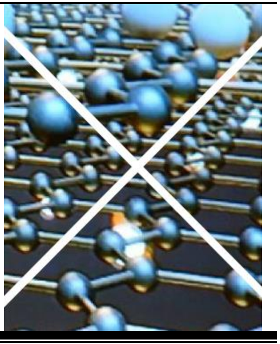
TIJMET, Vol. 0004 (2021) 125-132

The International Journal of
Materials and Engineering Technology

ISSN: 2667-4033
TIJMET ID: 210402005 (8 pages)
Type of the Paper: Research Article
Received: 20.10.2021 Revised: 07.12.2021 Accepted: 21.12.2021 Published (Online): 23.12.2021
Journal homepage: http://dergipark.gov.tr/tijmet



PRODUCTION OF CATHODE COPPER FROM LEACH LIQUOUR BY SELECTIVE ELECTROWINNING PROCESS

ELİF UZUN KART*[1a], ZEYNEP HAZAL YAZĞAN[1b]

[1]Department of Metallurgy and Materials Engineering, Marmara University, 34722, Istanbul, Turkey
*elif.uzun@marmara.edu.tr

Abstract

This work is aimed to have a direct Cu extraction from leach solution of chalcopyrite concentrate as an alternative to conventional smelting, refining and electrorefining methods. First of all, main aspects of kinetics of chalcopyrite leaching in sulphuric acid solution and transformation reactions of chalcopyrite at high temperatures were reviewed in detail, as well as processing and beneficiation of sulphide (chalcopyrite) copper ores. Consequently, the classic atmospheric acid leaching experiments was applied to oxidative roasted concentrate with a copper grade 21.1 under agitation by stirring. Therefore, the formation of a passive layer of sulphur on the chalcopyrite surface was concluded to be the main reason of the blocked reactions in the leach solution. The supply of elemental sulphur, sulphides in the solution should be removed in order to increase the dissolution rate. Therefore, the sulphides in the chalcopyrite were transformed into sulphates and oxides by heat treatment at 500 °C prior to leaching process. Furthermore, Cu extraction was resulted in high recovery yields of 99.82%. At the end of the leaching, the electrowinning experiments were carried out for 10 hours at 2.5 V to leach liquor with a high Cu and low Fe content and a 99.999% purity cathode copper (A Grade) was obtained and all iron ions remained in the solution.

Keywords: Cathode copper, atmospheric acid leaching, selective electrowinning.

1. Introduction

Copper, which has been known since ancient times, ranks the first in mineral exploration with its industrial importance, appearance, alloying ability, low corrosion, malleability, and high thermal and electrical conductivity. Copper has various usages such as construction, agricultural applications, electrical and general engineering applications, and has contributed greatly to the

---

How to cite this article:
Uzun Kart, E., Yazğan, Z.H., Production of Cathode Copper From Leach Liquour by Selective Electrowinning Process, The International Journal of Materials and Engineering Technology, 2021, 4(2): 125-132.

ORCID ID:
[a]0000-0002-4950-2162, [b]0000-0002-3502-5545

progress of humanity until our present day [1]. Copper ores are generally found in the form of sulfide minerals, oxidized minerals, and complex minerals in the nature. The most important copper ores are chalcolite (Cu_2S), chalcopyrite ($CuFeS_2$), and malachite [$CuCO_3 \cdot Cu(OH)_2$]. Other copper ores that are available are bornite, and azurite. Approximately 85% of the known copper reserves consist of sulfide and 15% oxide minerals [1], [2]. Copper is usually produced by smelting concentrates that are obtained by crushing and flotation, followed by sulfide ore mining. Higher-grade chalcopyrite concentration is obtained with flotation enrichment. Copper smelting method, which is one of the traditional methods, is generally used to obtain copper matte in the evaluation of chalcopyrite concentrate. However, these methods, which involve smelting processes, require high costs. Also, the greenhouse gas that is released to the nature at a high rate and the dusting of the concentrate fed into the atmosphere under open-air conditions affect the environment negatively [3], [4]. In our present day, pyrometallurgical methods are replaced by more economical and environmentally friendly hydrometallurgical methods due to these effects in environmental conditions and impurities such as heavy metals (Pb, As, Hg etc) are abundant in the environment and contribute largely to the sustainability and equilibrium of ecosystem processes. However, because of their bioaccumulation, nondegradability, and the excessive amounts in which they exist, these metals contaminate the food chain and subsequently become a source of toxicity to human beings and the entire ecological function) in the formation of ore. In pyrometallurgy solid wastes that contain heavy metals, dust and gas problems are getting attention than hydrometallurgy because of sustainable process without any dust, gas and heavy metal discharges.[5].

Hydrometallurgy is among the well-established and well-known branches of extractive metallurgy, and has emerged recently as a leading technology, and has been quite successful in many extractive processes playing important roles in the production and processing of nuclear metals and materials. Hydrometallurgy is done to recover by-products, separate intermediates, isolate impurities, or increase the efficiency of downstream unit processes [6]. It consists of a series of separation processes, starting with the leaching of ores or concentrates and ends with highly pure cathodes, powders, or compounds that are recovered from the solutions [7],[8]. As a unit process, the use of solvent extraction in hydrometallurgy extends from a variety of feed materials to a wide variety of metals, and includes low-grade ores, scraps, tailings, and dilute aqueous solutions. One of the advantages of hydrometallurgy is that the leaching of chalcopyrite as a slow factor in its pure state happens fast in a sulfated setting and a high rate of elemental sulfur is released in this respect. The formation and accumulation of sulfur also enable atmospheric leaching reducing the costs in the neutralization of acid that forms during the leaching process [9]. In general, the processes that are involved in hydrometallurgy are roasting, leaching, and electrowinning. Electrowinning is among the oldest known electrolytic processes, and is used widely in modern metal recovery, mining, and refining. Although the majority of copper production is performed with pyrometallurgical methods today, there has been a significant increase in copper production from oxide and sulfide ores by electrowinning in recent years [10]. In the electrorefining method, which is after the pyrometallurgical methods, although the anode is a copper product, they come from smelting process and it is the anode that is consumed to produce cathode copper in 99,99% Cu purity. Although the electrolysis process happens here, the precious metal impurities in the anode are collected in the electrolysis cell as anode sludge. The anode is the charged solution itself in electrowinning and is produced by the leaching process, then fixed, and inexhaustible anodes are employed to obtain electric current cycle. In this way, anode sludge does not occur [11]. The copper in the ores is leached out in the electrowinning process as valuable ions by using an acid solution, which contains positively and negatively-charged ions as electrolyzed, the positive charges are moved around a cathode, and the negative charges around the anode, in other words, copper ions are collected around the cathode [11].

The cathode (1), anode (2) and overall reactions (3) in the electrowinning of copper are as follows [12]:

$$Cu^{+2} + 2e^- \rightarrow Cu\ (E° = +0,34V) \quad (1)$$
$$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-\ (E° = -1,23) \quad (2)$$
$$Cu^{+2} + H_2O \rightarrow Cu° + 1/2O_2 + 2H^+ \quad (3)$$

2. Experimental Procedure

In electrowinning, approximately 8-10 times more energy is consumed (2.0 kW h/kg) than in electrorefining (0.25 kW h/kg), which has led to the start of studies to reduce energy consumption. In the electrowinning of copper, the presence of iron in the charged solution is a disadvantage [10]. Cathode copper was obtained in the present study from atmospheric acid leaching liquor with selective electrowinning. Cathode copper was obtained in the present study from atmospheric acid leaching liquor with selective electrowinning that is aimed to deposite only copper ions on the cathode and to remain all iron ions in the solution.

Chalcopyrite concentrate that was obtained from North Anatolia region was used in experimental works. The chemicals that were used on the concentrated sample, where hydrometallurgical methods were applied, were: Merck-quality sulfuric acid (96%, d: 1.84 g/cm3), Merck-quality benzotriazole (d:1.36 g/cm3) and de-ionized water [13]. An 8x5x0.2cm anode and cathode were employed for the electrowinning trials. Stainless steel (AISI 304L series low carbon austenitic stainless steel) was preferred as the cathode and graphite as the anode. A potentiostat with a capacity of 30V, 6A was used as the electricity (DC) source.

With the presence of a passive layer that originated from sulfur on the surface of the chalcopyrite concentrate atmospheric leaching process. Uzun, et. al., 2017 obtained as a result of their study the optimum roasting conditions of chalcopyrite concentrate to partial sulphates and oxides in atmospheric pre-heating treatment was applied at 500°C for 3 hours and in the same study atmospheric leaching conditions also were optimized 65°C, 120 g/L H_2SO_4 concentration under atmospheric conditions for 180 minutes and a high copper and low iron charged solution was obtained [14]. The leaching process was performed by using a propeller to provide mixing into the reaction vessel that was placed in a water bath as shown in Figure 1, and a magnetic stirrer with ceramic heating plate that has bushing for connecting a contact thermocouple to set the temperature at desired value.

Figure 1. Experimental setup of leaching.

Electrowinning experiments were used to obtain cathode copper from the charged solution obtained by atmospheric acid leaching. An experimental setup was used in the electrowinning experiments as shown in Figure 2, and the anode and cathode that were immersed in the copper-charged solution were connected to the power source. Electrowinning was used to the charged solutions containing Cu^{+2} and $Fe^{+2,3}$ ions for 2-10 hours at room temperature (30±1°C) and at electric potential difference values of 2-10V in the experiments. The distance between the anode and the cathode was 4.5 cm, and it was kept constant in all experiments [15]. The surface of the cathode copper, which is removed from the solution after the electrowinning process, was coated with benzotriazole by immertion in its solution, which is a physical coating process, and was then washed with de-ionized water and was dried at 60°C under atmospheric conditions to prevent sudden oxidation because the copper collected on the cathode had a highly reactive surface [16].

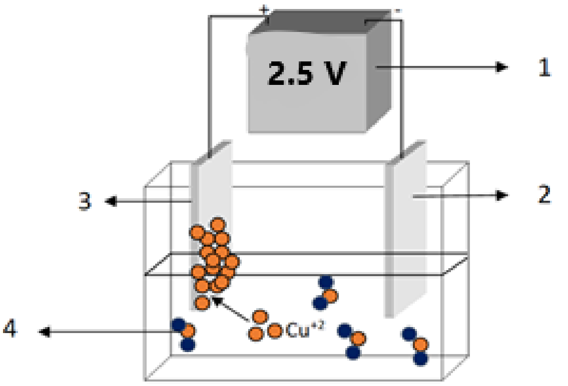


Figure 2. Experimental setup of electrowinning (1: power supply, 2: graphite anode, 3: stainless steel cathode, 4: Cu^{+2} ions)

3. Results and Discussion

Approximately 100 kg chalcopyrite concentrate that was extracted from the North Anatolia deposit and enriched at the pilot scheme was obtained with a density of $2.81 g/cm^3$ and a humidity of 7.82%. Obtaining the charged solution that was needed for electrowinning was provided with this concentrate, whose elemental analysis is given in Table 1 that was analyzed by ICP-OES and mineralogical (XRD) analysis is given in Figure 3 [1,14].

When the peaks in the pattern in the XRD pattern taken for the mineralogical analysis of the concentrated sample given in Figure 3 were examined, the 2ϴ angle was 29°, and chalcopyrite yielded the highest density in its own peaks and the peaks of other minerals. Chalcopyrite was observed at low-peak heights when the 2ϴ value was 34°, 49°, 58°, and 59°, respectively. After chalcopyrite, the highest peak 2ϴ angle was found to be 33°, and it was formed by the reflection of pyrite and sphalerite in the same area. Also, pyrite and sphalerite appeared at the same peak at 28°, 48°, and 55° angles, respectively. The peaks in which pyrite and sphalerite were seen alone were 36° and 70°, respectively, and when their sizes were compared, it was found that the sphalerite rate was very low. As a result of the mineralogical analyses with an optical mineralogist microscope, it was also supported by the result of this analysis that chalcopyrite that had the highest percentage (65%) also had a high density, and the least amount (5%) was found at low density [1,14].

Table 1. Elemental contents of chalcopyrite concentrate that was used to obtain the charged solution

Mineral	%	Element	%
$CuFeS_2$	65	Cu	21.1
FeS_2	30	Fe	33.34
ZnS	5	S	36.44
SiO_2	1.12	Zn	1.26

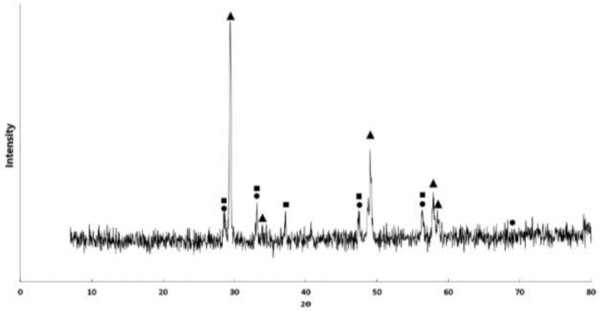


Figure 3. Mineralogical (XRD) pattern of the chalcopyrite concentrate that was used for the pregnant solution (chalcopyrite:▲; pyrite:■ ; sphalerite:●) [1], [14].

The sulfides in the concentrate were converted into sulfates and oxides with pre-heat treatment under atmospheric conditions at

500°C to decrease the effects of the passive surface that formed on the surface of the chalcopyrite concentrate [17]. The XRD pattern after the heat treatment applied to the concentrated sample is given in Figure 4 (b), and it is seen here that the dominant peaks were hematite, iron sulphate, and chalcocyanate. It was also found that the most dominant chalcopyrite peak that had a value of 2Θ at 29° in the concentrated sample decreased much after the heat treatment, and almost disappeared. The disappearance of the pyrite and sphalerite peak at 28° (as seen in Figure 4 (a)) with the heat treatment shows that it is a sphalerite peak rather than a pyrite one. It is also seen that pyrite and hematite exist together in the heat-treated concentrate at the most dominant peak at 2Θ value at 32° (at the same peaks at 41°). Hematite peaks were at 24°, 32°, 36°, 41°, 50°, 55°, 57°, 63°, 65°, and 73° 2Θ, respectively. However, the tenorite that was expected following the heat treatment can be said to be very low in density because it shows a slight peak formation at odd angles [18][19][20][21].

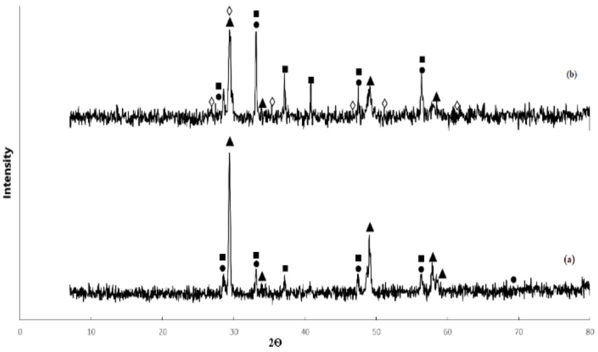


Figure 4. XRD patterns of (a) concentrate sample and (b) heat-treated concentrate (chalcopyrite:▲; pyrite:■; sphalerite:●; iron sulphate: ○; hematite:□; chalcocyanate: Δ; tenorite:▼) (*Patterns were shifted on the y-axis) [14]

After the heat treatment, 99.82% of the copper and 36% of the iron that were in the concentrates were recovered with the atmospheric stirred leaching process at a concentration of 120 g/L H_2SO_4 for 180 minutes at 65°C [22][9][23][24]. The optimum leaching conditions in this respect are given in Table 2. Electrowinning experiments were used for the charged solution after leaching under optimum conditions. The optimum leach liquour has 1.56% Cu^{+2} ions and 1.27%$Fe^{+2,3}$ ions. Experiments were performed between 2-10V, and it was found that, as the potential difference value increased, the copper collected in the solid phase in the electrolyte without adhering to the cathode and oxidized. Electrowinning experiment was performed at 10V for about 2 hours. Elemental analysis of the copper powder after the experiment was made, and it was found that 99.9% of it was copper oxide (Cu_yO_x). The copper oxide that appeared after electrowinning is shown in Figure 5. As a result of the experimental studies, it was found that copper cannot attach to the cathode surface when the value is below 2.5V, $Fe^{+2,3}$ ions in the solution are collected on the cathode together with Cu when this value is above 2.5V, or they pass into the solid phase in the electrolyte in powder form in the form of CuO at higher values, and a copper plate was not obtained at the desired purity [25]. It was concluded as a result of the electrowinning experiments that the optimum voltage value was 2.5V. Electrowinning experiments were performed at 2.5V between 2-10 hours to examine the effect of the time on the copper recovery efficiency, and it was found that the copper recovery efficiency increased depending on the increase in the time. The results of the tests are given in Table 3. The procedure of the experiment, which was performed under optimum electrowinning conditions (Table 4), the obtained cathode copper, feed-charged solution, waste solution, and electrowinning cell are given in Figure 6.

Table 2. Optimum leaching conditions

Leaching Temperature	65 °C
Leaching Time	180 min
Acid Concentration	120 g/L
Solid/Liquid	1/8
Mixing Speed	280 rpm

Table 3. Time-dependent copper winning yield values

Time (hours)	Cu Deposition (%)
2	17.43
4	37.40
6	50.77
8	68.19
10	83.97

Figure 5. Copper oxide (Cu_yO_x) obtained after electrowinning.

The chemical analysis of the cathode copper plate obtained as a result of the electrowinning test under optimum conditions is given in Table 4. The charged solution obtained in optimum leaching conditions was subjected to electrowinning under optimum conditions. X-ray diffraction (XRD) (Figure 7) and X-ray fluorescence (XRF) (Table 5) analyzes were used to the cathode copper plate obtained as a result of the trial. It was observed that the cathode copper plate contains 99.999% pure copper.

Table 4. Optimum electrowinning conditions

Electrolytic temperature, (°C)	30
Electrowinning time, (s)	10
Distance between electrodes, (cm)	4.5
Reaction voltage, (V)	2.5
Copper concentrate, (g/L)	15.6
Fe concentrate, (g/L)	12.7
pH value	1.28

Table 5. Chemical analysis of cathode copper

Element	%
Cu	99.999

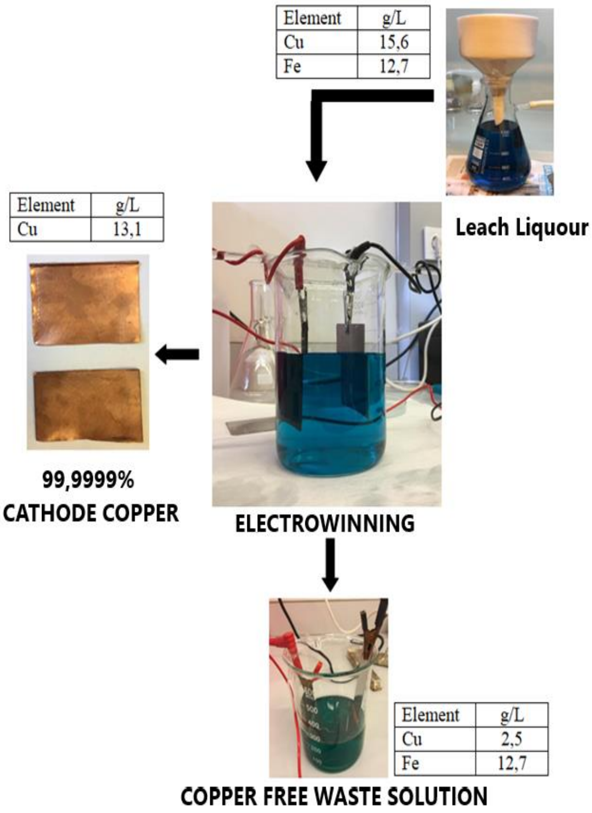


Figure 6. The procedure of the experiment, cathode copper obtained, feed-charged solution, waste solution, and electrowinning cell.

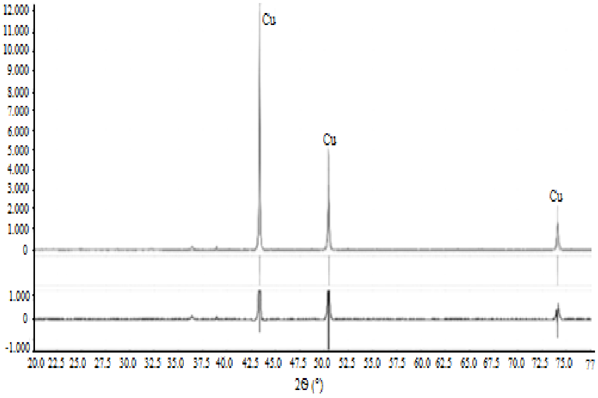


Figure 7. X-ray diffraction (XRD) patterns of the cathode copper plate.

4. Conclusion

In this study; cathode copper plate that had 99.999% Cu content was obtained by selective electrowinning method from chalcopyrite concentrate that had 21.1% Cu content. Atmospheric heat treatment was applied to the concentrate at 500°C for 3 hours to decompose the passive layer on the surface of chalcopyrite, and the copper was made to become sulphated and the iron oxidized. Stirred leaching was applied to the concentrate, whose surface characteristics were degraded, at 120 g/L acid concentration under atmospheric conditions at 65°C for 180 minutes, and the Cu recovery efficiency was calculated to be 99.82%, with a Fe recovery efficiency at 36%. It was found with the ICP-OES Elemental Analysis that the charged solution that was used for the optimization of the electrowinning experiments had 15.6 g/L Cu and 12.7 g/L Fe contents. As a result of the electrowinning experiments, the potential difference value was determined to be 2.5V and the copper collection time 10 hours. As a result of the optimum electrowinning experiments, although the copper recovery efficiency was found as 83.97%, the degree of selectivity was 100% leaving all the iron in the solution, and Cu content was obtained as plate cathode copper with 99.999%.

References

1. Uzun, E. Kalkopirit Konsantresinden Hidrometalurjik Yöntemle Katodik Bakır Üretimi. Hacettepe University. 2015.
2. Barceloux, D. G. Copper. J. Toxicol. - Clin. Toxicol. 1999, 37(2):217–230, doi: 10.1081/CLT-100102421.
3. Munoz, P. B., Miller, J. D., and M. E. Wadsworth. Reaction mechanism for the acid ferric sulfate leaching of chalcopyrite. Metall. Trans. B, 1979, 10(2):149–158, doi: 10.1007/BF02652458.
4. Romero, R., Mazuelos, A., Palencia, I., and Carranza, F. Copper recovery from chalcopyrite concentrates by the BRISA process. Hydrometallurgy. 2003, 70(1–3):205–215. doi: 10.1016/S0304-386X(03)00081-1.
5. Ugonna C. Nkwunonwo, Precious O. Odika, Nneka I. Onyia, "A Review of the Health Implications of Heavy Metals in Food Chain in Nigeria", The Scientific World Journal, vol. 2020, Article ID 6594109, 11 pages, 2020. https://doi.org/10.1155/2020/6594109.
6. Akdağ, M. Hidrometalurji: Temel Esasları ve Uygulamaları. 88th ed. Dokuz Eylül Üniversitesi Mühendislik-Mimarlık Fakültesi Yayınları, 1992.
7. T. K. M. C. K. Gupta. Hydrometallurgy in Extraction Processes. 1990,Volume II.
8. Peters, E. Hydrometallurgical process innovation. Hydrometallurgy. 1992. doi: 10.1016/0304-386X(92)90026-V.
9. Ruiz, M. C., Montes, K. S., and Padilla, R. Chalcopyrite leaching in sulfate-chloride media at ambient pressure. Hydrometallurgy. 2011, 109(1–2);37–42. doi: 10.1016/j.hydromet.2011.05.007.
10. Panda B., and Das, S. C. Electrowinning of copper from sulfate electrolyte in presence of sulfurous acid. Hydrometallurgy. 2001, 59(1) :55–67. doi: 10.1016/S0304-386X(00)00140-7.

11. Oishi, T., Koyama, K., Konishi, H., Tanaka, M., and Lee, J. C. Influence of ammonium salt on electrowinning of copper from ammoniacal alkaline solutions. Electrochim. Acta. 2007, 53(1):127–132.
12. Ehsani, A., Deveci, H., and Erdemir, F. The Influence of Impurity Ions on The Electrowinning of Copper from Waste PCBs Leaching Solutions. 2012, May 2014, doi: 10.13140/RG.2.1.2701.5200.
13. Uzun Kart, E. Evaluation of sulphation baking and autogenous leaching behaviour of Turkish metallurgical slag flotation tailings. Physicochem. Probl. Miner. Process. 2021, 57(4):107–116.
14. Uzun, E., Zengin, M., and Atılgan, İ. Improvement of selective copper extraction from a heat-treated chalcopyrite concentrate with atmospheric sulphuric-acid leaching. Mater. Tehnol. 2016, 50(3):395–401.
15. Do, T. D., Hoang, H. V. T., Huynh, C., and Duong, T. V. T. An information theory-based approach for time series discord discovery. ICIC Express Lett. 2018, 12(10):1071–1078.
16. Meterfi, S., Meniai, A. H., and Chikhi, M. Elimination of Cu(II) from aqueous solutions by liquidliquid extraction. Test of sodium diethyldithiocarbamate (SDDT) as an extracting agent. Energy Procedia. 2012, 18(Ii):1165–1174. doi: 10.1016/j.egypro.2012.05.131.
17. Subramanıan, K. N., and Kanduth, H. Activation and Leaching Of Chalcopyrite Concentrate, CIM Bull. 1973.
18. McDonald, R. G., and Muir, D. M. Pressure oxidation leaching of chalcopyrite. Part I. Comparison of high and low temperature reaction kinetics and products. Hydrometallurgy. 2007, 86(3–4):191–205
19. Maurice, D., and Hawk, J. A. Ferric chloride leaching of a mechanically activated pentlandite-chalcopyrite concentrate. Hydrometallurgy. 1999, 52(3):289–312. doi: 10.1016/S0304-386X(99)00021-3.
20. Pan, H. D., Yang, H. Y., Tong, L. L., Bin Zhong, C., and Zhao, Y. S. Control method of chalcopyrite passivation in bioleaching. Trans. Nonferrous Met. Soc. China. 2012, 22(9):2255–2260. doi: 10.1016/S1003-6326(11)61457-X.
21. Dreisinger, D. Copper leaching from primary sulfides: Options for biological and chemical extraction of copper. Hydrometallurgy. 2006, 83(1–4):10–20. doi: 10.1016/j.hydromet.2006.03.032.
22. Padilla, R. Vega, D., and Ruiz, M. C. Pressure leaching of sulfidized chalcopyrite in sulfuric acid-oxygen media. Hydrometallurgy. 2007, 86(1–2):80–88. doi: 10.1016/j.hydromet.2006.10.006.
23. Venkatachalam, S. Treatment of chalcopyrite concentrates by hydrometallurgical techniques. Miner. Eng. 1991, 4(7–11):1115–1126. doi: https://doi.org/10.1016/0892-6875(91)90087-C.
24. Antonijević M. M., and Bogdanović, G. D. Investigation of the leaching of chalcopyritic ore in acidic solutions. Hydrometallurgy. 2004, 73(3–4):245–256. doi: 10.1016/j.hydromet.2003.11.003.
25. Musa, A. O., Akomolafe, T., and Carter, M. J. Production of cuprous oxide, a solar cell material, by thermal oxidation and a study of its physical and electrical properties. Sol. Energy Mater. Sol. Cells. 1998, 51(3–4):305–316. doi: 10.1016/S0927-0248(97)00233-X.