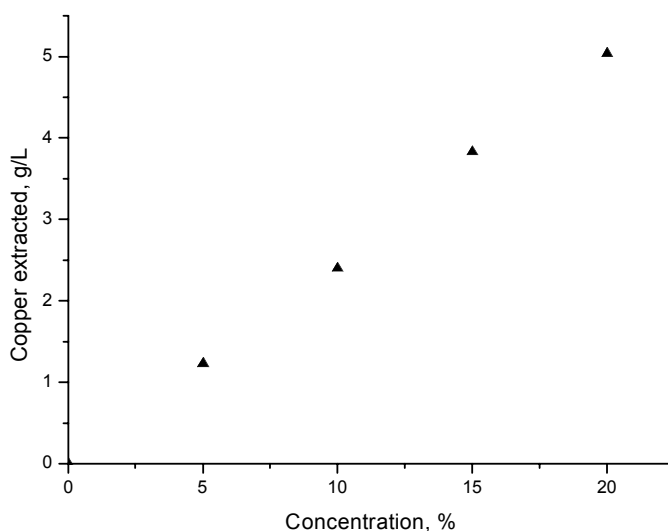


Fig. 1. Effect of the concentration of Lix 984 on copper extraction from HMCCLS: $\text{pH} = 0.6$; $\text{O}_o/\text{O}_a = 1:1$.

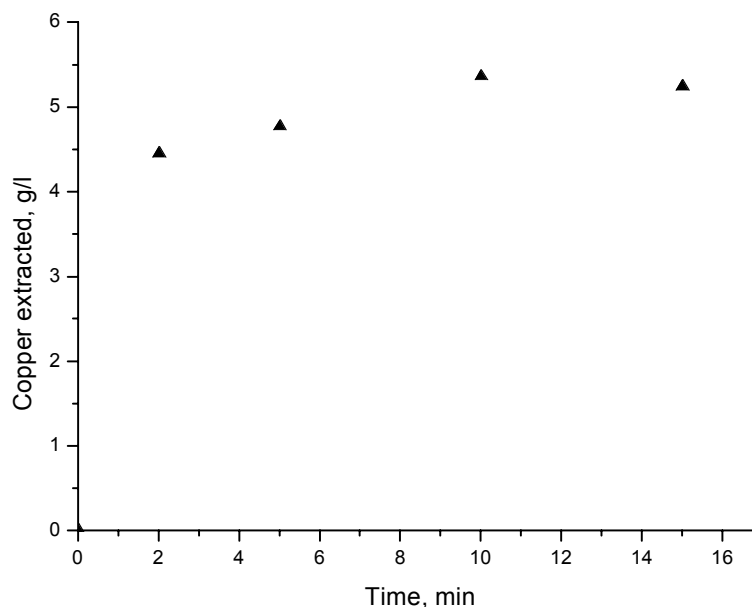
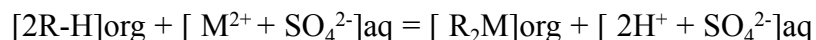


Fig. 2. Kinetic of copper extraction by Lix 984 20%, from HMCCLS:
pH = 0.6; $\phi_o/\phi_a = 1:1$.

From Extraction and re-extraction mechanisms by oximes given by the general following reaction [14], it appears that the pH of the solution is one of the most significant parameters controlling the extraction and the stripping of the elements :



With an aim of improving copper extraction, pH of the solution was adjusted to 1.7, by addition of NH_4OH 28% by volume. This pH adjustment leads to the following composition of the solution: 16.28 g/L Cu; 16.15 g/L Fe; 3.92 g/L Zn and 0.027 g/L Pb, and a formation of a white precipitate. The analysis of this precipitate by X-rays diffraction shows that it is amorphous with a possible presence of $PbSO_4$. The analysis by scanning electron microprobe (SEM) reveals the presence of SiO_2 and $PbSO_4$. The fact that the nitrogen, hydrogen and the fluorine are very light elements and cannot be

detected by the SEM, lets think that this product would also contain $(\text{NH}_4)_3\text{SiF}_6\text{NO}_3$ and $(\text{NH}_4)_2\text{SiF}_6$.

The tests on this solution, under the operating conditions of 10 minutes of contact time and $\text{Oo/Oa} = 1:1$, with 20% of concentration by volume of the extractant, allow to obtain the results shown in Table 1. It appears that, compared with that obtained in the case of the solution at $\text{pH} = 0.6$, the distribution coefficient of copper is improved at $\text{pH} 1.7$ reaching 1.05, being enhanced by 2.8 times. Extraction capacity of Lix 984 is consequently increased by 1.6 and remains also very selective with respect to copper.

The isotherms of distribution of McCabe - Thiele are obtained while varying the Oo/Oa , with 20% of extractants concentrations and a contact time of 10 minutes. The results of these tests are given in Fig. 3 and 4. They highlight that the extractant capacity of copper is enhanced by the adjustment of pH to 1.7. For total copper extraction from the crude pH solution (0.6), more than 7 stages of extraction with Oo/Oa of 3:1 are necessary, but at pH of 1.7, total copper can be achieved in only 3 stages with Oo/Oa of 1.5:1. The residual contents of copper are lower than 100 mg/L.

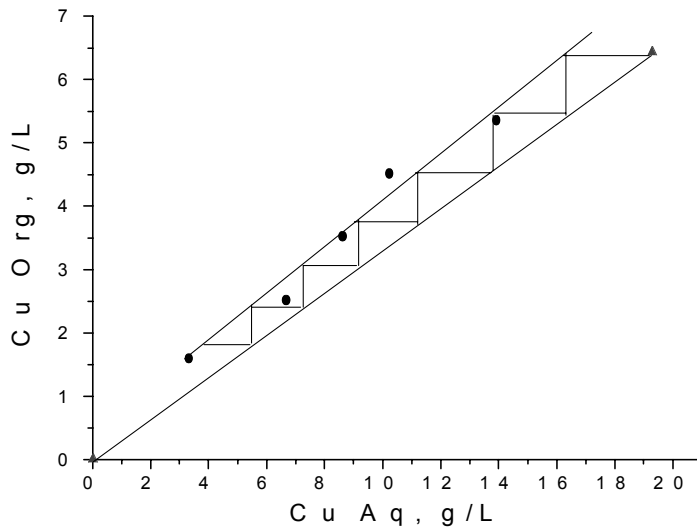


Fig. 3. Extraction isotherm of copper by Lix 984 20% v/v from HMCCLs: $\text{Oo/Oa} = 3:1$, $\text{pH} = 0.6$.

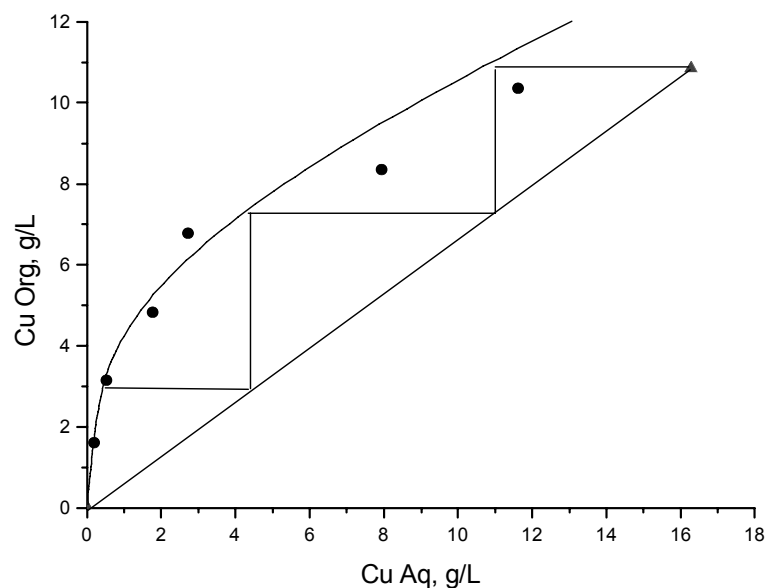


Fig. 4. Extraction isotherm of copper by Lix 984 20% v/v from HMCCLS; $\varnothing_o/\varnothing_a = 1.5:1$, $\text{pH} = 1.7$.

Table 1. Effect of the solution pH on the extraction of Cu, Zn, Fe and Pb by Lix 984 20% v/v from HMCCLS.

PH	Elements extraction, %			
	Cu	Fe	Zn	Pb
0.6	28	0	0	0
1.7	51	0	0	0

3.2. Re-extraction of copper from loaded organic phases

Copper stripping was studied on organic phase (Lix 984 20% v/v) charged by contact with the aqueous phase at pH of 1.7, $\varnothing_o/\varnothing_a = 1:1$, 15 minutes of contact time, ambient temperature and atmospheric pressure. The loaded organic phase obtained contains 8.2 g/L.

In this part of the work, the stripping solution was made of sulphuric acid

which is more employed for the recovery of copper from oximes, and in which the electrolysis of the contained copper is the conventional technique applied in the hydrometallurgy.

The variable parameters of the study were the concentration of the stripping solution, the kinetics of copper recovery and the O_o/O_a volume ratio. The constant parameters were the ambient temperature and the atmospheric pressure.

For the effect of the concentration of H_2SO_4 on copper re-extraction, concentrations of H_2SO_4 were: 0.5; 1; 1.5 and 2 M, 20 minutes of contact time between the phases and $\text{O}_o/\text{O}_a = 1:1$. The results presented in figure 5 showed that the backwash of copper from Lix 984 containing 8.2 g/L depends on the concentration of the sulphuric acid. The totality of copper is extracted when one uses H_2SO_4 2 M. From the kinetic of copper recovery study, the contact time varied from 2 to 20 minutes, and sulphuric acid concentration was fixed to 2 M, as well as O_o/O_a to 1:1. Results presented in Figure 6 highlight very fast kinetic for the copper re-extraction. With an equilibrium time approximately 5 minutes one re-extracts 7.66 g/L Cu, corresponding to the recovery of 93% Cu. If one prolongs the time of 15 minutes contact additional, copper recovery reaches 99.6%.

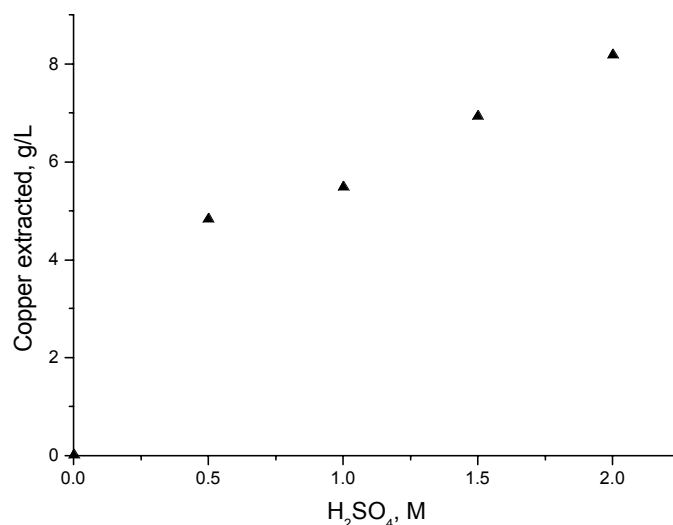


Fig. 5. Effect H_2SO_4 on the copper stripping from Lix 984 ;
 $\text{O}_o/\text{O}_a = 1$, contact time : 20 min.

Stripping operation under the conditions of concentration of H_2SO_4 2 M, variable O_o/O_a and a contact time of 20 minutes, result in the extraction of the totality of existing copper when $\text{O}_o/\text{O}_a = 0.5:1$ and $1:1$. However the aqueous phases obtained under these conditions contain less than 8.2 g/L Cu. By extraction at counter-current, using $\text{O}_o/\text{O}_a = 3:1$ (Fig. 7), totality of the copper contained in Lix 984 is reached in two stages of re-extraction. The aqueous phases obtained enriched in copper and their concentration is about 24.6 g/L Cu.

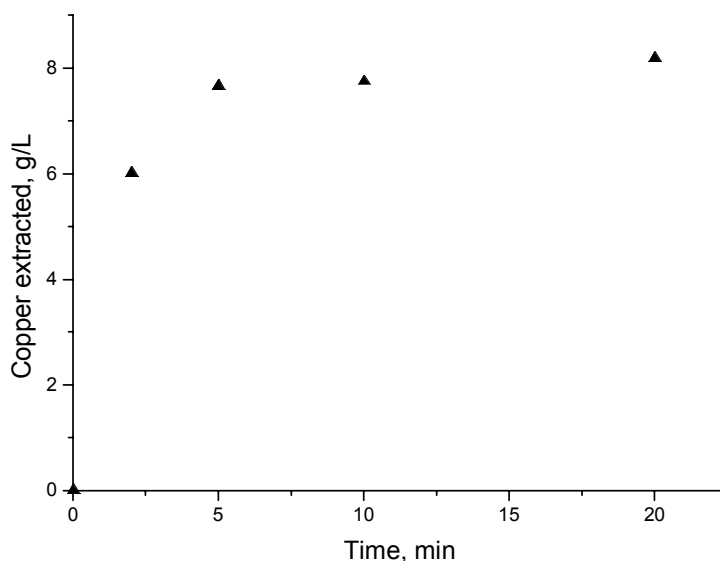


Fig. 6. Kinetic of the copper stripping from Lix 984; $\text{O}_o/\text{O}_a = 1$

4. Conclusions

Solvent extraction of copper from the nitro - fluorosilicic acid solutions was realised for the first time using oximes extractants. The results show that the pH of the crude solution is determinant on the capacity of the extractant. Lix 984 is selective toward copper in the presence of the other elements (Fe, Zn and Pb). However, a very acid pH negatively affects the extractant capacity of the reagent. Indeed, with pH 0.6, copper exhaustion of the solution by an

extraction with counter-current requires several stages, whereas with pH 1.7, the total extraction takes place only into 3 extraction stages. The recovery of the copper contained in the loaded organic phases is easily realisable by a sulphuric acid solution. This stage permits to obtain solution rich in copper which is able to be electrowon.

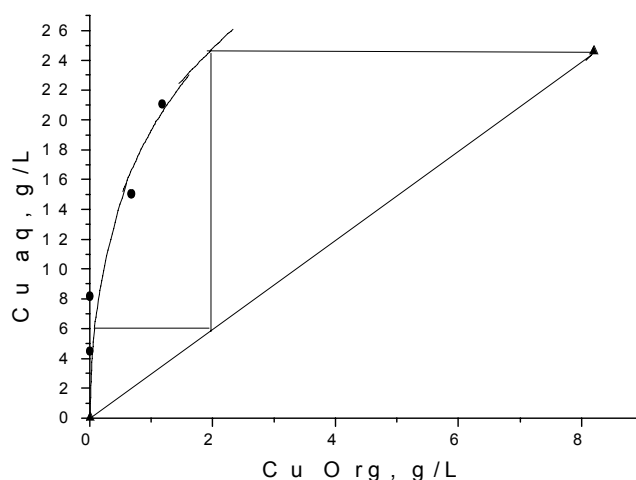


Fig. 7. Isotherm of copper stripping from Lix 984: $\text{Oo/Oa} = 3:1$

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