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COPPER RECOVERY FROM CHALCOPYRITE CONCENTRATE ACID LEACH SOLUTIONS BY ACORGA M5397

Khalid EL AMARI¹, El-Aid JDID², Pierre BLAZY³

¹ Laboratoire Géoressources, Unité Associée au CNRST (URAC 42), Faculté des Sciences et Techniques Guéliz, B. P. 549, 40000 Marrakech, Maroc; elamari@fstg-marrakech.ac.ma

² LEM UMR 7569, Nancy Université, ENSG-INPL-CNRS, 15 avenue du Charmois, B.P. 54 501, Vandoeuvre-Les-Nancy, France

³ ENSG-INPL, Rue du Doyen Marcel Roubault, B. P. 40, 54501 Vandoeuvre, France

Abstract: Chalcopyrite concentrate from Hajar Mine, Morocco, was leached with nitro-fluosilicic acid leach solution. The pregnant leach solution obtained contained 19.3 g/dm³ Cu, 18.1 g/dm³ Fe, 4.5 g/dm³ Zn and 0.03 g/dm³ Pb. Copper recovery from this pregnant leach liquor was performed by solvent extraction using Acorga M5397 diluted in Escaid 110. McCabe–Thiele distribution isotherms showed that at pH 1.7 complete and selective copper extraction can be achieved with $\phi_o/\phi_a = 1.5/1$ in 3 stages of extraction. Stripping of the loaded copper by treating the organic phases by a fresh sulphuric acid solution was easily realized.

Keywords: *Copper solvent extraction, solvent extraction selectivity, nitro-fluorosilic acid, AcorgaM5397*

Introduction

Metal copper production from ores can be performed by two main methods: conventional pyrometallurgical method (smelting/converting) and hydrometallurgical method (leaching followed by solvent extraction – electrowinning process, SX-EW) (Padilla et al., 2010).

Since 1900, when the world production was less than 0.5 teragrams (Tg) (500 thousand tonnes) world copper mining production has been growing by around 4% per year to reach nearly 16 Tg in 2009. SX-EW production, virtually non-existing before the 1960's, reached nearly 3.3 Tg in 2009 according to International Copper Study Group (2010). The ore quality is of increasingly lower grade with poor physical rock quality and high impurity level (Helle et al., 2010).

At the present pyrometallurgical route is the most frequently used technique to produce copper metal from chalcopyrite concentrates (Padilla et al., 2010; Habashi, 2007). However, copper production by heap leaching combined with SX-EW has become a gigantic operation (Habashi, 2007). According to Watling (2006), more than 20% of refined copper is produced via hydrometallurgy.

Other processes like bacterial leaching, roast-leach, chloride leaching, and pressure oxidation especially for dirty or low grade sulphide concentrates receive much more attention (Pradham et al., 2008; Dreisinger, 2004; Blazy and Jdid, 2002). However the importance of hydrometallurgical techniques involving SX - EW for recovery of copper from oxides and also some sulphide ores is growing rapidly (International Copper Study Group, 2010). They had gained wide acceptance as one of the new tools of hydrometallurgy, and are becoming the key processes in copper hydrometallurgy.

Copper solvent extraction from pregnant sulphuric acid leach solutions is widespread commercially with the use of LIX reagents (Suttill, 1989; Arbiter and Fletcher, 1994). It is also performed from chloride solutions in Cuprex process (Dalton et al., 1991) and ammoniacal solutions using some LIX reagents as LIX 54, 26, 34, 622N... (Arbiter and Fletcher, 1994; Dalton et al., 1991; Yoshinari and Katsutoshi, 1988; Henkel Corporation; Panigrahi et al., 2009).

Chalcopyrite is the most abundant copper sulphide mineral and most refractory regarding chemical leaching as well as bioleaching (Koleini et al., 2010) and the leaching of chalcopyrite remains the most difficult stage of the process. In the case of Hajar Mine copper concentrate, Morocco, leaching stage was performed using a complex acid leach medium, mixture of nitric acid and fluorosilicic acid (El Amari et al., 2000). Previous work performed by El Amari et al. (2006) showed that copper dissolution was non selective and the pregnant leach solution was rich in copper, iron, zinc and lead. In the case of this complex solution LIX 984 was efficient and selective in separation of copper from Zn, Pb and Fe.

For the purpose of the present study, copper solvent extraction was carried out on the same pregnant leach nitro-fluorosilicic acid solution as in previous work (El Amari et al., 2006), but using a modified nonylsalicyl aldoxime reagent (Acorga M5397) to evaluate its selectivity and loading capacity of copper. The copper loaded organic phases were then subjected to a stripping stage using a fresh sulphuric acid solution.

Experimental

Pregnant leach solution (PLS) used in this study was obtained by the treatment of a sample of copper concentrate from Hajar Mine (Morocco) in $\text{HNO}_3\text{-H}_2\text{SiF}_6$ mixture. Leaching tests were carried out according to El Amari et al. (2000). Principal characteristics of this solution are listed in Table 1.

Table 1. Characteristics of the feed solution (PLS)

	pH	Eh (mV/ENH)	Cu (g/dm ³)	Zn (g/dm ³)	Fe (g/dm ³)	Pb (g/dm ³)
PLS	0.6	580	19.3	4.5	18.1	0.03

Commercial extractant Acorga M5397, provided by ICI Specialty Chemicals, is a chelating agent belonging to the oximes family. It is a blend of 2hydroxy-5-nonylsalicylaldoxime, a long chain alcohol and a metallurgical grade diluent. Escaid 110 was used for the dilution of the Acorga solvent in this study with.

The equilibrium distribution of copper between the organic and aqueous phases was determined by mixing equal volumes (50 cm³) of the two phases by rapid stirring with magnetic stirrer. After each test both phases were separated and the concentration of the elements concerned (Cu, Fe, Pb and Zn) in the aqueous phase before and after extraction was determined by Inductive Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES, to determine the rate of their recovery. Metal content in the organic phase was determined from the mass balance.

Results and discussion

To determine the effect of the most significant parameters governing the solvent extraction, namely: pH of the solution, the kinetics of the extraction, and extractant concentration in the solvent, the experiments were carried out at ambient temperature and atmospheric pressure, with organic phase (φ_o) to aqueous phase (φ_a) volume ratio of 1/1 ($\varphi_o/\varphi_a = 1/1$). The leach solution was rich in various metals. The concern of the study was to recover selectively copper, keeping the other elements in the initial PLS solution. The distribution isotherms of copper were established according to McCabe–Thiele diagrams that permit the determination of the theoretical number of counter-current stages of extraction.

The copper re-extraction from the loaded organic phase 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 φ_o/φ_a volume ratio.

Copper extraction from PLS

Effect of extractant concentration

Varying the concentration of the extractant in Escaid between 5 and 20% by volume, and keeping constant the other operational parameters: 15 minutes of contacting time, $\varphi_o/\varphi_a = 1/1$ and ambient temperature, the dependence of percentage extraction of copper on extractant concentration was established (Fig. 1). The results show the high extraction capacity of Acorga M5397 and the increases in the recovery of copper with extractant concentration. In spite of this good extraction capacity, the cop-

per distribution coefficient of 0.63 seems to be less important because of high concentration of this element in the initial aqueous solution. In the case of PLS Acorga M5397 is also very selective toward separation of copper from iron and zinc. Coextraction of lead reached about 17% at this Acorga concentration value. This could be due to the small concentration of lead in PLS. Taking into account lead/copper concentration ratio in PLS (less than 0.2%) one can neglect this coextraction. Loaded organic phase in these conditions contains 7.47g/L Cu and 5 mg/L Pb.

The rest of the experiments were performed at the extractant concentration of 20 vol%.

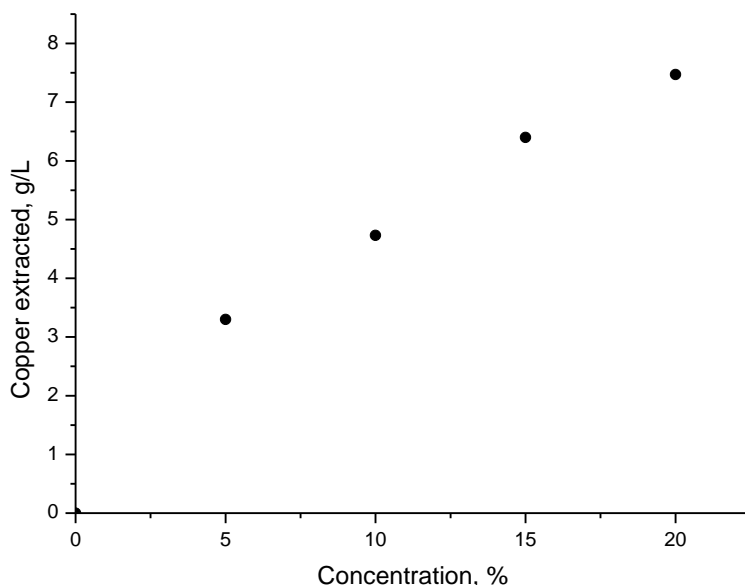


Fig. 1. Effect of concentration of Acorga M5397 on the copper extraction from PLS (19.3 g/ dm³ Cu) at pH = 0.6 and $\varphi_o/\varphi_a = 1/1$

Kinetics of extraction

The results presented in Fig. 2 were obtained at the concentration of the extractant of 20%, ambient temperature, φ_o/φ_a of 1/1, and the contact time varying from 2 to 15 minutes. Extraction reached the equilibrium in 10 minutes. The rate of extraction of copper amounted to about 38%. Iron and zinc remained in aqueous phase confirming the high selectivity of Acorga M5397 toward these elements. Lead was coextracted at the level of 15%.

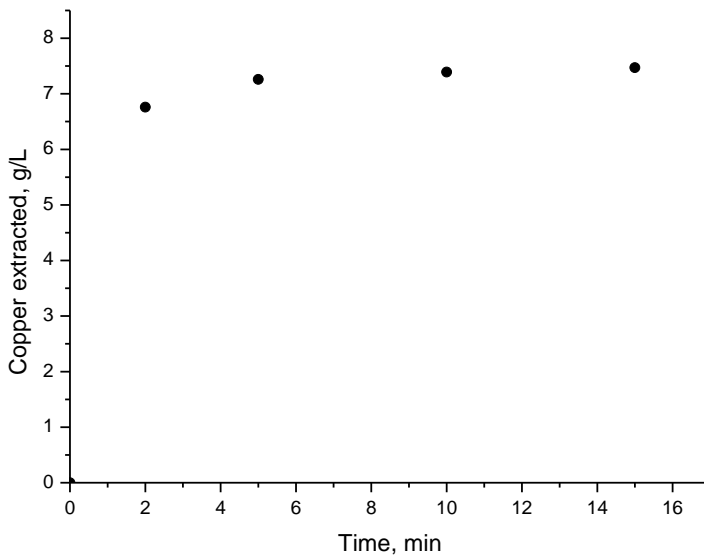


Fig. 2. Kinetics of copper extraction from PLS (19.3 g/L Cu) by Acorga M5397 20% at pH = 0.6 and $\varphi_o/\varphi_a = 1/1$

Effect of Organic/Aqueous ratio

The effect of φ_o/φ_a ratio was studied by varying the φ_o/φ_a from 1/2 to 10/1, with 20% Acorga M5397 (v/v) in Escaid 110, contact time 10 min and pH of 0.6. Results, listed in Table 2, suggest a decrease in copper raffinate with increase of φ_o/φ_a . Coextraction of iron and zinc did not exceed 3%. Coextraction of lead reached 43% for φ_o/φ_a of 10/1.

Table 2. Concentration of metals in raffinate (φ_a) and of Cu in the organic phase (φ_o) during extraction of copper with Acorga M5397 (pH 0.6)

φ_o/φ_a ratio	φ_a in equilibrium				φ_o in equilibrium
	Cu (g/dm ³)	Fe (g/dm ³)	Zn (g/dm ³)	Pb (g/dm ³)	Cu (g/dm ³)
Feed	19.30	18.10	4.50	0.03	
1/2	14.66	18.02	4.42	0.019	9.22
1/1	11.80	18.04	4.50	0.025	7.47
2/1	7.78	18.10	4.33	0.022	5.745
3/1	5.86	18.10	4.48	0.020	4.47
5/1	4.02	17.98	4.46	0.026	3.05
10/1	2.24	17.55	4.37	0.017	1.703

Based on data of Table 2, the McCabe–Thiele copper distribution isotherm (Fig. 3) shows that in such a very acidic solution more than 6 extraction counter-current stages with a φ_o/φ_a of 2/1 are necessary to recover 88% of copper from the PLS.

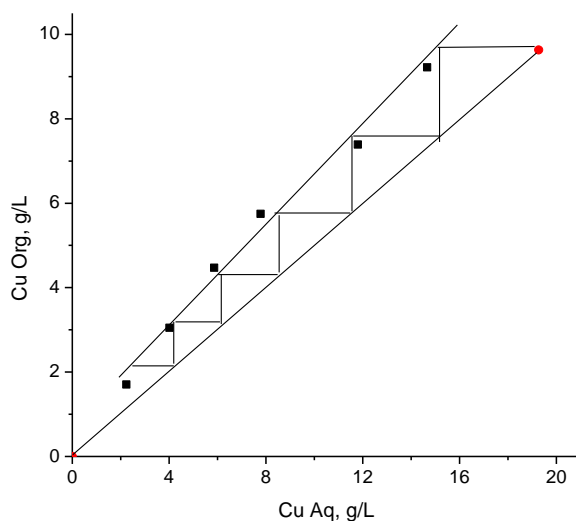
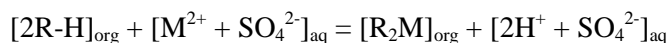


Fig. 3. The McCabe–Thiele diagram for copper extraction from PLS (19.3 g/dm³ Cu) with Acorga M5397 20% at $\phi_o/\phi_a = 2/1$ and pH = 0.6

According to the extraction and re-extraction mechanisms by oximes reagents, given by Rao et al. (2000) and Kitobo et al. (2010), it appears that pH of the solution is one of the most significant parameters controlling the extraction and the re-extraction of the metal ions.



where: M^{2+} – metallic ion in aqueous solution,

$[2R-H]_{\text{org}}$ – extractant dissolved in the organic phase,

$[R_2M]_{\text{org}}$ – charged metal organic complex dissolved in the organic phase.

The extraction coefficient can be determined as:

$$\log E = \log k + 2 \log [HR]_{\text{org}} + 2 \text{pH}$$

where k is the equilibrium constant.

To improve the copper extraction pH of the solution was adjusted to 1.7 by adding of NH₄OH to 28% by volume. This pH adjustment leads to the composition of the solution listed in Table 3. The decrease of Cu, Zn, Fe and Pb in the final solution is due to the formation of a white precipitate (El Amari et al., 2006).

Table 3. Characteristics of aqueous feed solution (PLS) after pH readjustment

	pH	Eh (mV/ENH)	Cu (g/dm ³)	Zn (g/dm ³)	Fe (g/dm ³)	Pb (g/dm ³ L)
PLS	1.7	506	16.28	3.92	16.15	0.027

The effect of φ_o/φ_a ratio on this solution is presented in Table 4. Compared with those obtained in the case of PLS at pH = 0.6, the distribution coefficient of copper was improved, reaching 1.63 with the increase of copper loading capacity of Acorga M5397 by a factor of about 1.4 (for φ_o/φ_a 1/1). Extraction rates of iron and zinc did not change confirming the high selectivity with respect to copper. Extraction of lead reached 15%.

Table 4. Concentration of metals in raffinate (φ_a) and of Cu in organic phase (φ_o) during extraction of copper with Acorga M5397 (pH 1.7)

φ_o/φ_a ratio	φ_a in equilibrium				φ_o in equilibrium
	Cu (g/dm ³)	Fe (g/dm ³)	Zn (g/dm ³)	Pb (g/dm ³ L)	Cu (g/dm ³)
Feed	16.28	16.15	3.92	0.027	
1/2	10.47	15.76	3.87	0.027	11.62
1/1	6.18	16.03	3.92	0.023	10.10
2/1	1.67	16.15	3.92	0.027	7.31
3/1	0.69	16.15	3.92	0.024	5.20
5/1	0.32	16.15	3.92	0.024	3.19
10/1	0.13	15.90	3.92	0.024	1.62

The distribution isotherm, measured under the same conditions of the solution but at pH = 1.7 (Fig. 4) from data of Table 4 shows that one can theoretically exhaust the solution in three counter-current stages by Acorga M5397 20% v/v using φ_o/φ_a of 1.5/1. In two stages 94% of copper could be recovered, the residual content of copper is less than 1 g/dm³.

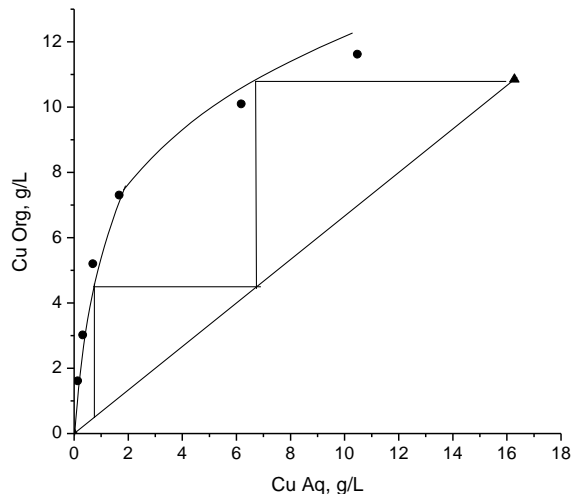


Fig. 4. The McCabe–Thiele diagram for copper extraction from PLS (16.28 g/dm³ Cu) with Acorga M5397 20% at $\varphi_o/\varphi_a = 1.5/1$ and pH = 1.7

Stripping of copper loaded Acorga M5397

Copper stripping was studied on organic phase charged by contact with the aqueous phase at pH of 1.7, $\varphi_o/\varphi_a = 1/1$, 15 minutes of contact time, ambient temperature, atmospheric pressure and 20% Acorga M5397 (v/v) concentration. The loaded organic phase contained 9.74 g/dm³.

At this stage of the study the stripping solution was made of sulphuric acid which is mostly used for the recovery of copper from oximes, and in which the recovery of copper by electrolysis 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 φ_o/φ_a volume ratio. The constant parameters were the ambient temperature and the atmospheric pressure.

Tests were carried out with the variable concentration of the fresh sulphuric acid solution (0.5 M to 2 M), $\varphi_o/\varphi_a = 1/1$ and the contact time of 20 minutes. From the results presented in Fig. 5 one can deduce that copper recovery from the organic phase charged with 9.74 g/dm³ is complete only when the concentration of sulphuric acid reaches 2 M. Then, the kinetics of copper recovery was determined by varying the time of contact between 2 and 20 minutes, and fixing φ_o/φ_a to 1/1. Figure 6 highlights relatively fast kinetics for the copper stripping. For an equilibrium time of approximately 10 minutes one re-extracts 98% Cu.

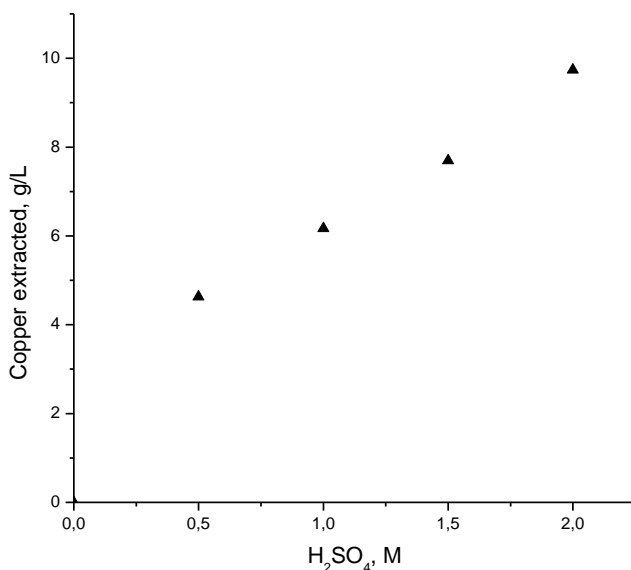


Fig. 5. Effect of H₂SO₄ concentration on copper stripping from loaded organic phase of Acorga M5397 (9.74 g/L Cu), $\varphi_o/\varphi_a = 1$, contact time 20 min

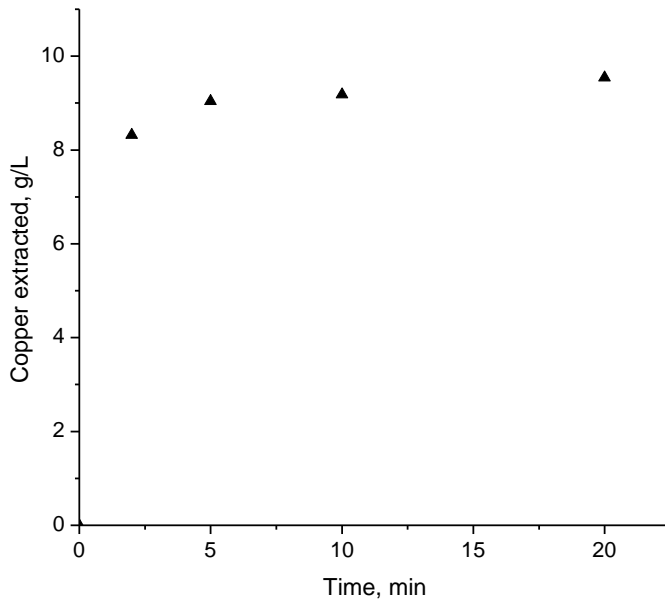


Figure 6. Kinetics of copper stripping from loaded organic phase of Acorga M5397 (9.74 g/dm³ Cu) at $\varphi_o/\varphi_a = 1$; 2M H₂SO₄

The effect of the variation of φ_o/φ_a , ranging between 0.5 and 3 was studied by working at a contact time of 10 minutes and 2 M H₂SO₄. Results are presented in Table 5. It can be seen that one can extract in only one contact stage all copper, when the φ_o/φ_a is between 0.5 and 1/1, with the corresponding copper contents in aqueous solutions attaining 4.88 g/dm³ and 9.75 g/dm³, respectively. With a high φ_o/φ_a (3/1) one can re-extract only 70% Cu in a single contact stage, but aqueous solution is more enriched in copper (20.42 g/dm³).

Table 5. Concentration of copper in the raffinate (φ_a) and in the organic phase (φ_o) during stripping with Acorga M5397 (pH 1.7)

φ_o/φ_a ratio	φ_a in equilibrium	φ_o in Equilibrium
	Cu (g/ dm ³)	Cu (g/ dm ³)
Feed		9.74
1/2	4.88	0
1/1	9.74	0
2/1	15.32	2.08
3/1	20.42	2.93

The plot of the Mc Cabe–Thiele diagrams (Fig. 7) from the data of Table 5 shows that by operating copper stripping at counter-current with a φ_o/φ_a of 3/1, total recovery

of copper can theoretically be reached in 3 stages of re-extraction. The obtained aqueous phase contains about $29 \text{ g/dm}^3 \text{ Cu}$.

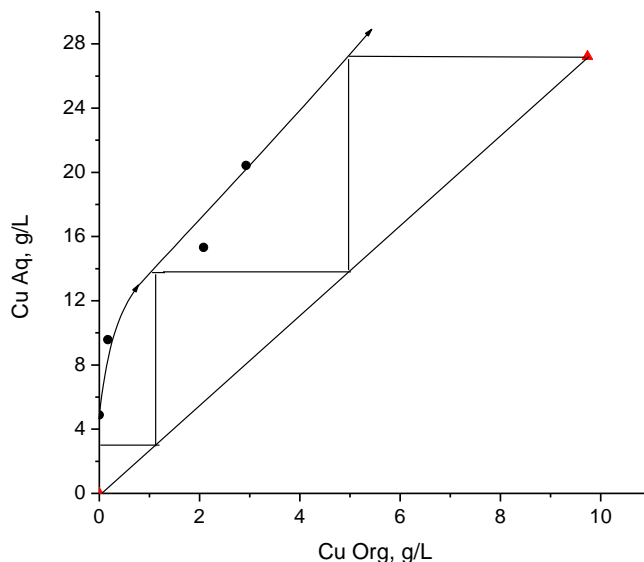


Figure 7. The McCabe–Thiele diagram for copper stripping from loaded organic phase of Acorga M5397 (9.74 g/L Cu) at $\varphi_o/\varphi_a = 3$

Conclusions

The complexity of the pregnant leach nitro-fluorosilic acid solution, obtained from the Hajar Mine Copper concentrate, is due to the difficulty of dissolving chalcopyrite by conventional agents. The good dissolution rates obtained by this leaching agent are affected by the weak selectivity toward copper (iron, zinc and lead are also leached). Nevertheless, the use of Acorga M5397 to extract selectively copper was effective. Coextraction of lead was noted, but can be neglected taking into account the lead/copper concentration ratio in the PLS (less than 0.2%).

Loading extractant capacity was improved by increasing the pH of the PLS. Compared to LIX 984, which belongs to the same solvent family, and used under the same conditions by El Amari et al. (2006), loading capacity of Acorga M5397 was higher without being less selective.

With pH 0.6, copper exhaustion of the solution by counter-current extraction requires more than 6 stages, whereas with a solution pH of pH 1.7, 94% of initial copper in the PLS could be recovered in only two counter-current extraction stages with Acorga M5397. The total extraction could be achieved in three stages.

The recovery of the copper contained in loaded organic phase Acorga M5397 was easily performed by sulphuric acid solution (2M H₂SO₄), allowing to obtain concentrated copper solution for electrowinning.

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