ISBN 978-86-82673-11-8
9 788682 673118

Proceedings of
XVI BALKAN INERAL PROCESSING CONGRESS
Belgrade, Serbia, June 17-19, 2015

Mining Institute Belgrade

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Proceedings of
XVI BALKAN MINERAL PROCESSING CONGRESS

Belgrade, Serbia, June 17-19, 2015

55 years of Mining Institute Belgrade

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VOLUME II

VOLUME II

Edited by

Nadežda Ćalić, Ljubiša Andrić,
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MINING INSTITUTE BELGRADE

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2015

XVI BALKAN MINERAL PROCESSING CONGRESS
BOOK OF PROCEDINGS

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For the publishers: MSc Milinko Radosavljević, director, Mining Institute Belgrade

Printed by: Colorgrafx, Belgrade

Issued in: 2015.

Circulation: 300

ISBN 978-86-82673-11-8 (MI)

CIP - Каталогизација у публикацији -
Народна библиотека Србије, Београд

622.7(082)

BALKAN Mineral Processing Congress (16th ; 2015 ; Belgrade)
Proceedings of XVI Balkan Mineral Processing Congress, Belgrade, Serbia, June 17-19, 2015. Vol. 2 / [congress organizers] Mining Institute Belgrade [and] Academy of Engineering Science of Serbia [and] University of Belgrade ; edited by Nadežda Ćalić ... [et al.]. - Belgrade : Mining Institute : Academy of Engineering Science of Serbia : University of Belgrade, 2015 (Belgrade : Colorgrafx). - VII str., str. 593-1147 : ilustr. ; 30 cm

Tiraž 300. - Str. VII: Foreword / Nadežda Ćalić. - Bibliografija uz svaki rad. - Registar.

ISBN 978-86-82673-11-8 (MI)

1. Ćalić, Nadežda [уредник] [аутор додатног текста]
2. Mining Institute (Belgrade)
а) Руде - Припрема - Зборници

COBISS.SR-ID 215733516

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XVI BALKAN MINERAL PROCESSING CONGRESS

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DESIGN OF A HIGH CURRENT EXTRACTION/STRYPPING SYSTEM USING EXTRACTION AND STRIPPING ISOTHERMS

Milena Danovska[1], Dejan Karanfilov[1], Mirjana Golomeova[2], Boris Krstev[2], Afrodita Zendelska[2]

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Abstract: The isotherms define the capacity of some extragent for its capability to extract required metal (in this case copper). They are used to evaluate how the system extraction/stripping works, or expected to work. The construction of extraction isotherm consists of the following stages: preparation of laboratory extragent, the organic phase is brought into contact with the electrolyte, optimization of the extraction equilibrium isotherm. Similarly, construct and stripping isotherm: organic solvent, brought into contact with retread solution, stripping isotherm is optimized, but in this case the balance is achieved of the aqueous solution-poor electrolyte from electrolysis with saturated organic. The given test follows the conclusion of stages of extraction required for extraction 97% copper and stages required for 99% copper stripping.

Keywords: solvent extraction, isotherm, copper leaching, stripping.

INTRODUCTION

Solvent extraction (SX) has been recognized as a one of the most important separation techniques for metals in solutions. The technology is increasingly being used in hydrometallurgy to separate, purify and concentrate metals such as nickel, cobalt, copper, zinc, uranium and rare earths. In the meantime a considerable amount of work has been carried out and reported (Szymanowski, 1993; Habashi, 1999; Ritcey, 2006; Flett, 2005; Apostoluk et al., 2009). A number of plants have been designed and operated to extract copper from leach solutions of various compositions. Until recently typical pregnant leach solutions (PLS) contained 0.5 - 4 g/l Cu. Such leach liquors are usually generated in heap and dump leaching of copper oxide ores or byproducts, which are readily leached under ambient conditions.

In recent years, there has been a considerable development of hydrometallurgical processes for copper extraction applying SX combined with electrowinning (EW) for the production of high-grade electrolytic copper. As a result, more than 20% of world copper production is currently produced from heap leaching–SX operations of oxide copper ores. The low capital and operating costs of SX plants together with the easy operation and the production of top quality electrolytic metals close to the mine site make the economics of the SX processes very attractive, being suitable and feasible in the range of small to medium capacities, where conventional smelting process is not applicable.

Copper flotation sulfide concentrates are mainly processed by means of smelting, converting and electrorefining, the unit operations that have dominated the World copper industry for technical and economic reasons. Research and development for hydrometallurgical alternatives to traditional pyrometallurgical processes has remarkably intensified in the recent years. A wide range of chemical and biological processes for copper recovery from concentrates has been developed (Dreisinger, 2006; Gupta, 1990; Habashi, 1999; 2005; 2007; Jansen and Taylor, 2000; Marsden, 2007; Peacey et al., 2003; Ramahadran et al., 2007). These processes appeared to be successful in leaching of copper from polymineral and chalcopyrite concentrates, purifying the leach solutions (PLS) using modern separation processes, mainly solvent extraction, and recovering a high value, high purity copper metal product. Chmielewski (2012) discussed the possible role of hydrometallurgy in more effective processing of polymetallic concentrates or by-products from Polish copper industry. In the past ten years, a great deal of attention has been paid to development of hydrometallurgical treatment of complex copper sulfidic ores, by-products and concentrates (Hyvärinen and Hämäläinen, 2005; Dreisinger, 2006). This type of material requires more aggressive, oxidative leaching methodsand application of Fe(III) ions and oxygen or bacteria assisted environment. Higher grades of solids are employed in the

leaching operations resulting in more concentrated leach liquors with higher metal content than those produced in heap leaching. Usually leaching of sulfide concentrates is realized with the use of iron(III) salts and sulfuric acid as a leaching medium. Leach liquors generated in the process can contain 20 - 80 g/l Cu, 0 - 30 g/l Fe and other metal values which have to be sequentially recovered (Kordosky, 2002). Moreover, the acidity of leach liquors changes in the pH range from below 1 to around 2. According to Eq. (1) the extraction reaction of metal cations M n+ by extractant HA is reversible towards hydrogen ions.

$$M\ n+\ MAn(o) + nH+\Delta(a) + nHA \qquad [1]$$

It means that for each mole of copper extracted, the raffinate acidity is increased by one mole. In solutions where copper concentrations can be in excess of 40 g/l a significant amount of acid is generated to the raffinate. This in turn can shift the equilibrium towards stripping reaction. A solution is to use a stronger copper Solvent extraction of copper(II) from concentrated leach liquors 359 extractant, which will be able to extract copper at higher acidity, but which in turn requires more acid to be stripped. One can also increase the concentration of extractant in order to extract more copper. This can in turn result in more viscous organic phases, particularly the loaded organic, leading to poorer phase separation performance with increased entrainment losses, and increased impurity transfer to the strip side. One can also operate at a higher organic to aqueous phase ratio (O/A). The choice of parameters depends on how high the copper concentration is and what else is in the ore or in the feed (Molnar and Verbaan, 2003).

Presented paper discusses the copper extraction behavior of commercial copper reagents with copper sulfide concentrate leach solutions. The performance of Acorga M5640 in Exsoll diluent were investigated. McCabe–Thiele diagrams were generated, copper net transfer values were compared and discussed.

Isotherms define the capacity of a extractant to extract the necessary metal. They are used to evaluate how the system works and extraction or stripping is expected to work.

EXPERIMENTAL

Once it is determined the composition of the aqueous phase and the percentage of organic matter in extractants, approached to consider the possibility of improving the extraction of copper through the construction of the extraction and stripping isotherm. pH of the aqueous solution to be extracted is measured and it was 1.8. Measured percentage of ACORGA 5640m is 22.16%. The transfer of copper from 1% extractant obtained a value of 0.33862 g/l. This value is derived from the sampling process as the mean of 13 measurements in 48 hours, which are given in the Table 1.

Table 1. Calculations of the average value of the content extracted copper in tree stage extraction process (process samples).

Table for calculating the extraction of 1% ACORGA 5640m				
$c(Cu)_{in}$	$c(Cu)_{out}$	ΔCu	%extrag.	c(Cu)1%
11	1.03	9.97	22.16	0.4049
10.2	2	8.2	22.16	0.333
10.45	1.4	9.05	22.16	0.3676
9.4	1.4	8	22.16	0.3249
10.3	1.4	8.9	22.16	0.3615
11.15	2.1	9.05	22.16	0.3676
11.9	2.37	9.53	22.16	0.387
11.65	2.85	8.8	22.16	0.3574
10	2.65	7.35	22.16	0.2985
10.65	2.7	7.95	22.16	0.3229
10.35	2.6	7.75	22.16	0.3148
9.85	2.59	7.26	22.16	0.2949
8.8	2.22	6.58	22.16	0.2672
10.438		8.338	average	0.33862

where c (Cu) log concentration of copper in the first stage of extraction, and c (Cu) onto the copper concentration of the third stage of extraction, i.e. Output of copper concentration in rafinate. ΔCu is the difference between the input and output concentration of copper ions in aqueous solution. With simple mathematical calculations, we get an approximate concentration of extractant required to better use:

10.4384 g/l Cu×0.9/0.33862 g/l Cu = 27.74 v/v% extractant.

Also, process measuring of copper content of the two stage stripping. There are 15 executed measurements for 48 hours. The obtained results are shown in Table 2.

Table 2, Calculations of the average value of the content stripping copper in two stage stripping process (process samples).

Cu output	c(Cu) input	ΔCu
48.15	33.05	15.1
46.8	34.1	12.7
45.95	33.15	12.8
50.6	36.1	14.5
48.2	33.25	14.95
48.3	33.35	14.95
51.1	32.15	18.95
52.15	33.2	18.95
52.6	31.8	20.8
48.85	33.85	15
52.1	36.45	15.65
52	33.95	18.05
51.75	32.8	18.95
43.4	32.95	10.45
42.2	31.8	10.4
48.943	33.463	15.48

The question is why the content of the extracted copper tree stage extraction is less than concentration of stripping copper? The answer will be obtained by constructing the extraction and stripping isotherm. The construction of extraction isotherm consists of the following stages:

1. The first phase is prepared with laboratory extractant 27.74 v/v% ACORGA 5640m in suitable organic solvent, Exsoll, derivative kerosene. The brought into contact with retreading, the copper concentration 10,1 g/l in the aqueous phase are mix in mixer settler within 3 minutes 1450 rpm, regarding O/V = 1. After separation of the phases, which lasts 3.5 minutes (time is not satisfactory, that is too long) copper from water stage passes into the organic phase, building organometallic complex extractant. The analysis of copper in the aqueous phase showed that in aqueous solution, present copper, which means that the copper content in the organic phase is 10.1 g/l. Such content can be fully extracted only in the laboratory and with new (unpolluted) organic.

2. In the second phase of the experiment, the organic phase is brought into contact with the electrolyte, the concentration of copper 30 g/l and the H_2SO_4 concentration of 180 g/l, 3 times per minute, compared to O/V = 1/1. The purpose of this procedure is getting a new organic solution in composition correspond stripping organic phase two stage continuous STRIPPING process.

In this case, based on laboratory tests, copper content in the electrolyte at the entrance to electrolysis (output re-extraction) is 38.943 g/l and 160 g/l H_2SO_4. Since loading, the re-extraction copper content is 30 g/l, it means that in the organic phase 2 will remain (38.943-30) g/l = 8.943 g/l and 10.1-8.943 = 1.157 g/l copper.

3. New laboratory prepared organic phase 2, the copper content of 1,157 g/l was used for further experiments that the construction of the extraction equilibrium isotherm, a Schedule 2, by bringing the steady state relationship of various organic phase 2 and the electrolyte poor and retreading. From the ratio of the phase O/V = 1, where c (Cu_{org}) = 1,157 g/l and c (Cu_v) = 10,1 g/l, after balancing the mixer specified content of copper in the aqueous phase in the amount of 0,59 g/l and the organic phase of the difference of the total copper and copper in an aqueous phase of 10,667 g/l. The results of the copper content in organic and aqueous phase in terms O/V = 1:1, and the results obtained for the different relationships between the phases are given in Table 3:

Table3, Equilibrium extraction parameters

Ratio O/A	organic Cu g/l	aqueous Cu g/l
10/1	12,04	0,07
5/1	12.28	0.09
2/1	12.96	0.17
1,5/1	13.26	0.26
1.0/1	13.7	0.59
1.0/2	14.19	1.24
1.0/5	14.35	1.94
Cu in extracted organic phase 1.157g/l		
Cu in regenerate 10.1 g/l		

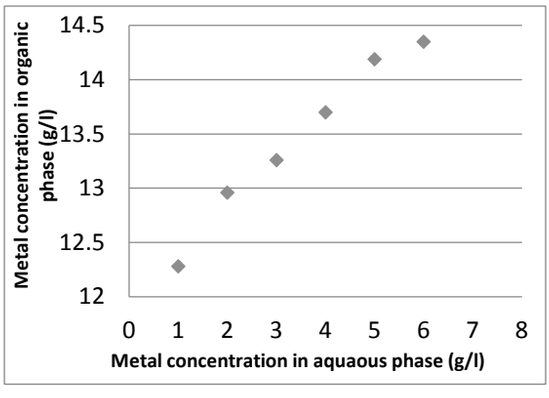

Figure 1, Extraction isotherm

From Fig. 1 we can see that under these conditions we need tree extraction stages for

nearly complete recovery of copper. First stage is from the beginning of the line to point 0.09, second to point 0.59 and third to point 1.24 on x-axis. This line may be considered as representing the fact that in any extraction stage the increase in metal concentration in the organic phase is equal to the decrease in metal concentration in aqueous phase multiplied by the phase ratio. It may or may not pass through the origin, depending on how low a metal concentration in the raffinate is desired.

In the similar way it is constructed and stripping isotherm:

1. Preparation of organic solvent content were 27.74 v/v% ACORGA 5640m in organic diluents, Exsoll. They are brought into contact with regenerate, so the copper concentration of 10.1 g/l in the aqueous phase, they are mixing in the mixer settler for a period of 3 minutes, 1450 speed per minute, compared O/V=1. Thus achieved is the maximum loading of organic phase with the copper content 14.35 g/l, which is used for preparing the stripping isotherm.

2. Stripping isotherm is obtained in the same manner, but in this case they are balanced the waterway-starved electrolyte solution by electrolysis of salt concentration of 30.7 g/l Cu and 190 g/l H_2SO_4 are laced organic 14.35 g/l Cu in different O/A ratio. By the balancing organic phase and poor electrolyte in the mixer settler, certain contents of copper in the aquatic phase, equaling 43.98 g/l, and in organic phase, copper is determined by the difference of the total copper and copper in the aqueous phase and its value is 1,07 g/l. The results on the contents of copper in organic and the aqueous phase ratio O/V = 1, and the results obtained in different relationships to the phases are given in Table 4.

Table 4, Equilibrium stripping parameters

Ratio O/V	Organic Cu g/l	Aqueous Cu g/l
10/1	1.76	81.3
5/1	1.38	73.2
2,5/1	1.21	67.7
1/1	1.07	63.8
1/2	1.01	62.3
1/4	0.98	61.2
Cu in loaded organic phase , g/l 14.35		
Cu in poor electrolyte, g/l 30,7		

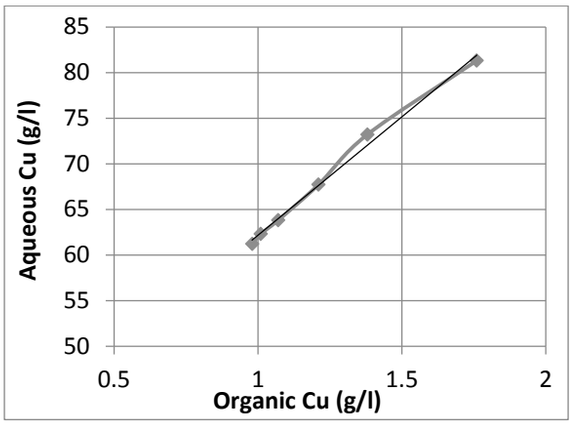

Figure 2, Equilibrium stripping isotherm

The given test follows the conclusion that using extractant ACORGA 5640m, can extract 97% copper three- stage extraction and 99% copper in two stage stripping. Negativity, which should work further difficult separation of the two phases, which is dependent on many factors such as: pH, viscosity, sulfuric acid concentration etc.

CONCLUSION

The obtained results demonstrated that investigated copper solvent extraction reagents are suitable for application to concentrated feed solutions from atmospheric or pressure leaching of copper concentrate. The stronger modified aldoxime reagent (Acorga) was shown to be superior and showed advantages in recovery and copper net transfer values. Therefore, high current extraction system is achieved and the given test follows the conclusion of stages of extraction required for extraction 97% copper and stages required for 99% copper stripping.

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