Journal of Chemical Technology and Metallurgy, 58, 6, 2023, 1139-1145

OPTIMIZATION OF DISSOLUTION OF COPPER FROM A NIGERIAN GOLDFIELDITE ORE FOR INDUSTRIAL UTILIZATION

Shemang Y. Chindo[1], Kehinde I. Omoniyi[1], Mustapha A. Raji[2], Usman Bello[3]

[1]Department of Chemistry, Ahmadu Bello University
P.M.B. 06, Zaria-810211, Nigeria
[2]Department of Industrial Chemistry, University of Ilorin
P.M.B. 1515, Ilorin-240003, Nigeria
[3]Centre for Biofuel and Biochemical Research
Chemical Engineering Department
Universiti Teknologi PETRONAS, Malaysia
E-mail: chindoshemang@gmail.com, israelflourish@yahoo.com

Received 07 March 2023
Accepted 07 July 2023

ABSTRACT

Conventionally, copper ores are treated and processed by a high-energy intensive pyrometallurgical process. However, the huge amounts of emission of obnoxious gases demand the development of a simple, low-cost, and environmentally friendly technique. In this work, the dissolution kinetics of goldfieldite ore in ammonia-ammonium chloride was investigated. The influence of some experimental conditions were critically developed. It was affirmed that the dissolution rate increased with increasing concentration, reaction temperature, and decreasing particle diameter. At optimized experimental conditions (0.5 mol L^{-1} NH_3-NH_4Cl, 75°C, 45 μm), 88.2 % copper dissolution was recorded with calculated activation energy, Ea, of 19.4 kJ mol^{-1}.

Keywords: *goldfieldite, optimization, leaching, activation energy, industrial utilization.*

INTRODUCTION

The scarcity of high-grade copper ores, which is largely due to the universal population growth and rise in consumption most especially in the high-tech sectors, has become a critical global threat in recent years [1]. As a crucial strategic metal, copper finds a wide array of utilizations in aviation, electronics, catalysis, and medicine, among others [2 - 4]; and thus, a key element in the removal of NOx and SOx from flue gases [5, 6]. At present, copper hydrometallurgy including leaching, solvent extraction, and precipitation, among others has developed appreciably and made the route draw global attention; thereby bringing novelty to the copper industry. Compared with energy-intensive copper pyrometallurgy, it has several distinct features such as effective recycling of valuable metals, ease of operation, low cost, and eco-friendliness, among others [7 - 9]. Almost 20 % of the global copper production is produced via hydrometallurgical routes, particularly by acidic and alkali leaching, solvent extraction, and electrowinning processes for low-grade ores.

However, numerous studies have been proposed for developing hydrometallurgical routes for leaching copper sulphide concentrates, at moderate and high reaction temperatures and pressure. Several leaching techniques, such as ammoniacal systems [10, 11], acid sulphate systems [12, 13], chloride systems [14, 15], nitrate systems [16], etc., have been examined. Thus, ammoniacal leaching has been commonly applied for the processing of non-ferrous metals from oxide ores and thereby allows for the maximum dissolution of the metal of interest leaving behind associated impurities including iron. These unwanted gangues led to a series of problems in processing the pregnant solution, such as the electrowinning of copper [17]. Also, the impurities present in the ore can cause high acid consumption. Although it has been reported that acid sulphate system is found with slow leach kinetics *cum* passivation of the mineral surface while the chloride systems gave more prevalent kinetics are highly corrosive [18, 19].

Hence, ammonia has become more popular as a lixivating agent in the present economic meltdown cum climate action conditions as a result of its low toxicity, low cost, and regeneration by evaporation process [20]. The aim of this investigation is therefore expected to address a persisting problem in Nigerian goldfieldite ore by sourcing an appropriate leachant (ammonia-ammonium chloride solutions) with lower environmental and safety risks.

EXPERIMENTAL

Material

The goldfieldite ore used in this investigation was provided from *Wase* (Nigeria). The raw ore was crushed, ground, and sieved using standard sieves to obtain desired particle fractions (45, 75, 90, and 125 µm). Deionized water was used throughout the experiments.

Leaching procedure

The leaching experiments were performed in a 500 mL glass reactor equipped with a mechanical stirrer, a thermometer to control the reaction temperature, and a condenser to prevent loss of solution by evaporation. A 10 g L^{-1} of the pulverized ore was added to the agitated solution at a defined lixiviant concentration at a specified reaction temperature, varied time intervals (5 - 120 minutes), and various ammonia-ammonium concentrations (0.05 - 0.6 mol L^{-1} NH_3-NH_4Cl). After the completion of the leaching examinations, the resultant solution was filtered, washed, dried and re-weighed. The concentration with the maximum fraction dissolved was used for the subsequent optimization of other parameters including reaction temperature and particle size variations [21 - 23]. At desired time intervals, 5 ml solution was withdrawn for analysis of copper and other associated impurities by atomic absorption spectrophotometer. However, the un-leached products obtained at optimal leaching conditions were analyzed by XRD and SEM-EDS analyses for material purity tests [24].

RESULT AND DISCUSSION

Ore characterization

The composition of the crude goldfieldite ore examined by EDXRF gave 57.89 wt. % SiO_2, 9.02 wt. % Al_2O_3, 8.91 wt. % CuO, 1.34 wt. % Fe_2O_3, 19.19 wt. % PbO, and 1.55 wt. % As_2O_3, respectively. However, the X-ray analysis indicates that the sample under investigation contains mainly *goldfieldite* ($Cu_{20.60}Te_{5.20}Sb_{1.71}$: 96-901-1756), *cerussite* ($Pb_{4.00}C_{4.00}O_{12.00}$: 96-901-3804), and *quartz* ($Si_{3.00}O_{6.00}$:

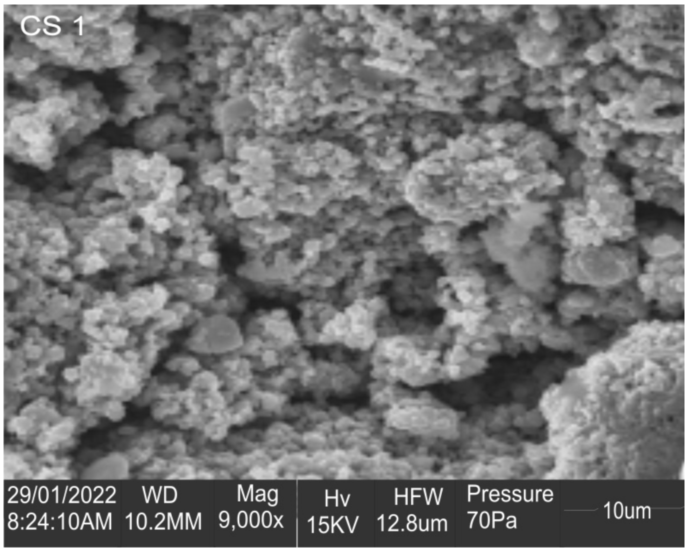

Fig. 1. SEM micrograph of the crude goldfieldite ore.

96-901-3322). However, the morphology of the crude goldfieldite ore was characterized by a bubble-cum-corrosion etching pits assembly as affirmed in Fig. 1 [25].

Also, in Fig. 1, areas showing a bright colour were characterized by a high percentage of silicon, aluminium, and lead could therefore be attributed to gangue minerals.

LEACHING INVESTIGATION

Effect of ammonia-ammonium chloride concentration

The influence of ammonia-ammonium chloride concentration on the extent of ore dissolution has been critically examined. The results are summarized in Fig. 2.

As can be observed in Fig. 2, initially the dissolution rate appreciably increased with the increase of ammonia-ammonium chloride concentration from 0.05 to 0.5 mol L^{-1}. A further increase in ammonia-ammonium chloride concentration to 0.6 mol L^{-1} gave a decrease in the dissolution rate. So, it is mandatory to keep up NH_3-NH_4Cl concentration at 0.5 mol L^{-1} during the goldfieldite leaching process [26].

Effect of reaction temperature

A series of experiments were performed to investigate the influence of reaction temperature on the dissolution rate. The temperature varied from 25°C to 75°C. The dissolution rate curves as shown in Fig. 3 indicate that the dissolution rate increased with an increase in reaction temperature.

The reaction temperature has a significant effect on the extent of copper dissolution from goldfieldite ore. At a temperature of 25°C, 47.2 % of copper was dissolved at 120 minutes of leaching, whereas at a temperature of 75°C, 88.2 % of copper was reacted only after 120 minutes of leaching. Hence, a decrease in copper dissolution was observed at 80°C for 120 minutes and could be attributed to the decomposition of ammonia-ammonium chloride solutions and their reaction with Cu(II) ions forming a precipitate [27].

Effect of particle size

The influence of particle size on the copper dissolution was studied for four size diameters (125, 90, 75, and 45 µm) at 75°C, in solutions containing 0.5 mol L^{-1} NH_3-NH_4Cl and a solid/liquid ratio of 10 g L^{-1} is shown in Fig. 4.

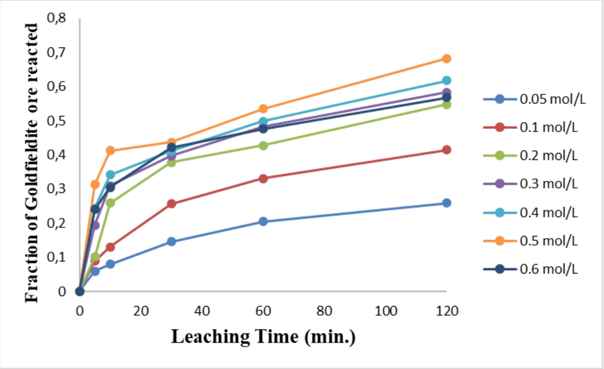

Fig. 2. Effect of $[NH_3$-$NH_4Cl]$ on the dissolution of goldfieldite ore. Conditions: $[NH_3$-$NH_4Cl]$ 0.05 - 0.6 mol/L, temperature 55°C, particle size 45 µm.

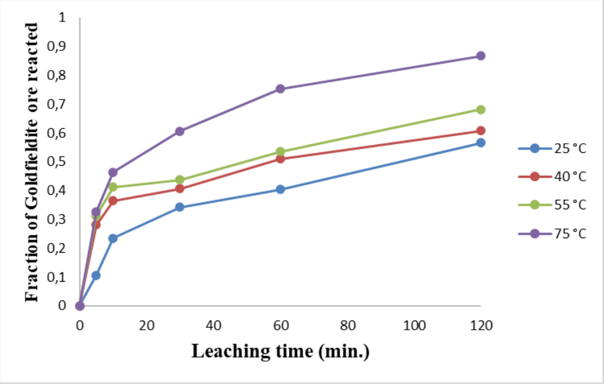

Fig. 3. Effect of temperature on the dissolution of goldfieldite ore. Conditions: $[NH_3$-$NH_4Cl]$ - 0.5 mol L^{-1}, temperature 75°C, particle size 45 µm.

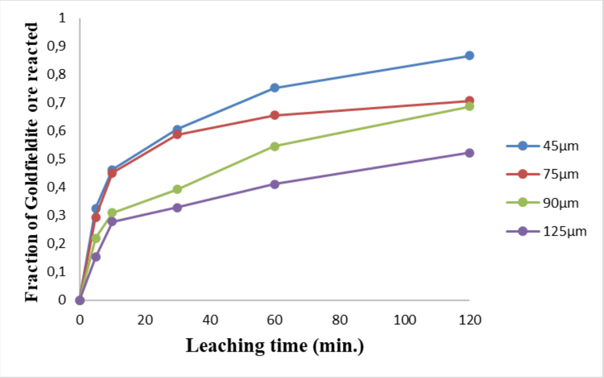

Fig. 4. Effect of particle size on the dissolution rate of goldfieldite ore. Conditions: $[NH_3$-$NH_4Cl]$ = 0.5mol L^{-1}, temperature = 75°C, solid-to-liquid =10g L^{-1}

As can be observed in Fig. 4, the rate of reaction increases as the size of the particles decreases. This effect is due to the increase in the interfacial area of the reaction as the solid particles become smaller [28].

KINETIC STUDIES

Tremendous attention has been paid to the investigation of the dissolution kinetics of non-homogeneous systems. Leaching is a basic unit operation involving recovering metal from ore by a lixiviant and the reactions occurring during the process are heterogeneous [21, 29]. The shrinking core model (SCM), maintains that the dissolution study considers that the leaching process is controlled either by the diffusion or chemical reactions. However, the stoichiometries for the SCM when either diffusion or chemical reactions are the rate-determining step can be summarized as follow [30]:

$$1-(1-x)^{1/3} = kt \tag{1}$$

$$1-\tfrac{2}{3}x-(1-x)^{2/3} = kt \tag{2}$$

where x - fraction of goldfieldite ore reacted; k - dissolution rate constant; t - leaching time.

From stoichiometries (1) and (2), when the process is chemical control, the R^2 value is 0.754; and if it is diffusion controlled, the R^2 is 0.958. The results of the fitting test of NH_3-NH_4Cl leaching depicted that the data fitted perfectly into reaction (2), as represented in Fig. 5.

The reaction order deduced from [NH_3-NH_4Cl] has a linear correlation value of 0.7432 as depicted (Fig. 6).

Also, calculating the activation energy of 0.5 mol L^{-1} NH_3-NH_4Cl leaching, the reaction temperature of the data was linearized in Fig. 7.

The kinetic rate constants for the reaction temperatures were estimated from the slopes of Fig. 7 and were used to make an Arrhenius plot as summarized in Fig. 8.

However, the activation energy of a diffusion-controlled is below 40 kJ mol^{-1}, while for a chemically controlled is greater than 40 kJ mol^{-1} [21, 22, 24]. Therefore, in this study, the calculated activation energy was 19.4 kJ mol^{-1} which indicates diffusion-based rate control.

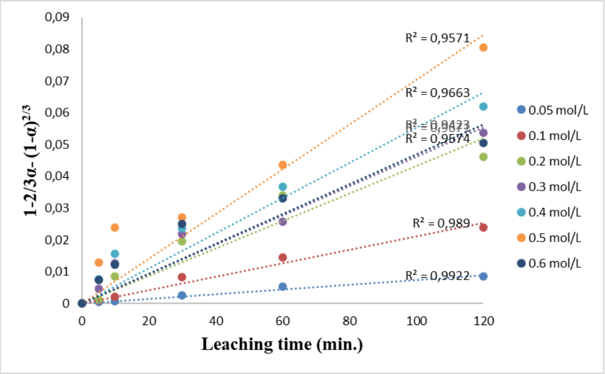

Fig. 5. The graph of $1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}$ versus leaching time.

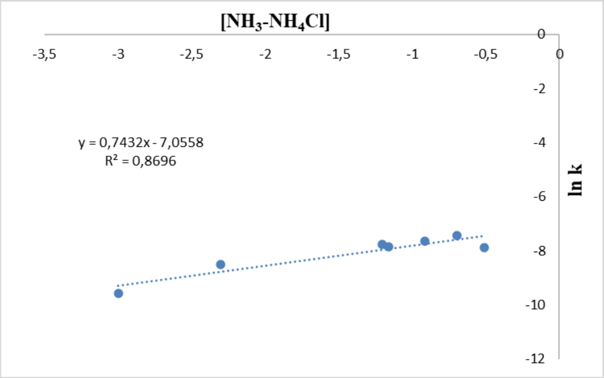

Fig. 6. The graph of ln k versus ln [NH_3-NH_4Cl].

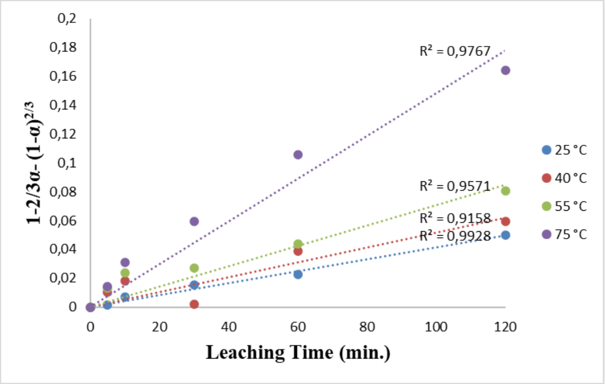

Fig. 7. The graph of $1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}$ versus leaching time.

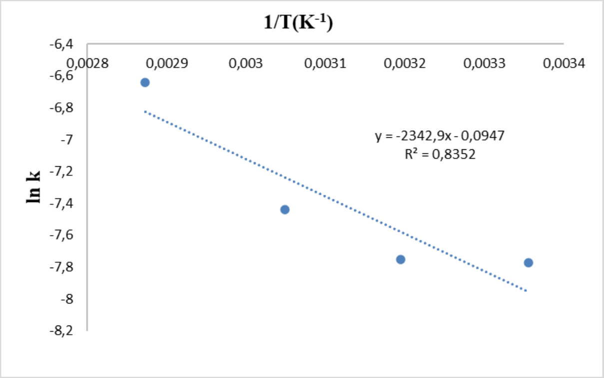

Fig. 8. The graph of ln k versus $1/\tau$.

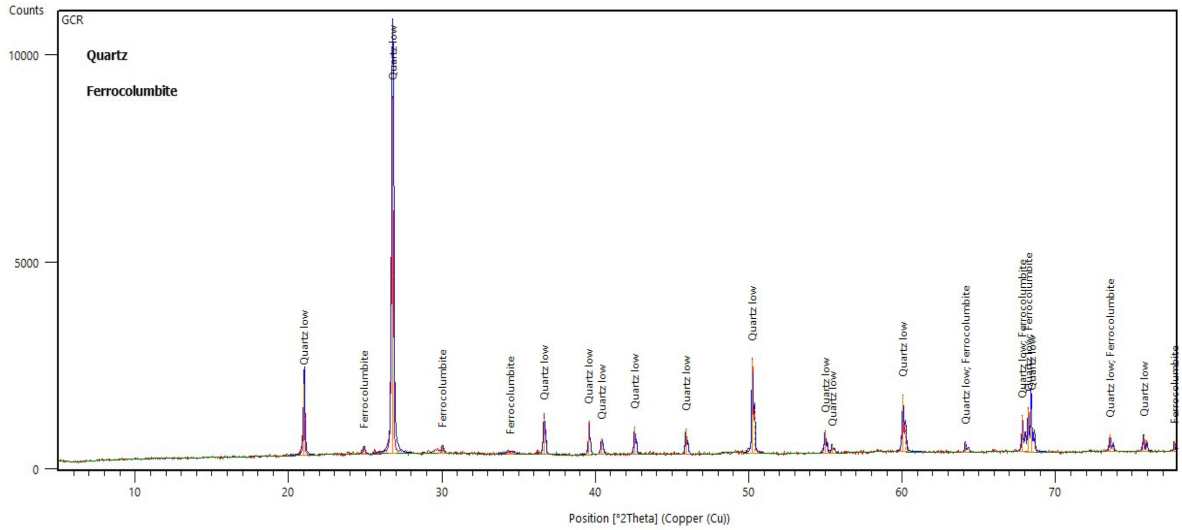

Fig. 9. X-ray diffraction pattern of the leached product.

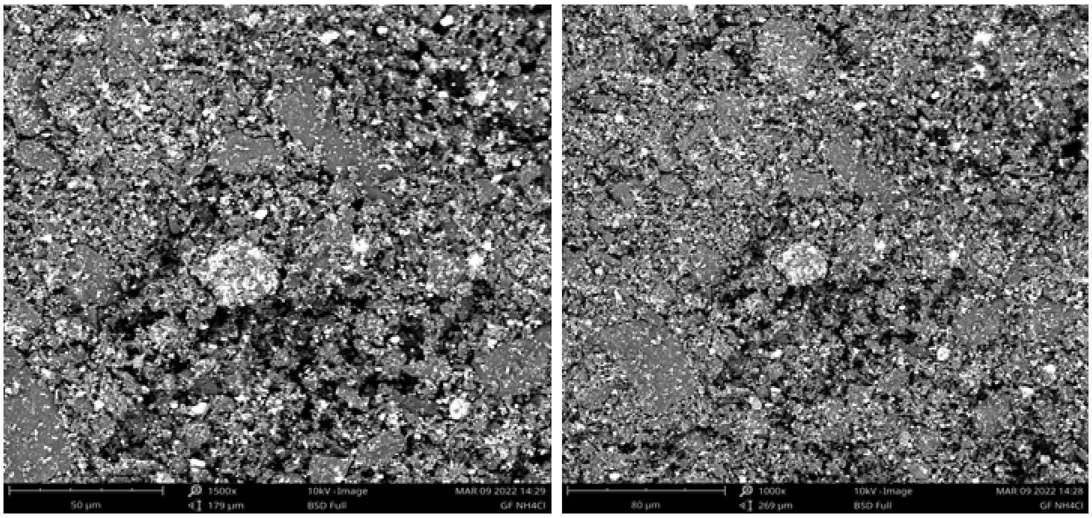

Fig. 10. SEM images of un-leached goldfieldite ore.

Material purity tests

The residual product achieved after 120 minutes of leaching in the 0.5 mol/L NH_3-NH_4Cl at 75°C, was subjected to XRD analysis. However, the major phases identified were *ferrocolumbite* ($Fe_{2.99}Mn_{0.89}Ti_{0.11}Nb_{7.58}Ta_{0.38}W_{0.01}Sc_{0.01}Ca_{0.00}Sn_{0.00}O_{24.00}$: 96-900-7253) and *quartz* ($Si_{6.00}O_{6.00}$: 96-101-1177) as summarized in Fig. 9.

SEM analysis of the un-leached product achieved at optimized conditions reveals that the goldfieldite sample dissolves, whereas associated impurities including quartz do not dissolve. Hence, supported the formation of a protective surface layer and hinder copper extraction from the raw ore as shown in Fig. 10 [31, 32].

CONCLUSIONS

The viable conditions in the alkali leaching of goldfieldite ore were determined to be reaction temperature, concentrations of ammonia-ammonium chloride, and particle diameter. The most suitable leaching conditions for ammonia-ammonium chloride solutions were: 0.5 mol L^{-1} NH_3-NH_4Cl, 75°C, and 45 µm. At the established conditions, about 88.2 % dissolution efficiency was achieved. The leaching rate is obeyed by the diffusion control reaction mechanism with calculated activation energy (*Ea*) of 19.4 kJ mol^{-1}. Hence, it is revealed that the alkali leaching of goldfieldite ore is a versatile hydrometallurgical route for copper dissolution.

REFERENCES

1. H. Wouters, D. Bol, Material Scarcity - an M2i Study. Materials Innovation Institute, Delft, The Netherlands, 2009.
2. P.P. Sun, H.I. Song, T.Y. Kim, B.J. Min, S.Y. Cho, Recovery of silver from the nitrate leaching solution of the spent $Ag/\alpha\text{-}Al_2O_3$ catalyst by solvent extraction, Ind. Eng. Chem. Res., 53, 52, 2017, 20241-20246.
3. U. Armbruster, A. Martin, A. Krepel, Hydrolysis and oxidative decomposition of ethyl acetate in sub- and super-critical water, Appl. Catal. B: Environ., 31, 2001, 263-273.
4. Z. Wang, J. Xi, W. Wang, G. Lu, Selective production of hydrogen by partial oxidation of methanol over Cu/Cr catalysts, J. Mol. Catal. A: Chem., 191, 2003, 123-134.
5. A. Fornalczyk, Industrial catalysts as a source of valuable metals, J. Achiev. Mater. Manuf. Eng., 55, 2012, 864-869.
6. C. Macken, B.K. Hodnett, G. Paparatto, Testing of the CuO/Al_2O_3 Catalyst–Sorbent in extended operation for the simultaneous removal of NO_x and SO_2 from flue gases. Ind. Eng. Chem. Res., 39, 2000, 3868-3874.
7. J.E. Dutrizac, The leaching of sulphide minerals in chloride media, Hydrometallurgy, 29, 1992, 1-45.
8. X. Fan, J. Peng, M. Huang, S. Zhang, L. Zhang, Study on innovative process of leaching of chalcopyrite, J. Mining and Metallurgical Engineering, 25, 3, 2005, 58-62.
9. J.P. Lotens, E. Wesker, The behaviour of sulphur in oxidative the leaching of sulphidic minerals, Hydrometallurgy, 18, 1987, 39-45.
10. M. Kuhn, N. Arbiter, H. Kling, Anacondás arbiter process for copper, Can. Min. Metall. Bull., 67, 1974, 62-71.
11. L. Beckstead, J. Miller, Ammonia, oxidation leaching of chalcopyrite-reaction kinetics, Metall. Trans. B 8, 1977, 19-29.
12. M.D. Sokić, B. Marković, D. Živković, Kinetics of chalcopyrite leaching by sodium nitrate in sulphuric acid, Hydrometallurgy, 95, 2009, 273-279.
13. Y.C. Guan, K.N. Han, The leaching kinetics of chalcopyrite (CuFeS2) in ammonium lodide solutions with iodine, Metall. Mater. Trans. B 28, 1997, 979-985.
14. K. Yoo, S.K. Kim, J.C. Lee, M. Ito, M. Tsunekawa, N. Hiroyoshi, Effect of chloride ions on leaching rate of chalcopyrite, Miner. Eng., 23, 2010, 471-477.
15. J. Lu, D. Dreisinger, Copper chloride leaching from chalcopyrite and bornite concentrates containing high levels of impurities and minor elements, Hydrometallurgy, 138, 2013, 40-47.
16. O. Gok, C.G. Anderson, Dissolution of low-grade chalcopyrite concentrate in acidified nitrite electrolyte, Hydrometallurgy, 134–135, 2013, 40-46.
17. A. Ekmekyapar, R. Oya, A. Kunkul, Chem. Biochem. Eng. Q., 17, 2003, 261-66.
18. H.R. Watling, Chalcopyrite hydrometallurgy at atmospheric pressure: 2. Review of acidic chloride process options, Hydrometallurgy, 146, 2014, 96-110.
19. T. Moyo, J. Petersen, M.J. Nicol, The electrochemistry and kinetics of the oxidative dissolution of chalcopyrite in ammoniacal solutions: Part I - Anodic Reactions. Hydrometallurgy, DOI: 10.1016/j.hydromet.2018.10.018.
20. X. Meng, K.N. Han, The principles and applications of ammonia leaching of metals-A review, Mineral Processing and Extractive Metallurgy Review, 16, 1996, 23-61.
21. A. Ekmekyapar, E. Aktaş, A. Kunkul, N. Demirkiran, Investigation of Leaching Kinetics of Copper from Malachite Ore in Ammonium Nitrate Solutions, Metallurgical and Materials Transactions B, 43B, 2012, 764-772.
22. M.A. Raji, A.A. Baba, R.B. Bale, A.G.F. Alabi, M.K. Ghosh, Removal of Iron impurities from a Nigerian Biotite-rich Kaolinite ore by a Sulphuric acid solution, Journal of Chemical Technology and Metallurgy, 55, 6, 2020, 2128-2135.
23. A.K. Panda, B.G. Mishra, D.K. Mishra, R.K. Singh, Effect of sulphuric acid treatment on the physico-chemical characteristics of kaolin clay, Colloids and Surfaces A: Physicochem. Eng. Aspects, 363, 2010, 98-104.
24. A.A. Baba, M.A. Raji, A.Y. Abdulkareem, M.K. Ghosh, R.B. Bale, C.O. Adeyemi, Dissolution Kinetics potential of a Biotite-rich Kaolinite ore for Industrial applications by Oxalic acid solution, Journal of Mining, Metallurgy and Exploration, 36, 6, 2019, 1091-1099.

25. S.Y. Chindo, Hydrometallurgical processing of Nigerian Goldfieldite and Chalcopyrite ores for Industrial Applications, PhD Thesis, Department of Chemistry, Ahmadu Bello University, Nigeria, 2022, pp. 1-192.
26. S. Yin, L. Wang, A. Wu, E. Kabwe, X. Chen, R. Yan, Copper recycles from sulfide tailings using combined leaching of ammonia solution and alkaline bacteria, Journal of Cleaner Production, 2018, DOI: 10.1016/j.jclepro.2018.04.116.
27. N. Glinka, Chimie Générale, Editions Mir, Moscou, 2, 1987, 234.
28. R. Padilla, D. Vega, M.C. Ruiz, Pressure leaching of sulfidized chalcopyrite in sulfuric acid-oxygen media, Hydrometallurgy, 86, 2007, 80-88.
29. D.W. Shiers, D.M. Collinson, N.J. Kelly, H.R. Watling, Copper extraction from chalcopyrite: Comparison of three non-sulfate oxidants, hypochlorous acid, sodium chlorate and potassium nitrate, with ferric sulfate, Minerals Engineering, 85, 2016, 55-65.
30. O. Levenspiel, Chemical Reaction Engineering, second ed., John Wiley and Sons Inc., New York, 1999.
31. A. Nabizadeh, V. Aghazadeh, Dissolution study of chalcopyrite concentrate in oxidative ammonia/ammonium carbonate solutions at moderate temperature and ambient pressure, Hydrometallurgy, 152, 2015, 61-68.
32. S.Y. Chindo, K.I. Omoniyi, M.A. Raji, Chalcopyrite Leaching in ammonia-ammonium Chloride Solutions: Insight into the Dissolution Kinetic Studies, Journal of Sustainable Materials Processing and Management, 2, 2, 2022, 91-98.