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COPPER (II) EXTRACTION FROM MULTICOMPONENT SULPHURIC-ACID SOLUTIONS BY MEANS OF LIX84I

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ABSTRACT

The process of copper extraction from a solution with the following composition in g/l: 2.38 Cu, 35.29Fe, 6.85Ni, 0.85Co, 2.90Mn and initial acidity 50.5 g/l H_2SO_4 *with a chelating extractant LIX84I diluted in kerosene was studied. The solution was obtained from the products (anode mud and electrolyte) of electrochemical anodic dissolution of a FeCuNiCoMn alloy. The influence of the main parameters of extraction: solution pH in the range from 1.5 to 3.0, Cu concentration (from 1.19 to 4.76 g/l), concentration of LIX84I in kerosene from 2 to 10 v/v %, aqueous to organic phase ratio* $(V_{aq} : V_{org})$ *within the range from 1:0.2 to 1:3 and the presence of* Fe^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+} *and* Mn^{2+} *ions in the solution on the extraction indices of the process: distribution (partition) coefficient* (D^{Me}), *degree of extraction* (E^{Me}) *and separation factor* $(\beta_{Cu/Me})$ *was determined. The selective capacity of an organic extraction agent LIX84I with respect to copper, in the presence of other metal ions in the solution was assessed. On the basis of experimental data, three-stage, counterflow copper extraction was proposed under the following optimal conditions: solution pH 2.5; LIX84I concentration in kerosene thinner - 6 v/v %,* $V_{aq} : V_{org} = 1:1$ *and phase contact time – 2min. The rate of copper extraction from the solution is 98.86 %.*

Keywords: solvent extraction, LIX84I, copper (II) recovery, FeCuNiCoMn alloy.

INTRODUCTION

The numerous research in the metal content (Mn, Fe, Cu, Ni and Co) of deep-sea nodules from the Clairon Clipperton region of the Pacific Ocean shows that it is commensurate with that of continental ores [1,2]. In combined pyro-hydrometallurgical nodule processing schemes [3,4], non-ferrous metals in the pyro-metallurgical part of the scheme concentrate into an intermediate product – FeCuNiCoMn alloy characterized by high iron content (>65 %) in comparison to that of Cu and Ni (~ 12-13 %) and especially of Co (~ 1 %). Mn content is about 5-6 %.

Several technology options of alloy dissolution were developed in some of our previous studies [5-8]. The conditions of electrochemical dissolution of the alloy in sulfuric acid and chemical compositions of the products obtained are presented in Table1.

It was found that about 97-98% of Fe, Ni, Co and Mn pass into the solution while Cu is distributed between the cathode deposit (66 %), the electrolyte (33 %) and anode mud (1 %).

Electrowinning is most frequently applied for obtaining of metallic copper of high purity in the metallurgical practice, the main requirements to the electrolyte being with respect to iron (< 2 g/l) and nickel

Table 1. Conditions of FeCuNiCoMn alloy electrochemical dissolution and chemical compositions of products obtained.

Parameters of electrolysis process	Products after electrolysis	Elemental composition				
		Fe	Cu	Ni	Co	Mn
52 g/l H_2SO_4 ia– 300 A/м^2 U- 1.5 V T – 298 K W - 15 l/dm^3	Electrolyte, g/l	34.78	2.32	6.82	0.89	2.82
	Cathode deposit, %	1.14	98.68	0.13	0.01	0.04
	Anodic slime, %	25.94	2.87	1.50	0.23	3.83

(< 10 g/l) [9]. From Table1 it can be concluded that such electrolyte can be produced solely from the cathode deposit. The other products: mud and electrolyte, require advance preparation due to the low copper concentration as well as high iron concentration.

Our study of literature on the subject [10-14] showed that most commonly, the extraction process using organic extraction agents (solvent extraction) is used to obtain concentrates of copper solutions during the recent years. One key advantage of the method is that it can be combined with the electrowinning process. Organic acids of the hydrooxyoxime species, the so-called chelates, with commercial title LIX-s (LIX63, LIX64, LIX70, LIX74, LIX84I, etc.), characterized by high selectivity with respect to copper in the presence of Fe, Ni, Co, Mn ions, and other metals are mostly used for copper extraction. The data cited in the literature, however, refer to solutions free of, or with low iron concentration and the extraction parameters are determined individually in each particular case.

The article presents experimental results for copper extraction from a multicomponent solution with high iron concentration using an organic extractant - LIX84I diluted in kerosene.

EXPERIMENTAL

Experiments were carried out with a solution obtained after dissolution of anode mud in the electrolyte. The chemical composition of the solution is shown in Table 2. LIX84I, a derivative of the hydrooxyoximes [15], was used as an extraction agent. Some extraction systems of defined compositions were prepared in advance by addition of a chelating extractant diluted in kerosene.

The experiments were performed in glass separating funnels with 100 ml capacity. Shifting of the aqueous and organic phases was done by the method of overturning with by means of a rotating machine at a rotation speed of 35 min^{-1}. After reaching the extraction equilibrium (15-30 s), some samples were taken from the aqueous phase in order to determine the concentrations of: Cu, Fe, Ni, Co and Mn by the atomic absorption method. A Perkin–Elmer 5000 spectrophotometer was used for the purpose.

The following parameters were examined: pH of the solution, time of contact between the aqueous and organic phases, concentration of the extractant in the organic phase ($C_{LIX\,84I}$), copper concentration in the solution C_{In}^{Cu}, ratio between the volumes of aqueous and organic phases ($V_{aq} : V_{org.}$) and the presence of other metals in the solution on the distribution coefficient (D^{Me}), the separation factor $(\beta_{Cu/Me})$ and the degree of copper extraction (E^{Cu}) from the solution.

The equilibrium concentrations of metals in an organic phase were calculated after the formula:

$$C_{org.}^{Me} = C_{aq}^{In} - C_{aq}^{end} \quad (1)$$

where: C_{aq}^{In} and C_{aq}^{end} were respectively: initial and final metal concentrations in an aqueous phase. The equilibrium between organic and aqueous phases was characterized by the distribution coefficient:

$$D^{Me} = [C_{org.}^{Me} / C_{aq}^{Me}], \quad (2)$$

which was also used to determine the degree of metal extraction - E^{Me}:

Table 2. Chemical composition of the solution, g/l.

Fe	Cu	Ni	Co	Mn	H_2SO_4
35.29	2.38	6.85	0.89	2.90	50.5

Table 3. Effect of pH on the extraction indices of copper.

No	pH	C_{aq}^{Cu} ,g/l	$C_{org.}^{Cu}$, g/l	^{Cu}	E^{Cu},%
1	1.5	2.38	No extraction takes place		
2	2	1.43	0.95	0.66	39.75
3	2.5	0.56	1.82	3.25	76.47
4	3	Hydrolyses of Fe^{3+}			

$$E^{Me} = \{(D^{Me}.V_{org}/V_{aq})/1+(D^{Me}V_{org}/V_{aq})\}x100,\% \qquad (3)$$

where: V_{org} and V_{aq} were respectively volumes of the organic and aqueous phases. At equal volumes:

$$E^{Me} = \{D^{Me}/(1+D^{Me})\}x100,\% \qquad (4)$$

the separation factor of copper from the metals in the solution was determined as ratio between the metal and copper separation factors:

$$\beta_{Cu/Me} = \frac{D^{Cu}}{D^{Me}} \qquad (5)$$

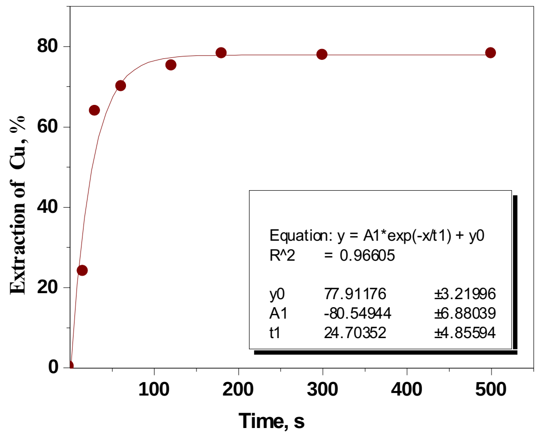

Fig. 1. Effect of contact time between aqueous and organic phases on copper extraction at $C_{In}^{Cu} = 2.38 g/l$.

RESULTS AND DISCUSSION

Effect of the solution pH

According to [15], copper extraction with LIX-s takes place within a very narrow range of solution pH from 2 to 2,5. A series of experiments was performed to verify this parameter at different values of pH= 1.5, 2, 2.5, 3 and constant other parameters: $C_{LIX\,84I} = 6$ v/v %, initial copper concentration $C_{In}^{Cu} = 2.38 g/l$, $V_{aq} : V_{org.}$ =1:1 and time of contact 2 min.

Table 2 shows that the concentration of H_2SO_4 in the solution is 50.5 g/l. That is why a two-stage neutralization of the solution was performed in order to achieve a definite pH level. Initially, slaked lime was added until pH 1.8, followed by the addition of concentrated solution of $CuCO_3$ up to pH 2, 2.5 and 3, respectively. This was done to produce gypsum with minimum impurities (0.05 % Fe, 0.04 % Cu, 0.03 % Ni, 0.04 % Mn and traces of Co), which can be used in the construction. A similar method is proposed in [16]. The experimental results are presented in Table 3.

It can be seen that the maximum degree of copper extraction is reached at pH 2.5. At pH 1.5 copper extraction does not take place, and at pH>2.5 hydrolyses of the ferric ions is observed.

Effect of phase contact time

The time needed to reach equilibrium between the copper ions in aqueous and organic phases was examined within the range 30-500 s for the following constant parameters: pH 2.5, $C_{In}^{Cu} = 2.38 g/l$, $C_{LIX\,84I} = 6$ v/v % in kerosene and $V_{aq} : V_{org}$ =1:1. The obtained experimental results are illustrated graphically in Fig. 1.

The exponential relation obtained has a high correlation factor (0.98805) and indicates that the time

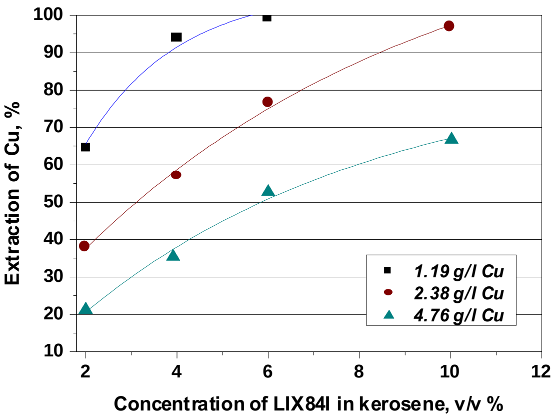

Fig. 2. Effect of $C_{LIX\,84I}$ in kerosene on copper extraction at different C_{In}^{Cu} and constant $pH = 2.5$ and $V_{aq} : V_{org.}$ =1:1.

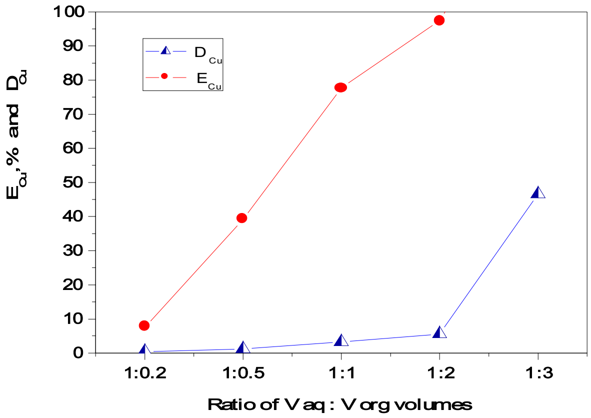

Fig. 3. Effect of the ratio of $V_{aq} : V_{org.}$ volumes on copper extraction at C_{In}^{Cu} =2.38g/L and $C_{LIX\,84I} = 6$ v/v %.

Table. 4. Effect of the conditions of extraction on the quantitative copper indices

No	C_{In}^{Cu}, g/l	C_{LIX84I}, $\%_{vol}$	$V_{aq}:V_{org.}$	Concentration g/l		D^{Cu}	E^{Cu},%
				C_{aq}^{Cu}	$C_{org.}^{Cu}$		
1	2.38	2	1:1	1.48	0.90	0.61	37.89
2	2.38	4	1:1	1.02	1.36	1.33	57.08
3	2.38	6	1:1	0.56	1.82	3.25	76.47
4	2.38	10	1:1	0.07	2.31	33.0	97.05
5	1.19	2	1:1	0.42	0.77	1.83	64.66
6	1.19	4	1:1	0.07	1.12	16.0	94.12
7	1.19	6	1:1	0.01	1.18	119	99.17
8	4.76	2	1:1	3.74	1.02	0.27	21.25
9	4.76	4	1:1	3.23	1.52	0.47	31.97
10	4.76	6	1:1	2.22	2.54	1.11	52.69
11	4.76	10	1:1	1.31	3.45	2.63	72.45
12	2.38	6	1:0.2	1.71	0.67	0.39	7.23
13	2.38	6	1:0.5	1.05	1.03	1.22	37.89
14	2.38	6	1:2	0.36	2.02	5.61	91.82
15	2.38	6	1:3	0.05	2.33	46.6	99.29

needed to reach equilibrium is ~ 120 s. Such high rate of copper extraction is of great significance for technological implementation of the process in the continuous case.

Effect of Cu concentration in the solution, LIX84I in organic phase and aqueous to organic phase volume ratio

Table 4 summarises the experimental results concerning the effect of initial copper concentration in the solution within the range from 1.19 to 4.76 g/l, the concentration of LIX84I from 2 to 10 v/v % in kerosene and the volume ratio of aqueous to organic phases from 1:0.2 to 1:3 on the quantitative indices (D^{Cu} and E^{Cu}, %) of copper extraction. The experiments were performed at pH 2.5 and time of contact between aqueous and organic phases τ 120 s. Fig. 2 shows relationships of $E^{Cu} = f(C_{LIX84I})$, %, obtained at different initial copper concentration in the solution and constant other parameters. It can be seen that at the same concentration of LIX84I in organic phase, the degree of copper extraction depends on its initial concentration in the solution. That fact can be explained with differences in the times required for achievement of equilibrium in the system. The effects of the aqueous phase/organic phase volume ratios on $D^{Cu}$and E^{Cu} are illustrated on Fig. 3. They are built for $C_{In}^{Cu} = 2.38 g/l$ and C_{LIX84I} = 6 v/v %.

Table 5. Extraction characterristics of the metals present in the solution and their separation factors using C_{LIX84I} = 6 v/v % in kerosene.

Me^{n+}	$Me_{initial}$ g/l	Me_{phase} g/l		D^{Me}	E^{Me},%	$\beta_{Cu/Me}$
Cu^{2+}	2.38	V_{aq}	0.56	3.25	76.47	-
		$V_{org.}$	1.82			
Ni^{2+}	6.85	V_{aq}	6.67	0.026	2.53	124.2
		$V_{org.}$	0.18			
Co^{2+}	0.89	V_{aq}	0.83	0.072	6.72	48.94
		$V_{org.}$	0.06			
Mn^{2+}	2.90	V_{aq}	2.75	0.054	5.12	59.81
		$V_{org.}$	0.15			
Fe^{2+} Fe^{3+}	31.83	V_{aq}	33.75	0.046	4.40	70.22
	3.46	$V_{org.}$	1.54			
Fe^{2+} Fe^{3+}	25.41	V_{aq}	33.17	0.074	6.89	43.64
	10.21	$V_{org.}$	2.45			

It is obvious that increase of the organic phase volume, resp. the concentration of LIX84I, results in increase of copper extraction. The experience of plants implementing the extraction process for extraction of copper from low-concentration solutions (2-3 g/l) indicates that it would be more advisable to work at a lower ratio of phases (for example, 1:0.5 or 1:1) and to perform two- or three stage extraction [14].

Effect of metal impurities in the solution

According to M.A. Meretukov [17], chelating extractants of the hydroxyoxime species in certain conditions can also extract, beside copper, the ions of

Table 6. Chemical compositions of the streams before and after the three-stage counter-current simulation.

Stream	Metal concentration, g/l				
	Cu	Fe	Ni	Co	Mn
Leach liquor	2.38	35.29	6.85	0.89	2.90
Raffinate (R3)	0.027	34.29	6.67	0.87	2.83
Loaded organic	2.35	1.0	0.18	0.02	0.07

Table 7. Degree of copper extraction from the solution after "n"- stage counter-current simulation.

Stage	C_{In}^{Cu},g/l	Concentration, g/l		Extraction efficiency, %
		C_{aq}^{Cu}	$C_{org.}^{Cu}$	
1st	2.38	1.020	1.36	57.08
2nd	0.71	0.188	2.19	92.12
3rd	0.21	0.027	2.35	98.86

$Ni^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}$, etc. The high concentration of these ions in the examined solution (Table 2), with the exception of Co^{2+}, shows the feasibility of their co-extraction together with copper. The so-called separation factor $\beta_{Cu/Me}$ is used for assessment of the selectivity of the extraction agent used with respect to copper against the rest of metals present in the solution. The experiments were performed with two solutions of different concentrations of ferro- and ferrite ions with the following parameters: $pH = 2.5, C_{LIX84I} = 6$ v/v %, and $V_{aq} : V_{org.} = 1:1$, $\tau = 120s$. The values of D^{Me}, E^{Me},% and $\beta_{Cu/Me}$ are presented in Table 5.

Analysis of the results shows that E^{Me},% of $Ni^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}$ does not exceed 7 %. The factors of their separation from copper ($\beta_{Cu/Me}$) have significant numeric values which testifies for high selectivity of LIX84I with respect to copper. It should be noted that increase of the concentration of Fe^{3+} ions in the solution is not advisable because the separation factor is seriously reduced. That, on the one hand, results in poorer copper extraction indices, and on the other – in decreased extraction capacity of the extractant.

Determining the number of counter-current stages of copper extraction

In practice, multi-stage counter-current extraction is most commonly used for copper extraction from low-concentration solutions [12,14]. The number of required extraction stages , can be determined theoretically through the so-called extraction isotherm or experimentally [17]. For the study performed by us, the second method was chosen. The counter-current batch simulation scheme of the experiment is shown in Fig. 4.

Copper concentration in the solution, after the n-th degree of extraction, was determined by the equation:

$$C_{aq}^{n} = C_{aq}^{In}\left(\frac{V_{aq}}{D^{Cu}V_{org} + V_{aq}}\right)^{n} \tag{5}$$

After each extraction stage the solution was sampled for atomic absorption analysis. The experimental results are presented in Tables 6 and 7.

Analysis of the results shows that after a three-stage counter-current extraction the degree of copper extraction in the organic phase is 98.86 %. Other species passing into it are in g/l: 1.0 Fe, 0.18 Ni, 0.02 Co and 0.07

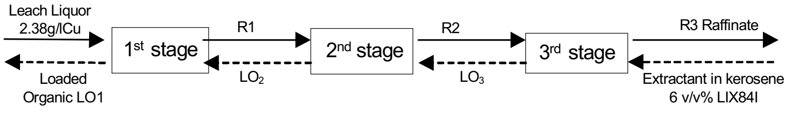

Fig. 4. Counter-current batch simulation scheme for copper extraction.

Mn. Therefore the organic phase has to be flushed before the re-extraction process. The concentration of copper in the rafinate product is 0.027 g/l and after removal of the iron and manganese, it will be transferred for extraction of nickel and cobalt.

CONCLUSIONS

On the basis of the experimental study performed, optimal technology parameters of copper extraction from multicomponent solution with composition in g/l: 2.38 Cu, 35.26 Fe, 6.85 Ni, 0.89 Co, 2.90 Mn and 50.5 g/l H_2SO_4 using an organic extraction agent LIX84I in kerosene as a solvent were determined. It was obtained from the products (electrolyte and anode mud) of electrochemical dissolution of FeCuNiCoMn alloy. The maximum degree of copper extraction (98.86 %) was achieved after three-stage counter-current extraction with the following parameters: solution pH 2.5; $C_{LIX\,84I}$ = 6 v/v %; $V_{aq} : V_{org.}$ = 1:1; T=298 K and time of contact between phases 120 s. Neutralization of the solution was performed in two stages, with slaked lime to pH 1.8 and copper carbonate to pH 2.5. The impurities content in the gypsum produced after the first stage was as follows in $\%_{mass}$: 0.05 Fe, 0.04 Cu, 0.03 Ni, 0.04 Mn and traces of Co.

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