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**SELECTIVE SEPARATION OF COPPER FROM RICH-IN-IRON BIOLEACHING SOLUTION BY MEANS OF PROCESSES OF SOLVENT EXTRACTION WITH LIX 984 N AND STRIPPING WITH SULPHURIC ACID**

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**ABSTRACT:** The separation of copper and iron from model bioleaching solutionby means of solvent extraction was studied in dependence on the concentration of LIX 984 Nin organic phase (O), pH value of aqueous phase (A), time for mixing of both phases, and phases ratio (O:A). The optimal conditions of copper extraction were as follow: the concentration of LIX 984 N – 8 %, phase ratio (O: A) – 1:1, pH value of aqueous phase – 1.75, and mixing time of 8 minutes. The effect of temperature on the separation process at above-mentioned optimal conditions was studied at 5, 10, and 15º C, respectively. As a result of this, the extraction isotherms at the relevant temperatures was drawn, as well as copper extraction constants and the average rates of copper extraction were determined by means of Langmuir equation and pseudo-first equation rate, respectively. Above–mentioned parameters were also determined for stripping of copper with 180g/l H2SO4 at O:A ratio of20:1 when the process was realized as a one-stage as well as a three-stage process, respectively.

Keywords: copper, solvent extraction, stripping, kinetic, Kd

**СЕЛЕКТИВНО КОНЦЕНТРИРАНЕ НА МЕД ОТ БОГАТ НА ЖЕЛЯЗО ПРОДУКЦИОНЕН РАЗТВОР ЧРЕЗ ПРОЦЕСИТЕ НА ТЕЧНОСТНА ЕКСТРАКЦИЯ С LIX 984 N И РЕЕКСТРАКЦИЯ СЪС СЯРНА КИСЕЛИНА**

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**РЕЗЮМЕ:** Разделянетона медта и желязото от моделен продукционен разтворчрез процеса течностна екстракция беше изследвано в зависимост от концентрацията на LIX 984 N в органичната фаза (O), pH на водния разтвор (A), времето за смесване на двете фази и фазовото отношение (О:А). Оптималните условия за течностна екстракция на мед от разтвора бяха както следва: концентрация на LIX 984 N – 8 %, отношение на фазите (O:A) – 1:1,pHна водната фаза – 1,75, и време за разбъркване –8 минути. Влиянието на темепературата върху процеса при горе-споменатите оптимални условия беше изследвано при 5, 10и 15º C. В резултат на което, бяха получени екстракционнните изотерми при съответните температури, както и константата на екстракция и средната скорост на екстрахиране на мед, които бяха определени посредством уравнението на Лангмюир и уравнениеза скорост на процеса от псевдо-първи ред съответно. Горе-споменатите параметри бяха определени и при процеса на реекстрахиране на мед с 180g/lH2SO4присъотношениеO:A 20:1, когато той беше реализиран като едно стъпален и три стъпален процес, съответно.

**INTRODUCTION**

Two technological routes are applied nowadays for copper ores processing–pyrometallurgyand hydrometallurgy, respectively.Copper production by means of pyrometallurgyis appliedin case of chalcopyriteconcentrates is a raw material and the following processes are used – smelting, converting and electrorefining. However, due to the higher energy demand and stricter environmental regulations in Western countries, especially to sulfur and nitrogen emissions to the environment, the popularity of this route is steadily declining. Despite of the higher resistance of chalcopyrite, the pressure oxidation leaching (McDonald & Muir, 2007) as well as bioleaching (by means of acidophilic chemolithotrophic bacteria growing at moderate or extreme thermophilicconditionsmainly (Groudev et al., 2013)) are in process of researching as alternative ways to process chalcopyrite concentrates (Peacey et al., 2003).

Since 1970`s the role of hydrometallurgy in processing of copper ores is growing rapidly and now more than of 20 % of refined copper is produced via this route (Watling, 2006). The hydrometallurgy of copper is based on three main consecutive technological processes – a process of leaching, a process of concentration of dissolved copper, and a process of electrowinning (Jenkins, 2002; Zhang et al., 2011). The process of leaching in dependence on the quantity and quality of raw material could be realized in different way – bacterialleaching, chemical leaching, pressure oxidation, etc. As a result of this, the hydrometallurgy could be easily adapted to raw materials with completely different chemical content as well as mineralogy (Peacey et al., 2003; Walting, 2006).

Two techniques are applied nowadays into the practice toconcentrate already leached copper– ionexchange with resins and solvent extraction process. A lot of new products with higher capacity and better separation properties used in these processes are put on the market, which enables processing of low-grade copper ores to be connected with low capital and operating costs. Moreover, the production of top quality electrolytic metal is close to the mine site which makes the economics of the whole production activity very attractive and being suitable for small to medium-in-range enterprises, and to bein accordance with environmental regulations (Ritcey, 2006).

Solvent extraction technique is applied to extract not only copper ions presented in solution. Already leached cations are extracted usually into organic diluents by acidic or chelating extractants. For example, aromatic oxime molecules, known on the market as LIX (Cognis) and ACORGA (Avecia) are used to extract gold too. Lead, cadmium, zinc, nickel etc., are extracted by means of organophosphates such as mono(2-ethylexyl) phosphoric acid (H2MEHP), di(2-ethylexyl) phosphoric acid (D2EHPA), etc. (Ritcey. 2006). In relation to metal anions, they could be extracted by an ion-pair formation with long chain alkyl amines dissolved in an organic diluent when suitable salts or acids are presented in the aqueous phase. For example, a suitable complexing agent for chromium and mercury is tri-n-octylamine (TOA).

LIX 984 N is a solvent extraction reagent applied into practice after its dissolution in kerosene without a need of additional purification. LIX 984 N is a 1:1 volume blend of LIX 860N-I andLIX 84N-I, a mixture of 5-nonylsalicylaldoxyme and 2-hydroxy-5-nonylacetophenone oximein a high flash point hydrocarbon diluent which forms water insoluble complexes with various metallic cations in a manner similar to that shown below. Thisextractant contains no added modifier and it might be used for copper extraction from solutions containing soluble silica or finely divided solids (El Amari et al., 2006).

A common reaction describes the solvent extraction of leached cationsfrom pregnant solution is:

*Men+ + nRH(o)↔MeRn(o) + nH+(a)*

According to it, hydrogen ions and mostly their concentration governs the direction of the process. So, during the solvent extraction for each mole of extracted bivalent cation, the raffinate acidity is increased by twomoles. Thedirection of the process (from extraction to stripping) could be changed very easily by means of sulphuric acid addition. As a result of the higher concentration of hydrogen ions, the equilibrium conditions in the system are changed and the extracted copper is transferred from organic to aqueous phase respectively. By this process, the extraction capacity of the reagent is recovered and the next cycle of metal extraction could be initiated.

**MATERIALS AND METHODS**

The aqueous phase for solvent extraction was prepared by CuSO4.5H2O, FeSO4.7H20, FeCl3 and H2SO4 and the properties and concentration of main cations in the solution were as follow; pH –1.55; Eh –+ 492 mV; acidity – 345 mmol/l;Fetotal – 8480 mg/l; Fe3+ - 1975 mg/l; and Cu – 515 mg/l.

Table 1.

*Effect of the initial pH of pregnant solution on copper extraction by LIX 984 N*

|  |  |  |
| --- | --- | --- |
| pH of the aqueous phase | Cu in raffinate, mg/l | Efficiency of solvent extraction, mg/l |
| 1.50 | 70.6 | 86.3 |
| 1.75 | 50.5 | 90.2 |
| 2.00 | 33.7 | 64.8 |
| 2.25 | 25.8 | 63.2 |
| 2.50 | 15.5 | 55.0 |

Table 2.

*Effect of concentration of LIX 984 N in kerosene on copper extraction from pregnant solution*

|  |  |  |
| --- | --- | --- |
| Concentration of LIX 984 N, % | Cu in raffinate, mg/l | Efficiency of solvent extraction, mg/l |
| 2 | 75.2 | 85.4 |
| 4 | 65.9 | 87.2 |
| 6 | 53.6 | 89.6 |
| 8 | 44.3 | 91.4 |
| 10 | 43.8 | 91.5 |

Table 3.

*Effect of ratio organic to aqueous phase (O:A) on copper extraction from pregnant solution by LIX 984 N*

|  |  |  |
| --- | --- | --- |
| Ratio O : A | Cu in raffinate, mg/l | Efficiency of solvent extraction, mg/l |
| 1:1 | 46.4 | 91.0 |
| 1:2 | 66.4 | 87.1 |
| 1:4 | 96.3 | 81.3 |
| 1:6 | 142.1 | 72.4 |

Table 4.

*Effect of extraction time on copper extraction from pregnant solution by LIX 984 N*

|  |  |  |
| --- | --- | --- |
| Extraction time, min | Cu in raffinate, mg/l | Efficiency of solvent extraction, mg/l |
| 2 | 316.2 | 38.6 |
| 4 | 193.1 | 62.5 |
| 6 | 79.3 | 84.6 |
| 8 | 46.9 | 90.9 |
| 10 | 41.5 | 91.9 |

LIX 984N, (Henkel Corporation, Germany) was diluted in kerosene and was used to solvent extraction of copper from model solution without further purification. The stripping reagent was 180 g/l H2SO4. All correction of pH was made with Na2CO3. pH measurements was carried out by aWTW pH-meter.

The equilibrium distribution of copper between the organic (O) and aqueous (A) phase at the relevant experimental conditions was determined by mixing of their exact volumes with an overhead stirrer FALC at 300 rpm. After each test both phases were separated by means of a separatory funnel and the concentration of copper in the aqueous phase before and after extraction was determined by spectrofotometric methods(APHA, 1995).Metal content in the organic phase was determined from the mass balance.

After the optimal conditions for copper extraction from pregnant solution was determined, the effect of temperature on the process was studied. That experiment was carried out in a chamber in which constant temperature (at 5, 10, and 15ºC, respectively) was maintained during the test. In order to exhaust the extraction capacity of 8 % LIX 984 N, six consecutive cycles of solvent extraction were carried out at each temperature. The concentration of copper and iron in raffinate were determined after each cycles of extraction. The extraction isotherms at 5, 10, and 15º C respectively were drawn and the relevant constants for copper extraction (KL) were determined by means of Langmuir equation. The rate constants (k)of copper extraction at the relevant temperatures were determined by means of pseudo-first order kinetic expression (Halder et al., 1997). The selective separation between copper and iron as a result of solvent extraction was evaluated by means of distribution coefficients (Kd) and a separation factor(*βCu/Fe*), respectively.

The stripping of copper was carried out with the organic phase received after the equal mixing of the volumes of loaded LIX 984 N that was produced as a result of the study of extraction process at 5, 10, and 15ºC. The temperaturethat was maintained during the process was 35ºC; the stripping agent was 180 g/l H2SO4 and the applied O: A ratio was 20:1. The constant temperature was maintained by means of a JulaboSW 22 water bath. The stripping behavior of copper fromorganic to aqueous phase was studied by means of two different variant. In the first variant, the stripping of copper was realized as a one-stage process, and its total duration was 36 minutes. The aqueous phase was sampling periodically during the process, and as a result, the stripping isotherm for copper was drawn.In the second variant, the stripping of copper was realized as a three-stage process. After each stage, copper concentration wasdetermined in aqueous as well as in organic phase, and the next stage of stripping was realized with fresh solution of sulfuric acid. On that base, the relevant McCabe-Thiele diagrams of copper distribution between two phases were drawn.

The average rate for stripping of copper as well as the rate constant for copper stripping was determined by the above-mentioned equations (Halder et al., 1997).

**RESULTS AND DISCUSSION**

A lot of experimental conditions have influence on the effectiveness of copper solvent extraction from pregnant solutions. Amongst them pH of the aqueous phase is a parameter that has a crucial role. As a thumb of rule, the concentration of iron and especially concentration of ferric iron is usually much higher or at least equal to that of the dissolved cupric ions in pregnant solutions produced as a result of bioleaching (Groudev et al., 2013). In that case, the efficiencyof selective copper separation and extraction is strongly dependent on the pH of the aqueous phase. It is well known that the extraction process is highly selective in the pH range of 1.5 – 2.0 (Kul&Cetinkaya, 2009; Zhang et al., 2011). For that reason, pH in a set of experiments was adjusted by Na2CO3addition. The highest value of copper solvent extraction was measured at pH 1.75 of the aqueous phase (Table 1). At higher pH, especially above 2.50, most of dissolved ferric iron ions hydrolyzed which led to formation of Fe(OH)2+, Fe(OH)2+ and Fe(OH)3complexes. These complexes adsorbed and co-precipitate a significant part of cupric ions which determined a reduction of copper extraction.

Table 5.

*Effect of ambient temperature on copper extraction from pregnant solution at optimal conditions by LIX 984 N*

|  |  |  |  |
| --- | --- | --- | --- |
| Index | Temperature, ºC | | |
| 5 | 10 | 15 |
| Cu in organic phase, mg/l | 2775 | 2802 | 2825 |
| Cu in raffinate, mg/l | 95.0 | 93.0 | 82.0 |
| Distribution coefficient of copper, KdCu | 29.2 | 30.1 | 34.4 |
| Extraction constant of copper, KL, L/ mmol | 0.270 | 0.269 | 0.268 |
| Average rate of copper extraction by 8 % LIX, VCuextracted,*gCu/l/ h* | 0.628 | 0.632 | 0.64 |
| Extractionrate constant of copper determined at 50 % saturation of 8 % LIX984 N, k, s-1 | 3.53x10-3 | 3.53x10-3 | 3.57x10-3 |
| Distribution coefficient of iron, KdFe | 0.14 | 0.14 | 0.13 |
| Separation factor, βCu/Fe | 208.6 | 215.0 | 264.6 |



**Fig. 1. Extraction isotherms of copper by LIX 984 N at the relevant temperature**

In a second set of experiments, the effect of concentration of LIX 984 N on solvent extraction of copper was studied. The optimal concentration of the extractive reagent is strongly dependent on the concentration of dissolved copper in the pregnant solution. The solvent extraction is a process short in duration and for that reason higher concentration of copper in aqueous phase requires a higher concentration of extractive reagent. On other hand, it is not advisable to use too high concentration of extractive reagent than the optimal because the separation process between copper and iron is worsening (Liu et al., 2008). So, the best copper extraction was received with 8 % and 10 % LIX 984 N at 8 minutes mixing time and at 300 rpm (Table 2). For that reason, 8 % LIX 984 N was determined as an optimal concentration.

Practically the concentration of LIX 984 N as well as the ratio of organic to aqueous phase (O:A) are the most important parameters which determine the efficiency of copper extraction as well as the final concentration of copper in enriched electrolyte. Organic to aqueous phase ratio which is used in practice widely is close to 1:1 (Ochromowicz&Chmielewski, 2013; Jenkins, 2002). Ratios with more volumes of the aqueous phase determine the lower rate of copper diffusion and extraction due to the higher difference in the specific gravities of both phases as well as and their immiscibility. For that reason, the highest copper extraction was measured at O:A ratio of 1:1(Table 3). The approach applied into the practice to receive organic phase with higher concentration of copper is connected with the application of lower O:A ratio combined with a higher concentration of the extractive reagent as well as to use a longer time of mixing of both phases (El Amari et al., 2006; Zhang etal., 2011).

In the fourth set of experiments, theduration of mixing of the both phases were studied. The solvent extraction as most of the chemical processes is time dependent. For that reason, the best resultsfor copper extraction were received for 8 and 10 minutes of duration of mixing (Table 4). However, the extra contact of both phases by agitation for another two minutes led to only 5.4 mg Cu/ l additional extraction from aqueous to organic phase. For that reason, 8 minutes was determined as an optimal time for solvent extraction of copper.

As a result of these experiments, relevant values of the most important technological parameters of solvent extraction ofcopper were determined as optimal as follow:

* Optimal pH of the pregnant solution for solvent extraction of copper - 1.75;
* Concentration of LIX 984N in organic phase – 8 %;
* Ratio organic to aqueous phase (O:A) = 1:1;
* Duration of agitation of organic and aqueous phase – 8 minutes.

After the optimal conditions for solvent extraction of copper from the pregnant solution were determined, the effect of the ambient temperature on the process was studied. Temperature of environment is well-known to have a significant effect on activity of ions in solutions as well as on the reactions they participate in. In addition to that, most of the plants for processing of pregnant solutions generated as a result of chemical as well as bacterial leaching are built nearby to the mineral depositsi.e. in the mountains at higher altitude where amplitude in ambient temperature through year is significant. For that reason, as a part of this study the efficiency of copper extraction was studied at 5, 10, and 15 ºC which are in the temperature range at elevation of 1200 – 1700 m above sea level for most of time of the year.

Six consecutive cycles of solvent extraction of copper were carried out for each temperature with aim to saturate extraction capacity of 8 % LIX 984 N containing in the organic phase. By means of periodical sampling during the first cycle of solvent extraction, the extraction isotherms for these temperatures were drawn (Figure 1). The results showed that even after the first cycle of solvent extraction when the saturation of extraction capacity of LIX 984 N was negligible, the temperature had a strong effect on the process. For example,

Table 6.

*Effect of the way of organization of stripping process on copper re-extraction by means of 180 g/l H2SO4and at Organic to Aqueous phase (O:A) ratio of 20:1*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Index | As an  one-step process | As an three-stage process | | |
| 1st stage | 2nd stage | 3rd stage |
| Cu in aqueous phase, g/l | 39.93 | 29.4 | 18.95 | 6.4 |
| Cu stripping, % | 71.3 | 52.5 | 71.2 | 84.2 |
| Cu in organic phase at the end of stripping, g/l | 0.80 | 1.33 | 0.38 | 0.06 |
| Average rate for stripping of copper, VCustripped,*gCu/l/ min* | 1.11 | 2.45 | 1.58 | 0.53 |
| Rate constant of stripping of copper, *k, s-1* | 2.13x10-4 | 1.07x10-3 | 1.75x10-3 | 3.19x10-3 |



***Fig. 2. Stripping isotherms of copper by 180 g/l H2SO4 at O:A ratio of 20:1 realized as one-stage process***

the difference in copper extraction after the first minute of mixing for the relevant temperatures was negligible. However, the difference in amount of the extracted copper by means of LIX 984 N steadily increased, so that at the end of the first extraction cycle copper extraction efficiency at 5, 10, and 15 ºC were 93.6, 96.3, and 97.7, respectively. These values were determined by the extraction rate constant and the average rate of copper extraction which had increased with increasing the temperature (Table 4). As a result of this, the highest value of the distribution coefficient of copper (KdCu) as well as the lowest value of distribution coefficient of iron (KdFe) was measured at 15 ºC. So, the highest value of the separation factor between two cations (βCu/Fe) which were presented in the pregnant solution was measured at that temperature. During the next five cycles of solvent extraction the difference of the copper extraction at these temperatures steadily increased and the concentration of copper in organic phase after the sixth extraction cycle was 2775, 2802, and 2825 mg/l, respectively (Table 5). These results determined that average efficiency of copper extraction for the six cycles solvent extraction at 5, 10, and 15 ºC were 89.9, 90.7, and 91.4 %, respectively. For that reason, the practical way to improve the extent of copper extraction at 5 ºC or even lower temperature would be to use higher concentration of extractive reagent in organic phase or to increase the agitation time of both phases.



**Fig. 3.McCabe-Thielediagramforstrippingofcopperfrom saturated 8 % LIX 984 N by 180 g/l H2SO4 at O:A ratio of 20:1 realized asa one-stage process**



**Fig. 4.McCabe-Thielediagramforstrippingofcopperfrom saturated 8 % LIX 984 Nby 180 g/l H2SO4 at O:A ratio of 20:1 realized asa three-stage process**

The process following the solvent extraction was the transfer of already extracted copper from the organic back into the aqueous phase by means of a process of stripping. For that purpose, highly concentrated solution of sulfuric acid was used which enabled the additional separation and concentration of cupric ions as well as recovery of the extractive properties of LIX 984 N.

There are two factors which have strong effect on the process. One of them is the concentration of sulfuric acid which has effect on the process` rate as well as on the properties of the extractive reagent when the used concentration is higher. For that reason, concentration of sulfuric acid, which is most used widely in the practice, is in the range of 150 – 250 g/l (Ritcey, 2006; Jenkins, 2002). The second important factor for the effective stripping process is the ratio between organic and aqueous phase (O:A). its value determined the power of concentration of copper due to its transfer from organic to aqueous phase. Understandably, as the copper concentration in the enriched solution is higher as the efficiency ofstripping process is better due to the lower operation costs of copper deposition oncathode by electrowinning process (Peacey et al., 2003).For that reason, two different variant of stripping of copper at O:A = 20:1 at temperature of 35 ºC were studied – as an one-stage as well as three-stage process, respectively.

At the end of one-stage-variant, the concentration of copper in the enriched solution was 39.93 g/l, which referred to 75.1 % efficiencyof copper transfer from organic to aqueous phase (Table 6, Figure 2). Total duration of process was 36 minutes, however the rate constant of copper transfer decreased significantly after the fifteenth minute since the start of the process (Table 67, Figure 2). As a result of this, the residual copper concentration in the organic phase was still high - 0.80 g/l (Figure 3).

In the second variant, the stripping was realized as three consecutive-connected-processes and the residual cooper concentration in the organic phase after the third cycle of stripping was decreased to 0.06 g/l. By this way, more than of 99 % of copper in the organic phase was successfully transferred into the aqueous phase. Understandably, the copper concentration in enriched electrolytes were lower (29.4, 18.95, and 6.4 g/l, respectively) in comparison to that received as a result of the one-stage stripping process (Figure 4). However, the average rate of copper stripping for the first stage of stripping was more than twofold higher in comparison to the rate measured for the one-stage variant. In similar way, the rate constants of copper stripping for each stage of the second variant were with an order higher in comparison to the value measured for the one-stage variant of the process (Table 6). The better results of three-stage process for stripping of copper could be explained with a higher amount of volume of sulfuric acid that was used. By this way, theexchange between hydrogen ions and already extracted copper was enhanced which determined the higher rate of copper diffusion from organic back to the aqueous phase.

**CONCLUSIONS**

1. pH of the pregnant solution, concentration of LIX 984 N, organic to aqueous phase (O:A) ratio as well as the duration of agitation of both phase during the solvent extraction process had strong effect on separation and transfer of copper from aqueous to organic phase.
2. The best result for copper extraction from studied pregnant solutions was received at 15 ºC. Its value was determined by the higher average rate of copper extraction from the aqueous phase as well as the higher value of the rate constant. As a result of this, the separation between copper and iron, which were presented in the pregnant solution, was considerably enhanced. When the process have to be realized at 5 ºC or even lower temperature, the lower rate of copper diffusion from aqueous to organic phase could be compensate by the higher concentration of extractive reagent as well as the longer agitation time of both phases.
3. Organic to aqueous (O: A) ratio had strong influence on the stripping of copper also. If used O: A ratio is higher than 10:1,it will be better the stripping process to be organized as a counter-current batch process consisting of two stages. By this way, the whole duration of the process would be decreased as well as the average rate of copper stripping and the value of rate constant would be increased respectively. Meanwhile, the residual concentration of copper in the organic phase after the stripping would be decreased significantly which improved the processes` mass balance as well as the full recovery of extractive properties of LIX 984 N for the next cycle of solvent extraction of copper.

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