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Dissolution Potential of a Nigerian Complex Covellite Ore by Ammonia-Ammonium Chloride Solution

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Abstract
With continuous industrial demands and as the market potential of purified copper in Nigeria and around the world is on the increase, the development of cheap and eco-friendly methods for the processing of mixed and lower grade copper ores become paramount. Consequently, this study examines the effect of ammonia-ammonium chloride concentration, temperature and particle size on the extent of covellite ore dissolution for predicting optimal copper extraction conditions. The results of the dissolution rates were found to be influenced by ammonium ion concentration, reaction temperature and particle size. At optimal leaching conditions, 82.9% of the initial 10 g/L covellite ore reacted within 120 minutes. The un-leached products (~17%) examined by X-ray diffraction was found to contain siliceous impurities that could be processed further to serve as a by-product for some defined industries. In all, the dissolution data was accordingly analysed and found to follow the shrinking core model for the diffusion controlled reaction. The calculated activation energy of 31.16 kJ/mol supported the proposed mechanism, assumed to be first order relation.

Keywords: Covellite ore, Leaching; Ammonia-ammonium chloride; Dissolution kinetics.

1. INTRODUCTION

To date, the depletion of higher grade ore deposits and the need for environmentally sound processing has led to continuous recovery of metal by hydrometallurgical treatment from lean and complex ore, especially from low-grade ores and waste rocks tailings which has apparently come to the forefront in recent years (Baba *et al.*, 2013; Zhi-Xhong *et al.*, 2012; Zhao *et al.*, 2004; Wu and Liu, 2001). Copper ore exists mainly in the form of sulphide and oxide minerals, such as chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), chalcocite (Cu_2S), covellite (CuS), enargite (Cu_3AsS_4), cuprite (Cu_2O), tenorite (CuO), azurite [$Cu_3(CO_3)_2(OH)_2$], malachite [$Cu_2(CO_3)(OH)_2$] and chrysocolla [$(Ca, Al)\ 2H_2Si_2O_5(OH)_4 \cdot nH_2O$].

Covellite (CuS) is a copper sulphide mineral that represents a large copper resource and perhaps, the most abundant member of the Cu-S system forming a variety of geologic conditions as a secondary mineral during enrichment and oxidation zones of copper sulphide deposits (Rickard, 1972). Due to the aforementioned impurities, treatment of the ore for its industrial suitability is necessary.

Various treatment methods such as the pyrometallurgy, electrolytic and hydrometallurgical approaches are prominent. However, the first two techniques, owing to high energy consumption, design and environmental concerns are not economically viable. Consequently, the hydrometallurgical alternative that involves leaching, solvent extraction, precipitation and unit operations addressed the above concerns as it is cost-effective (Künkül *et al.*, 2013; Gupta and Murkerjee,1990). For example, leaching is an important hydrometallurgical operation required to bring metal values from the ore surface with aqueous solution containing appropriate leachant which may be acidic or basic (Baba *et al.*, 2014; Baba *et al.*, 2013; Liu *et al.*, 2010). The type and concentration of the leachant is often controlled to allow some degree of selectivity for the metal or metals to be recovered for defined beneficiation through solvent extraction and precipitation routes (Künkül *et al.*, 2013; Gupta and Murkerjee, 1990). Many workers have examined copper ores purification for possible industrial utilization by hydrometallurgical method in different media with limited data on covellite ore treatments. In the dissolution and kinetic studies of copper ore using different reagents such as hydrochloric acid, sulphuric acid, ammonia, ammonium chloride and ammonium sulphate among others have indicated that the extraction of copper increases with increasing leachant concentration, reaction temperature with decreasing particle size fraction over time due to its decreasing surface area (Baba *et al.*, 2014; Zhi-Xiong *et al.*, 2012; Liu *et al.*, 2010; Reilly and Scott, 1976). Optimization of the aforementioned parameters defined the extent of the ore dissolution over time and often used for the dissolution kinetics assessment in the prediction of appropriate mechanism for copper extraction and purification studies (Ekmekyapar *et al.*, 2015; Künkül

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et al., 2013; Yartari and Copur, 1996). However, the use of ammoniacal leachant offers the possibility of ease of metal complexation and high extraction efficiency.

This study examined the effects of leachant concentration, reaction temperature and particle sizes on the extent of covellite ore dissolution in ammonia-ammonium chloride solution for establishing the copper optimal extraction conditions.

2. EXPERIMENTAL

Materials and instrumentation

The ore used in the study was obtained from the Mines around Wukari in Taraba State, Nigeria. After crushing and grinding, the ore was sieved using the American Society for Testing and Materials (ASTM) standard sieves to three size fractions: 90 + 75, 112 + 90 and 250 + 112 µm. Unless otherwise stated, -70 + 75 µm size fraction was used for specific characterization. The elemental analysis of the ore was carried out using an X-ray fluorescence (XRF, MINI PAL 4 EDXRF spectrometer). The mineralogical purity of the ore was examined using an EMPYREAN X-ray diffractometer (Shimadzu XRD model 6000 XRD). The surface morphology was also analyzed using Scanning Electron Microscopy: Leo1450 with LaB6 filament. The samples were viewed at 10 kV and at 13 mm working distance. The elements detected was analysed with a Bruter X-Flash detector using Esprit 1.82 software (Baba *et al.*, 2017a).

Method

The dissolution experiments were carried out in a 250 mL Pyrex glass reactor, equipped with a magnetic stirrer, reaction temperature control unit and a cooler to avoid loss of solution by evaporation. The ranges of reaction parameters were between - 90 + 75 µm for particle size, 25-75°C for temperature, and 0.05 - 0.6 mol/L for ammonia/ammonium chloride concentration. For each experimental run, after adding predetermined concentration of ammonia/ammonium chloride into the reactor and heated the reaction system to a desired temperature, 10 g/L of covellite ore was added into the ammoniacal solution, and the reactor content was then stirred at a constant stirring speed at intervals of 5 and 120 minutes (Baba *et al.*, 2017a). At the end of the reaction period, the content of the reactor was filtered, the amount of covellite ore reacted was evaluated from the difference in weight of the amount reacted or unreacted at various constant times up to 120 minutes, after oven-dried at about 60ºC for 1 hour. The post-leached residue at optimal conditions during 120 minutes treatment (75 ºC, 0.5 mol/L NH_3/NH_4Cl) was subjected to XRD and SEM examinations for better understanding of the dissolution mechanism.

3. RESULTS AND DISCUSSION

Ore characterization

The elemental chemical analysis of the **-** 90 + 75 µm ore fraction was examined in our previously reported work using XRF (Baba *et al.*, 2017) and found to contain 19.5 % CuO, 36.86 % Fe_2O_3, 24.6 % S, 8.1 % MoO_3, 5.8 % SiO_2, 1.9 % Al_2O_3 and 1.52 % Ag_2O as the major constituents. Other compounds detected occurring from low to trace level include: MnO (0.429 %), CaO (0.33 %), Eu_2O_3 (0.30 %), BaO (0.22 %), K_2O (0.21 %), TiO_2 (0.18 %), CeO (0.04 %) and Sc_2O_3 (0.01 %). The EDS analysis of the ore apparently corroborates the result of EDXRF to give S (36.85 %), Cu (33.76 %) and Fe (29.39 %). Also, the powdered X-ray diffraction (XRD) of the Covellite ore gave phase composition dominated by covellite (CuS), chalcopyrite ($CuFeS_2$) and putoranite **($Cu_9(Fe, Ni)_9S_{16}$)**. The XRD data also identified the presence of other associated compounds including siderite ($Fe(CO_3)$) and graphite (C). The surface morphology of the raw covellite ore under investigation indicated the presence of pores and crackles of the fine ores filled with other minerals coated with coarse surface (Baba *et al.*, 2017a).

Leaching studies

Effect of ammonia/ammonium chloride (NH_3/NH_4Cl) concentration

The effects of ammonia/ammonium chloride concentration (0.05 - 0.6 mol/L) on the extent of covellite ore dissolution at 55°C at various leaching times with moderate agitation were examined. The fraction of the ore reacted at various leaching times plotted for different NH_3/NH_4Cl concentration is shown in Figure 1.

Figure 1 indicates that the dissolution rate increases with increasing ammonium chloride concentration. This apparently suggests that the concentration of NH_3/NH_4Cl has a significant effect on the leaching of covellite ore and could be attributed to two reasons, one of which is that ammonium chloride can form a buffer solution with ammonia at constant solution pH; and secondly NH_4^+ could possibly react with OH^- to form NH_3, which subsequently increases the concentration of

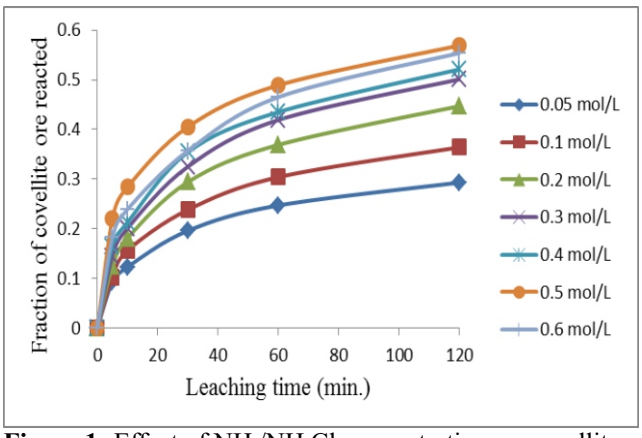

Figure 1: Effect of NH_3/NH_4Cl concentration on covellite ore dissolution.

***Experimental conditions*:** 1.75 mol/L NH_3, NH_4Cl concentration = 0.05 0.6 mol/L, Temperature = 55°C, Particle size = -90 + 75 m, Solid/liquid ratio = 10 g/L with moderate stirring.

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reactant and thus increases the leaching rate (Liu *et al.*, 2010). For example, covellite ore dissolution reached 56.9% and 54.7% by 0.5 and 0.6 mol/L NH_3/NH_4Cl solution respectively within 120 minutes. It can also be deduced that the amount of covellite ore reacted with 0.5 mol/L and 0.6 mol/L is almost equal coupled with the fact that after 0.5 mol/L leachant concentration, reactions ceased and there was not much difference in the dissolution rate; 0.5 mol/L NH_3/NH_4Cl was kept for further studies.

Effect of reaction temperature

The effect of reaction temperature on the extent of covellite ore dissolution was examined over the temperature range of 27°C - 75 °C as shown in Figure 2.

It is evident from Figure 2 that increasing the reaction temperature relatively improved the covellite ore dissolution rate. However, the reaction seemed to be slower at lower temperatures (25°C - 40°C), but improved moderately from 55°C - 75°C. At 75°C, the ore dissolution reached 82.9 % within 120 minutes. This may have been caused by the increase in volatilization rate of ammonia as the temperature increased; thus, loweroperating temperature was often suitable to reduce reagent consumption (Liu *et al.*, 2010).

Effect of particle size

The effect of particle size on the extent of covellite ore dissolution was studied using three particle sizes: (-90 + 75m, -112 + 90 m, and -250 + 112 m) by 0.5 mol/L NH_3/NH_4Cl solution at 75°C as summarized in Figure 3.

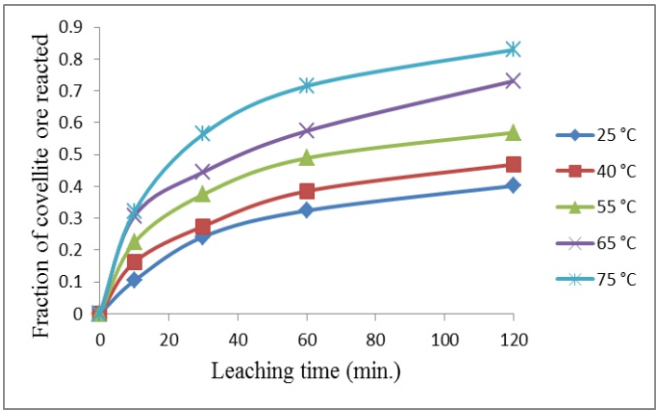

Figure 2: Effect of temperature on covellite ore dissolution at various leaching time.

Experimental conditions: 1.75 mol/L ammonia, 0.5 mol/L ammonium chloride, Temperature = 25°C -75°C, Particle size = -90 + 75 m, Solid/liquid ratio = 10 g/L with moderate stirring.

Figure 3 depicts that as the particle diameter decreased, the extent of ore dissolution increases owing to increased particle surface area. At a set of experimental conditions, about 58.2%, 69.7% and 82.9% of the ore were reacted using particle sizes -250 +112, -112 + 90 and -90 +75 µm respectively within 120 minutes. These indicated that the leaching velocity of copper increased as the particle size of the ore decreased.

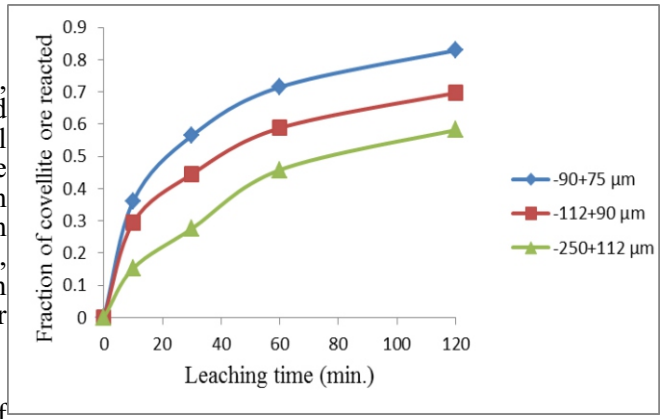

Figure 3: Effect of particle size on covellite ore dissolution at various leaching time.

Experimental conditions: 1.75 mol/L ammonia, 0.5 mol/L ammonium chloride, Temperature = 75 °C, Particle size = -90 + 75 m, Solid/liquid ratio = 10 g/L with moderate stirring.

Dissolution Kinetic Analysis

For a liquid/solid reaction system, the reaction rate is generally controlled by one of the following steps: diffusion through the liquid film, diffusion through the ash/product layer or the chemical reaction at the surface of the solid particles (Baba *et al.*, 2017b; Ekmekyapar *et al.*, 2003; Bell *et al.*, 1995; Scott, 1963). The rate of the process would be controlled by the slowest of these sequential steps. The reaction model between a liquid and a solid may be given as (Baba *et al.*, 2017b; Ekmekyapar *et al.*, 2003):

$$A_{(fluid)} + bB_{(solid)} \longrightarrow \text{Products} \qquad (1)$$

Let the time of completion of the leaching process be t^*, the fractional conversion of covellite be α and at any time t. The integrated equations for liquid/solid heterogeneous reactions with respect to film diffusion control is (Scott, 1963):

$$t = t^*[1 - (1 - \alpha)] \qquad (2)$$

For a chemical controlled reaction, it is consistent with the following expression (Ekmekyapar *et al.*, 2003; Baba *et al.*, 2017b):

$$t = t^*[1 - (1 - \alpha)^{1/3}] \qquad (3)$$

and for ash diffusion control yields:

$$t = t^*[1 - \alpha - (1 - \alpha)^{2/3}] \qquad (4)$$

The value of t^* in Equations (2) - (4) depends on the reaction parameters relative to the kinetic models. For example, in a chemical reaction controlled model as defined by Equation (3), t^* is consistent to the expression (Bell *et al.*, 1995):

$$t^* = \rho BRo/bksCA \qquad (5)$$

ρB is the molar density of the solid reactant (mol.m^{-3}), R_o is the radius of the solid particle (m), b is the stoichiometric coefficient of the solid, k_s is the surface reaction rate constant (m. min^{-1}) and C_A is the leachant concentration (mol.m^{-3}).

To determine the kinetic parameters and rate-controlling step for the dissolution of covellite ore, the experimental data in Figures 1 - 4 have been analyzed on

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the basis of liquid/solid heterogeneous reaction model Equations (2) and (3). The data did not fit these models. However, data fitting using a diffusion-controlled reaction through solution boundary or the diffusion through a solid product layer, (Equation 3) gave straight lines with average correlation (R^2) of 0.947 as shown in Figures 4 - 7.

The validity of the experimental data into the integral rate was tested by statistical and graphical methods. The kinetic analysis of the effect of leachant concentration on the extent of ore dissolution were found to be consistent with the diffusion controlled model as summarized in Figure 4.The experimental rate constants, k_d, were determined from the slopes derived from Figure 4 and the plot of $\ln k_d$ versus $\ln[NH_3/NH_4Cl]$ were made as shown in Figure 5.

As seen from Figure 5, the slope of the resulting plot indicates that the reaction order with respect to NH_4^+ ion is 0.65. The slope of 0.65 with correlation coefficient 0.994 is assumed to be first order relationship with respect to the leachant concentration at defined molarities.

The apparent rate constant, k_d, calculated from the slopes of the straight lines in Figure 6 was used to

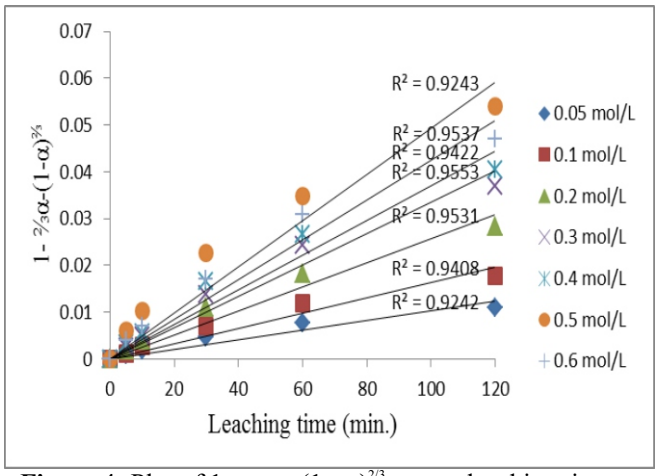

Figure 4: Plot of 1 - α - (1 - α)$^{2/3}$ versus leaching time at different NH3/NH4Cl concentration.

Experimental conditions: Same as in Figure 1.

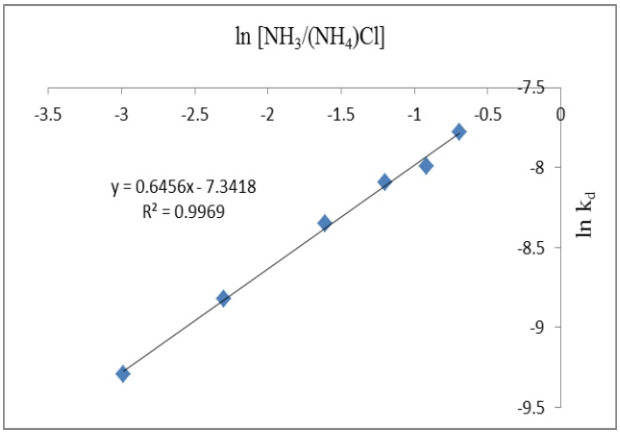

Figure 5: Plot of ln k_d versus ln $[NH_3/NH_4Cl]$

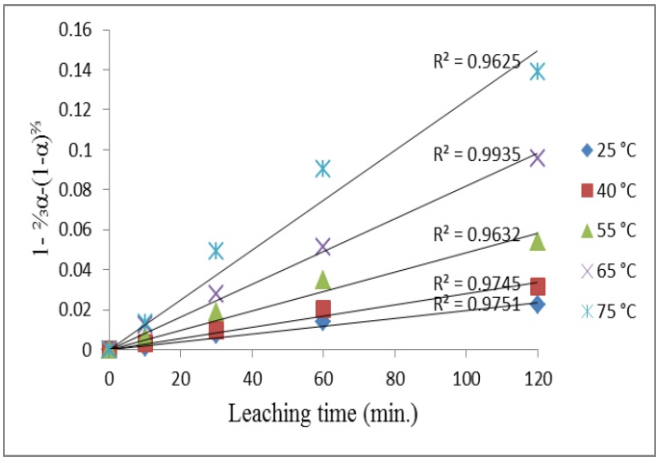

Figure 6: Plot of 1 - α - (1 - α)$^{2/3}$ versus leaching time at different temperature

Experimental conditions: Same as in Figure 2.

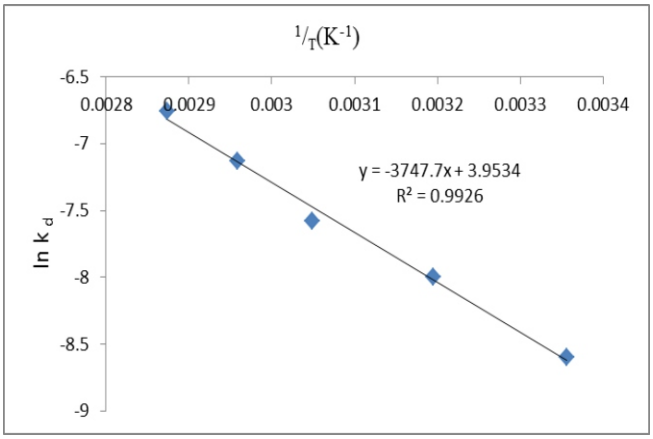

Figure 7: Plot of $\ln k_d$ versus 1/T.

obtain Arrhenius relation shown in Figure 7 in the estimation of activation energy, *Ea* for the dissolution process and was calculated to be 31.16 kJ/mol.

This value clearly suggests a diffusion control reaction as earlier proposed by several investigators on other varieties of copper ores dissolution from different sources (Liu et al., 2010; Künkül *et al.*, 1994).

Also, the data in Figure 2 was linearized using Equation (4) to obtain the results represented in Figure 6.

Residual Product Analysis

To assess the nature of the unreacted species at optimal leaching conditions, the leached product obtained was analysed using XRD and SEM techniques shown in Figures 8 and 9 respectively. The XRD affirmed the unleached products to consist mainly of silica with few traces of iron compound: magnetite as shown in Figure 8.

In addition, the SEM image of leached residues at optimal leaching conditions show very clean surface with small amounts of a precipitate assumed to be siliceous impurities constituting ~17% of the unreacted component during the leaching process. The micrograph of the solid particles before leaching presents a surface of ore grains etched with striations marks and pores and crackles as observed in Figure 9A.

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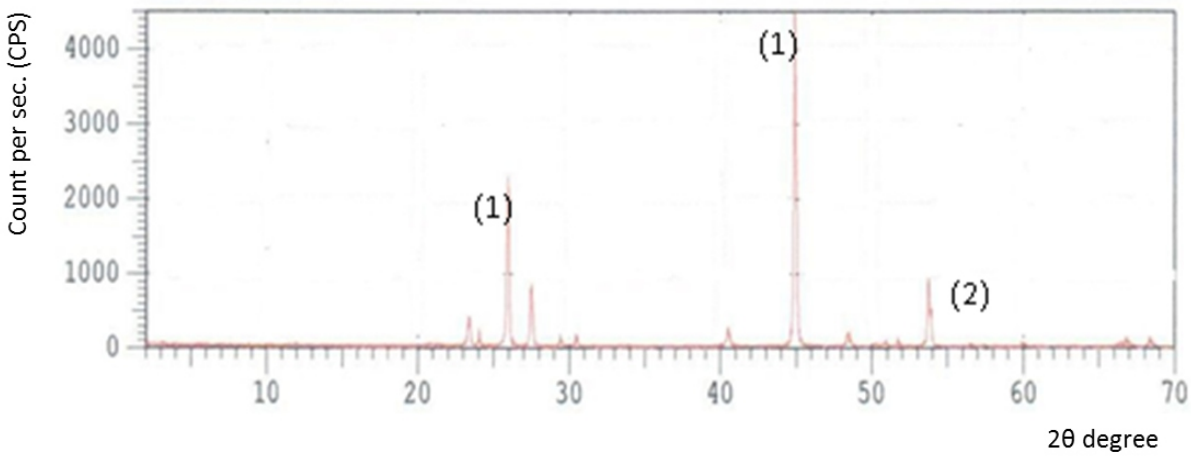
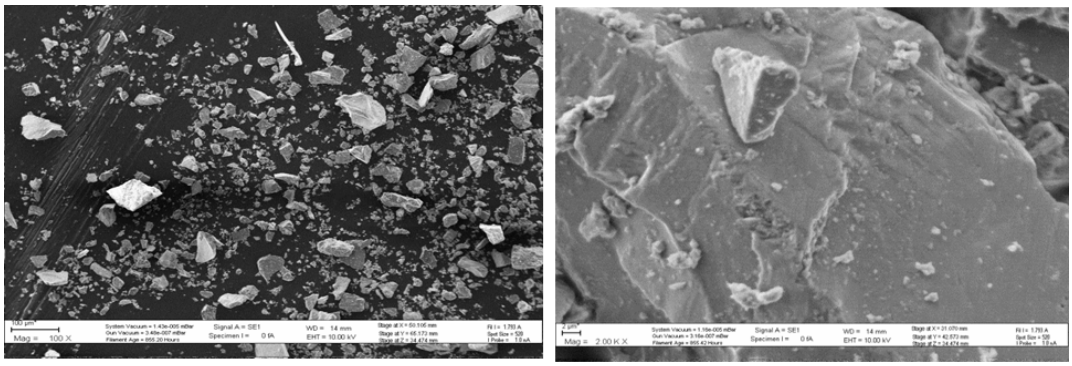


Figure 8: X-ray diffraction pattern of the leached residual product, showing the primary compound identified with its Joint Committee on Powder Diffraction Standard file number used in peak attributions: (1) SiO_2 (quartz) {045-1375}, (2) Fe_2O_3 (magnetite) {025-1402}.



A B

Figure 9: SEM image of raw ore and ammonia/ammonium chloride leached product at optimal leaching conditions: A: raw ore; B: leached ore.

Consequently, the micrograph of the leached residues presents distinct surfaces. The covellite ore was nigh reacted and could not be observed in the leached residues by EDs (S=19.31%, Fe=49.43% and Si=16.80%).

4. CONCLUSIONS

In this study, the mineralogical characterization of a complex covellite ore reveals that the ore is rich in covellite and other major minerals identified were chalcopyrite and putoranite. Ammoniacal leaching of the ore shows that copper extraction from covellite ore firmly depends on the concentration of ammonia-ammonium chloride, reaction temperature and the leaching time with decrease in ore particle size. Analysis of the leach residue indicates that the leachant is strongly selective in iron and co-iron removal impurities. At optimal leaching conditions, 82.9% of the covellite ore reacted within 120 minutes. The dissolution kinetic evaluation with appropriate shrinking core model indicates that the rate of covellite ore is diffusion controlled and the derived activation energy of 31.16 kJ/mol supported the proposed dissolution reaction.

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REFERENCES

Baba, A.A., Ayinla, K.I., Adekola, F.A., Bale, R.B., Ghosh, M. K., Alabi, A. F., Sheik, A. and Folorunso, I. O. (2013). Hydrometallurgical application for treating a Nigerian Chalcopyrite ore in chloride medium: Part I. Dissolution kinetics assessment, International Journal of Minerals, Metallurgy and Materials, 20(11):1021-1028.

Baba, A.A., Balogun, A.F., Bale, R.B., Adekola, F.A. and Alabi, A.G.F. (2017a). Treatment of a Nigerian Covellite ore, Part I: Dissolution kinetics study by Ammonia solution. Russian Journal of Non-ferrous Metals, 58(1):1-7.

Baba, A.A., Olaoluwa, D.T., Alabi, A.G.F., Balogun, A. F., Ibrahim, A.S., Sanni, R.O. and Bale, R.B.. (2017b). Dissolution behaviour of Beryl ore for optimal industrial beryllium compound production. Canadian Metallurgical Quarterly, DOI: 10.1080/00084433.2017.14.03107.

Baba, A.A., Ghosh, M.K., Pradhan, S.R., Rao, D.S., Baral, A. and Adekola, F.A. (2014). Characterization and kinetic study on ammonia leaching of complex copper ore. Trans.

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Nonferrous Met. Soc. China, 24:1587−1595.

Bell, S.L., Welch, G.D. and Bennett, P.G. (1995). Development of ammoniacal lixiviants for the in-situ leaching of chalcopyrite. Hydrometallurgy, 39(1−3):11−23.

Ekmekyapar, A., Demirkıran, N., Künkül, A. and Aktaş, E. (2015). Leaching of Malachite Ore in Ammonium Sulfate Solutions and Production of Copper Oxide, Brazilian Journal Of Chemical Engineering, 32(01):155 165.

Ekmekyapar, A., Oya, R. and Künkül, A. (2003). Dissolution Kinetics of an Oxidized Copper Ore in Ammonium Chloride Solution Journal of Chemical and Biochemical Engineering Quarterly, 17(4):261−266.

Gupta, C. K. and Murkerjee, T. K. 1990. Hydrometallurgy in Extraction processes, CRC Press, USA.

Künkül, A., Gülezgin, A. and Demirkiran, N. (2013). Investigation of the Use of Ammonium Acetate as an Alternative Lixiviant in the Leaching of Malachite Ore, CI&CEQ 19(1):25−35.

Künkül, A., Kocakerim, M. M., Yapici, S. and Demibrag, A. (1994). Leaching kinetics of malachite in ammonia solutions, Int. J. Miner. Process, 41:167-182.

Levenspiel, O. (1972). Chemical Reaction Engineering, Wiley,New York, pp 361371.

Liu, W., Tang, M., Tang, C., He, J., Yang, S. and Yang, J. (2010). Dissolution kinetics of low grade complex copper ore in ammonia-ammonium chloride solution, Trans. Nonferrous Met. Soc. China, 20:910−917.

Reilly, I. G. and Scott D.S. 1976. The leaching of cupric sulfide in ammonia [J]. Ind Eng Chem Process Des Dev, 15(1):60−67.

Rickard, D.T. (1972). Covellite formation in low temperature aqueous solutions. Mineral Deposita (Berl.), 7:180-188.

Scott, W.W. (1963). Standard methods of chemical analysis; Van Nostrand., New York.

Wu, H. and Liu, Y. (2001). Study on copper recovery from tailing by means of leaching progress [J]. China Mining Magazine, 10(6): 65−67. (in Chinese).

Yartasi, A. and Copur, M. (1996). Dissolution kinetics of copper (II) oxide in ammonium chloride solutions [J]. Minerals Engineering, 9(6):639−698.

Zhao G., Wu, H., Zhang, Y. and Liu, Q. (2004). Ammonia leaching for tailings from a copper mine [J]. Nonferrous Metals, 56(3):54−56. (in Chinese)

Zhi-Xiong, L., Yin, Zhuo-Ian, Y., Hui-Ping, H., and Chen, Qi-Yuan, C. (2012). Leaching Kinetics of low-grade copper ore containing calcium-magnesium carbonate in ammonia-ammonium sulfate solution with persulfate, Trans. Nonferrous Met. Soc. China, 22:2822-2830.

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