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Leaching kinetics of a Nigerian complex covellite ore by the ammonia-ammonium sulfate solution

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Abstract−Hydrometallurgical treatment of copper sulfide ore is increasingly establishing itself as a feasible route for the extraction of copper and recovery of associated precious metals value. This is attributed to the merits of this route, which include suitability for low-grade and complex ores, high recoveries, competitive economics, and other operational features. The leaching kinetics of Nigerian complex covellite ore was investigated in ammonia-ammonium sulfate solution. The concentration of ammonia and ammonium sulfate, the ore particle size, and the temperature were chosen as parameters in the experiments. The results show that temperature, concentration of ammonia-ammonium sulfate has favorable influence on the leaching rate of covellite ores; however, leaching rate decreases with increasing particle size. At optimal conditions (1.75 mol/L NH_4OH+0.5 mol/L $(NH_4)_2SO_4$, −90+75 μm, 75 °C, with moderate stirring) about 86.2% of copper ore reacted within 120 minutes. The mechanism of the leaching was further established by characterizing the raw ore and the leached residue by EDXRF - chemical composition, SEM - structural morphology and XRD - phase identification studies. From the X-ray diffraction analysis, the partially unreacted Cu and S phases were presumed to be CuO, and the iron present in the CuS phase was mainly converted to hematite ($Fe_2O_3 \cdot H_2O$), as the CuS phase disintegrated and remained in the residue afterward.

Keywords: Copper Sulfide, Covellite Ore, Ammonia, Ammonium Sulfate, Leaching, Diffusion Control Mechanism

INTRODUCTION

Due to environmental restrictions in conjunction with the high cost of fuel and necessity to process low-grade ores that cannot be economically improved by convectional pyrometallurgical routes, the development of hydrometallurgical adjunct to compete with the traditional metallurgical routes of copper production was prompted. The hydrometallurgical routes are usually preferred for the recovery of copper from the low grade, lean and complex copper ores because of low cost, short construction time, operational simplicity, good performance, and environmental advantages [1,2]. This has played an important role in the sustainable development of copper industry.

In addition, various hydrometallurgical methods using reagents such as bases, acids, and salts have been developed for copper dissolution from copper bearing minerals. Ammonia-ammonium sulfate leaching for copper recovery has advantages over other leachants. An important characteristic of leaching in ammonia-ammonium sulfate solutions among others is that pH is almost constant during the leaching. Also, ammonia and ammonium sulfate generate ammonium ions required for the dissolution reaction of covellite. Ammonia produced by ammonium ions forms stable complexes with metal ions and this leads to an increase in dissolution rate of covellite. The leachant used for copper leaching is generally sulfuric acid; however, other metals in ore matrix cause excess acid consumption. In addition, some impurities, particularly iron, dissolved in the leaching solution when sulfuric acid is used, cause some problems in further processing of the leached solution [3,4]. It is said that copper is selectively extracted from the leach solution by ammonia-ammonium sulfate.

Covellite (CuS) being a secondary copper sulfide mineral containing 66% copper, is now considered as dimer (two molecules of CuS forming Cu_2S_2) with the copper existing as Cu (I). Covellite occurs very often in nature, associated with chalcopyrite and chalcocite which are the main primary and secondary copper sulfides for the copper industry, respectively [5-7], but rarely found as a primary mineral in naturally occurring copper deposits. The leaching process of covellite is considered slow and in comparison with chalcopyrite and chalcocite, covellite leaches slower than chalcocite, but faster than chalcopyrite [6]. From a scientific perspective, covellite has drawn significant interest as a superconductor. It is known that both synthetic and natural CuS show excellent metal conductivity and condense into the superconducting state below 1.6 K [8,9]. Among the non-ferrous metals, copper is one of the

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most commonly used metals over thousands of years. The traditional industries continued to survive and flourish due to the art of making and shaping of copper and copper metal value. The promotion and security of copper as non-conventional energy sources and in solar heating is expected to dictate the use of the metal in large quantities in the nearest future [10]. Studies on covellite ore processing were focused on superconducting ability to extent their application and to characterize their properties. So far, only a few researches on hydrometallurgy technology for processing covellite ore have been reported in literature. Therefore, there is need to exploit covellite ore processing for metal extraction.

Leaching of high-grade and low-grade copper ores in ammoniacal media [11-16] or acidic media [17-20] has been reported. Consequently, ammonia/ammonium sulfate solution has been chosen as leachant in this study to investigate the leaching of complex covellite ore in ammonia-ammonium sulfate and the effects of concentrations of ammonia-ammonium sulfate, temperature and particle size on the leaching rate are reported.

EXPERIMENTAL

1. Materials

The covellite ore used for this study was sourced from Wukari, Taraba State of Nigeria. The covellite ore was crushed and reduced to fine particles using an acetone-rinsed mortar and pestle. The pulverized ore was sieved into three different particle sizes: −90+75, −112+90, and −250+112 μm using American Society for Testing and Materials (ASTM) standard sieve. Ammonia-ammonium sulfate solution was used as the leachant. All experiments, unless otherwise stated were performed using the −90+75 μm particle size fraction due to its high surface area.

2. Methods

The dissolution experiments were carried out in a 250 ml Pyrex glass reactor, equipped with a mechanical agitator, a reaction temperature control unit, and a cooler to avoid loss of solution through evaporation. After the addition of 100 ml of $NH_4OH/(NH_4)_2SO_4$ solution into the reactor and attaining temperature of 55 °C, 10 g/L of the covellite ore was added [11]. The covellite ore dissolution rate with $NH_4OH/(NH_4)_2SO_4$ solution at different concentrations (0.05 mol/L - 0.6 mol/L) was investigated. The ammonium sulfate ionizes in aqueous medium giving ammonium ion which is hydrolyzed to form ammonia:

$$(NH_4)_2SO_4 \rightarrow 2NH_4^+ + SO_4^{2-} \quad (1)$$

$$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+ \quad (2)$$

The ammonium ion provides the protons required for the dissolution of the covellite ore, whereas the ammonia produced forms stable complexes with the copper ions from the ore [4]. The concentration which gave the highest dissolution (0.5 mol/L) was subsequently used for the optimization of other leaching parameters including temperature (varied from 25 °C to 75 °C) and particle size. The activation energy, Ea and constants were evaluated from the Arrhenius plots. In all cases, the fraction of the covellite ore reacted, α, were calculated from the initial difference in weight of the amount reacted or unreacted at various time intervals up to 120 minutes after being oven-dried at about 60 °C. The post-leaching residual product at 75 °C in 0.5 mol/L $NH_4OH/(NH_4)_2SO_4$ was then analyzed by XRD and SEM techniques.

3. Characterization

The ground and leached covellite residue at optimal leaching were characterized using the MINI PAL 4 EDXRF spectrometer, Shimadzu X-ray diffractometer model 6000 and SEM model Leo1450 with LaB6 filament, respectively. The samples were viewed at 10 kV, 13 mm working distance and were carbon coated. The element analysis was done with a Bruker X-Flash detector using Esprit 1.82 software.

RESULTS AND DISCUSSION

1. Characterization of Raw Powder

1-1. Chemical Analysis

The elemental analysis of the −90+75 μm ore fraction contains

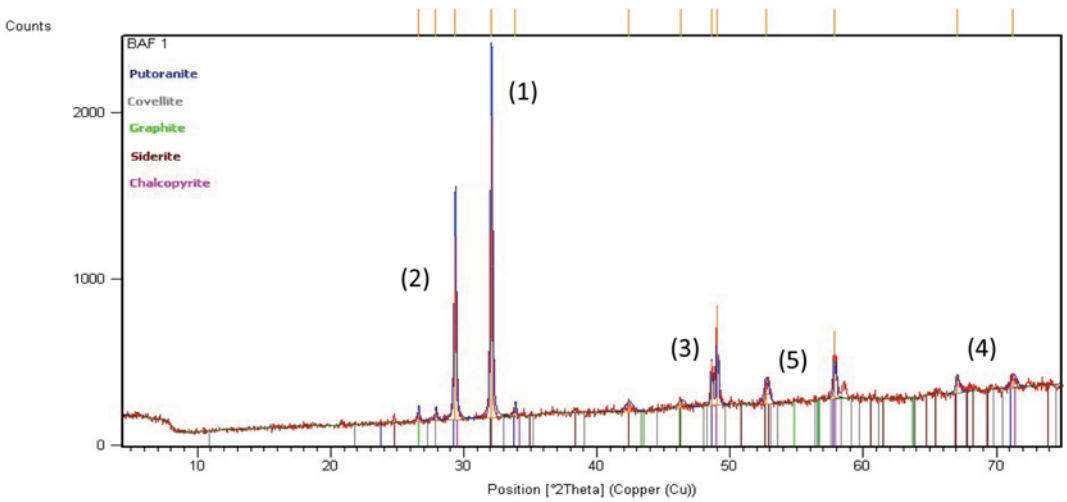

Fig. 1. X-Ray diffraction pattern of raw covellite ore showing presence of (1) CuS (covellite) {065-3928}, (2) $CuFeS_2$ (chalcopyrite) {001-0842}, (3) $Cu_9(Fe, Ni)_9S_{16}$ (putoranite) {041-1404}, (4) $Fe(CO_3)$ (siderite) {083-1764}, (5) C (graphite) {075-2078} as identified with the Joint Committee on Powder Diffraction Standard file number.

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: 0.429% MnO, 0.33% CaO, 0.30% Eu_2O_3, 0.22% BaO, 0.21% K_2O, 0.18% TiO_2, 0.04% CeO and 0.01% Sc_2O_3. The EDS analysis of the ore apparently corroborates the result of EDXRF to give S (36.85%), Cu (33.76%) and Fe (29.39%).

1-2. Mineralogical Analysis by XRD

Powder X-ray diffraction (Fig. 1) showed the ore was comprised primarily of covellite (CuS), chalcopyrite ($CuFeS_2$), $Cu_9(Fe, Ni)_9S_{16}$ (putoranite). The other associated mineral phases are $Fe(CO_3)$ and (siderite) C (graphite) that occurred in low to trace abundance (≤5%).

1-3. SEM Morphology

The surface morphology of the raw covellite ore was analyzed with scanning electron microscopy prior to leaching. The surface of ore grains was etched with striation marks, pores and crackles (Fig. 2), which were filled with other amorphous materials. EDS showed the ores to be mainly composed of 33.76% Cu, 29.39% Fe and 36.85% S (Fig. 3).

2. Leaching Studies

2-1. Effect of Ammonia/Ammonium Sulfate Concentration

The effect of $NH_3/(NH_4)_2SO_4$ concentration (0.05-0.6 mol/L) on the covellite ore dissolution at 55 °C at various leaching times with moderate stirring was investigated. The fraction of the ore reacted at various leaching times plotted for different $NH_3/(NH_4)_2SO_4$ concentration is shown in Fig. 4.

The plot (Fig. 4) shows that with increasing $NH_3/(NH_4)_2SO_4$ concentration the rate of dissolution increased with time. This suggests that the concentration of $NH_3/(NH_4)_2SO_4$ has a significant effect on the leaching of covellite and can be attributed to two reasons. First, the ammonium sulfate forms a buffer solution with ammonia and pH of the solution is kept at a certain value; and secondly, could be that ammonium ion is hydrolyzed to form ammonia, which will subsequently increase the concentration of ammonia reactant [16,21]. At a set of optimal conditions (55 °C, 120 minutes) about 57.3% and 58.7% of the ore reacted by 0.5 mol/L and 0.6 mol/L solution, respectively, at constant pH of 10.1. The pH of this solution is maintained at these concentrations. Hence, it is evident

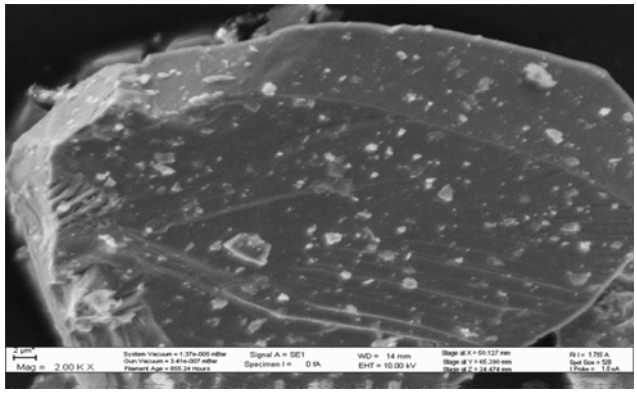

Fig. 2. SEM image of raw covellite ore.

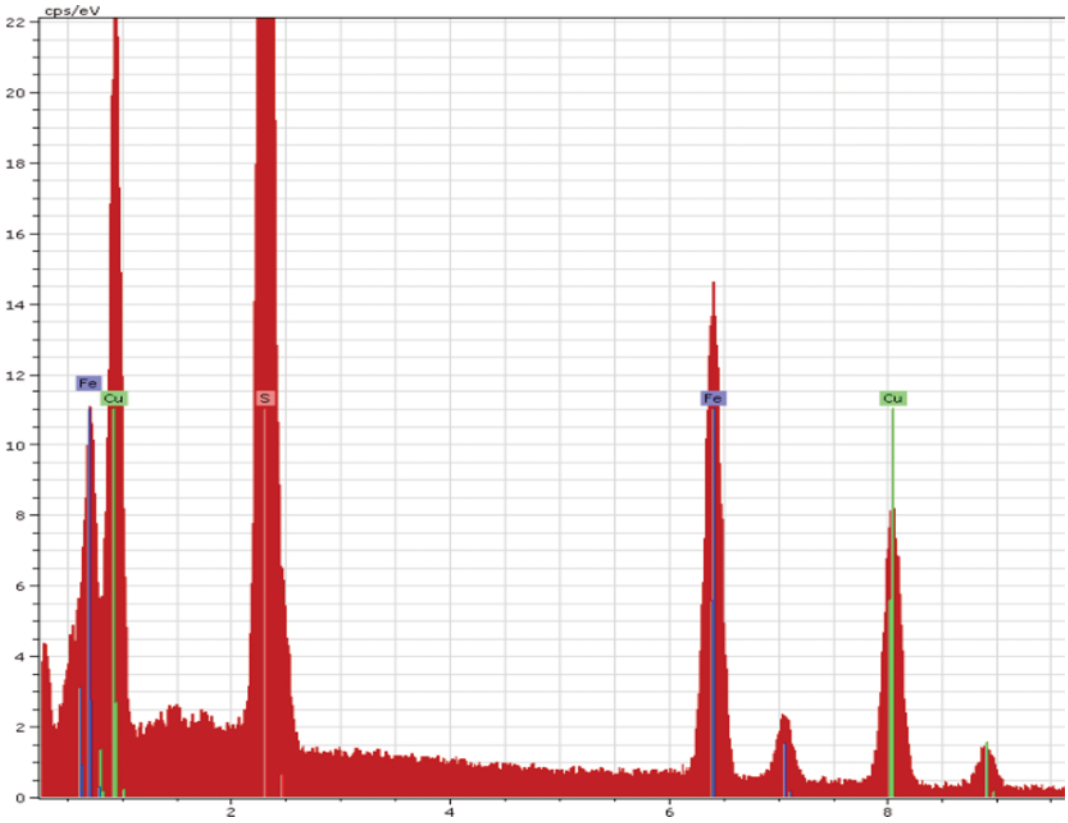

Fig. 3. EDS spectrum of raw covellite ore.

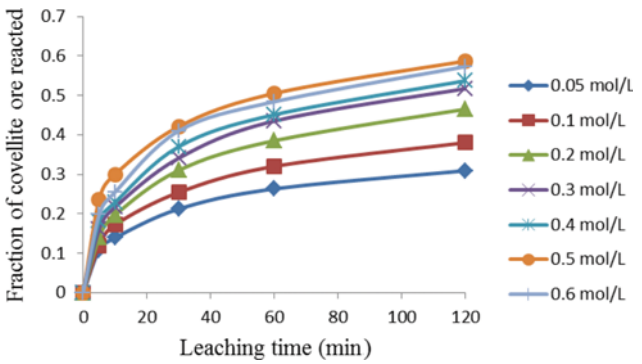

Fig. 4. Effect of $NH_3/(NH_4)_2SO_4$ concentration on leaching of covellite ore. Experimental conditions: $[NH_3/(NH_4)_2SO_4]$ concentration=0.05-0.6 mol/L, temperature=55 °C, particle size=−90+75 μm, solid/liquid ratio=10 g/L with moderate stirring.

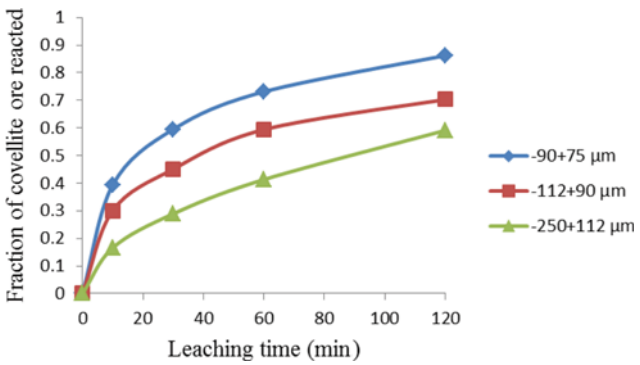

Fig. 6. Effect of particle size on leaching of covellite ore. Experimental conditions: $NH_3/(NH_4)_2SO_4$ concentration=0.5 mol/L, temperature=75 °C, solid/liquid ratio=10 g/L with moderate stirring.

that the amount of the ore reacted is almost equal at these concentrations and pH. For economic considerations, the optimum $NH_3/(NH_4)_2SO_4$ concentration used in this study was 1.75 mol/L NH_3 and 0.5 mol/L $[NH_3/(NH_4)_2SO_4]$ and kept for use to optimize some other leaching parameters, including reaction temperature and particle size. Covellite (CuS) dissolves in $NH_4OH/(NH_4)_2SO_4$ solutions by forming a stable $Cu(NH_3)_4^{2+}$ complex. For Cu-NH_3 system on Eh-pH diagram for example, the $Cu(NH_3)_4^{2+}$ complex formation is stable at pH ranges 9.0-10.5 [22]. Therefore, the possible dissolution reaction of covellite ore leaching by ammonia/ammonium sulfate solution is consistent with the following stoichiometry:

$$CuS+4NH_4OH+2(NH_4)_2SO_4 \rightarrow Cu[(NH_3)_4]^{2+}+3SO_4^{2}+4NH_4^{+}+4H_2 \quad (3)$$

Reilly and Scott [23] draw a similar conclusion that S^{2-} in the sulfide mineral is eventually oxidized to SO_4^{2-} in ammonia-oxygen solution.

2-2. Effect of Reaction Temperature

The effect of reaction temperature on the leaching of covellite ore was examined over the temperature ranges 25 °C-75 °C. The result is shown in Fig. 5.

As shown in Fig. 5, the extraction rate of copper increases with the increase of temperature. The extraction rate of copper after 120 minutes reaches 36.5% and 86.2% for 25 °C and 75 °C, respectively. This observation can be attributed to the fact that particles only react when they collide effectively with increasing dissolution temperature. This is in line with the fact that when a substance is heated, particles gain more kinetic energy and collide more frequently, thus speeding the rate of reaction [12]. Results of other similar studies affirmed that increasing the temperature of the system during dissolution increases the amount of the ore or material reacted at various leaching time. However, tests at higher temperatures (>75 °C) would be less suitable due to increase in loss of $NH_3/(NH_4)_2SO_4$ vapor [20].

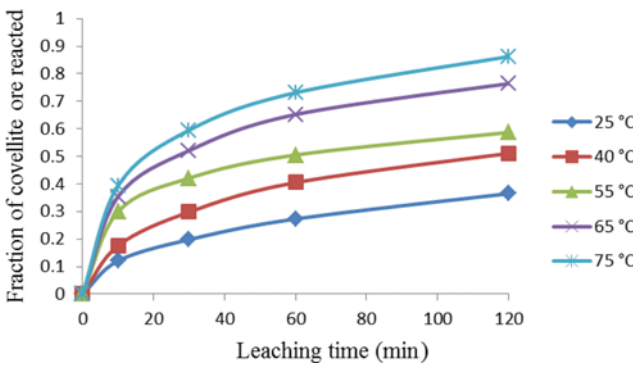

Fig. 5. Effect of reaction temperature on leaching of covellite ore. Experimental conditions: $[NH_3/(NH_4)_2SO_4]$ concentration=0.5 mol/L, temperature=25 °C-75 °C, particle size=−90+75 μm, solid/liquid ratio=10 g/L with moderate stirring.

2-3. Effect of Particle Size

The effect of particle size on the rate of covellite ore dissolution was studied using three particle sizes (−90+75 μm, −112+90 μm, −250+112 μm) in 0.5 mol/L $[NH_3/(NH_4)_2SO_4]$ solution. The result obtained is presented in Fig. 6.

From Fig. 6, about 59.1%, 70.3% and 86.2% of the ore was reacted using particle size −250+112, −112+90 and −90+75 μm, respectively, at a set of experimental conditions. It is obvious that the extraction rate of copper increases as the particle size decreases. When the particle size decreases, a corresponding increase in the surface area causes better exposure of copper ores to the solution.

3. Disscusion

3-1. Dissolution Kinetics Analysis

It has been assumed that the solid particles have spherical shape and do not change their dimensions during reaction. In addition, they contain reactive material uniformly embedded in an inert matrix [1,24,25]. By considering that insoluble gangue minerals covering the unreacted covellite surface form an ash layer, the unreacted-core model can be chosen for kinetics calculations.

Let us consider a solid particle B immersed in a fluid A, and reacting as:

$$A_{(fluid)}+b\ B_{(solid)} \rightarrow \text{products}$$

If the fluid A diffuses from r_0 to r_c and react at r_c, the reaction rate of the particle is controlled by diffusion through ash layer. By pseudo steady-state assumption, the material balance of component A can be written on the particle between r_0 and r_c for a spherical particle [4].

$$D\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dc}{dr}\right)=0 \tag{4}$$

By solving Eq. (4) and by making equal the rate of reaction to the diffusion rate, the time required for the particle to reduce the unreacted core from r_0 to r_c is obtained as follows [13,14]:

$$t=\frac{c_B}{bDc_0}\left[\frac{r_c^3}{3r_0}-\frac{r_c^2}{2}+\frac{r_0^2}{6}\right] \tag{5}$$

Eq. (5) can be written in terms of reacted fraction of the solid (α) as:

$$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}=\frac{6bDc_0}{c_Br_0^3}r \tag{6}$$

If the reaction rate is controlled by chemical reaction, the integrated rate equation is expressed by the following equation [1,26].

$$1-(1-\alpha)^{1/3}=\frac{bk_dc_0}{c_Br_0}t \tag{7}$$

These models have been applied to fluid-solid reactions systems [1,11-16]. The results of this study were evaluated according to Eqs. (6) and (7) that are theoretical models, and $1-(2/3)\alpha-(1-\alpha)^{2/3}$ versus t plots corresponding to ash layer diffusion model gave straight lines. Consequently, all the kinetic data were expressed using Eq. (6). The results indicate that the linear relationship between $1-(2/3)\alpha-(1-\alpha)^{2/3}$ and leaching time (t) gave average correlation coefficient of 0.9715 as shown in Fig. 7 is significant and thus suggests that covellite dissolution in this study is controlled by diffusion reaction.

From Fig. 7, the experimental rate constants, k_d, were determined from the slope of the straight line at various $NH_3/(NH_4)_2SO_4$ concentrations, and the plot of $\ln k_d$ versus $\ln[NH_3/(NH_4)_2SO_4]$ is shown in Fig. 8.

As seen from Fig. 8, the slope of the resulting plot indicates that the reaction order is 0.52 with respect to NH_4^+ ion with correlation coefficient 0.994.

Furthermore, the data in Fig. 5 at different temperatures were linearized by Eq. (6) and the result obtained is summarized in Fig. 8.

In the literature, it is stated that the diffusion controlled heterogeneous reactions are slightly dependent on temperature, while

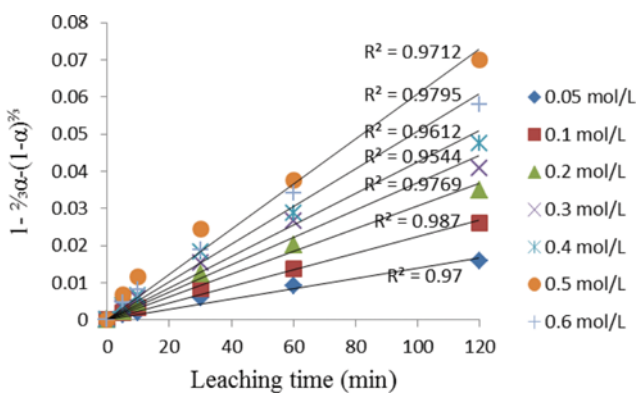

Fig. 7. Plot of versus leaching time at different $NH_3/(NH_4)_2SO_4$ concentration.

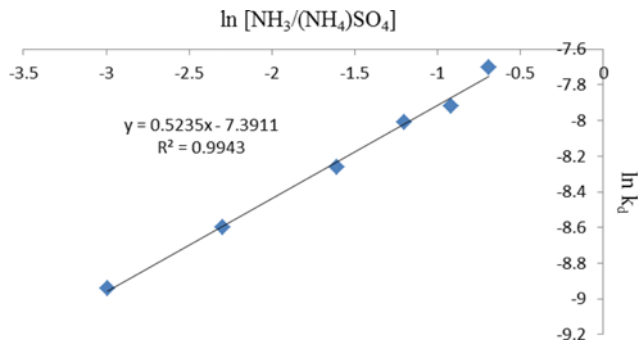

Fig. 8. Plot of ln k_d versus ln $[NH_3/(NH_4)_2SO_4]$.

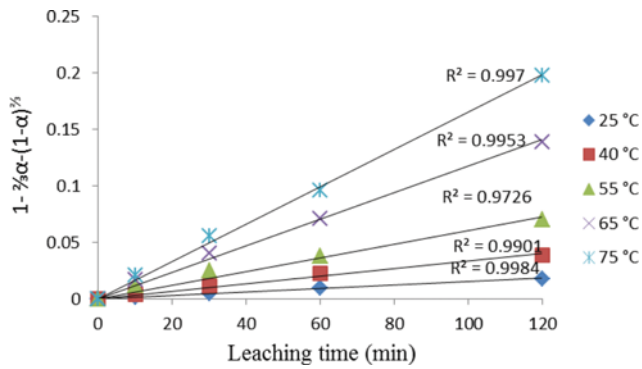

Fig. 9. Plot of $1-(2/3)\alpha-(1-\alpha)^{2/3}$ versus leaching time at different temperatures.

chemically controlled processes are strongly dependent on temperature. The activation energy of a diffusion controlled process is usually below 40 kJ/mol, while for a chemically controlled reaction, this value is usually greater than 40 kJ/mol [20,26]. Therefore, the value of the activation energy of a leaching reaction may be used to predict the rate controlling step of the process. According to the activation energy value determined in this study, the rate of process is controlled by the diffusion reaction.

The apparent rate constant k_d was calculated from the slopes of the straight lines in Fig. 8 and was used for the Arrhenius plot shown in Fig. 10. By using the rate constants derived from the slopes in Fig. 9, the Arrhenius diagram in Fig. 10 was drawn from which the activation energy, Ea, was calculated as 37.37 kJ/mol, which

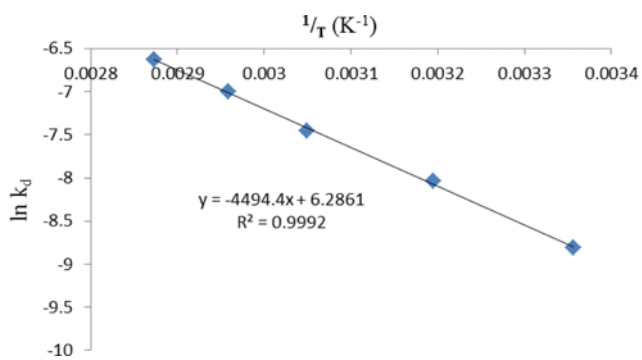

Fig. 10. Plot of $\ln k_d$ versus 1/T.

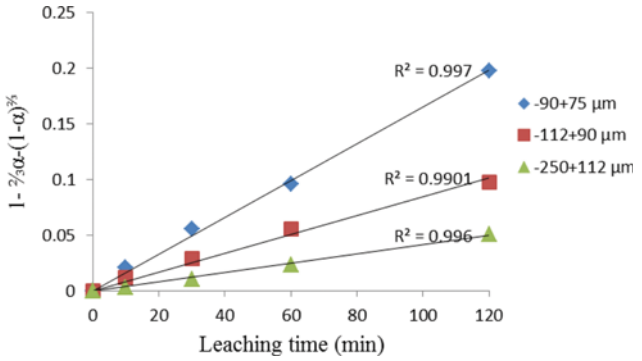

Fig. 11. Plot of $1-(2/3)\alpha-(1-\alpha)^{2/3}$ versus leaching time at different particle size.

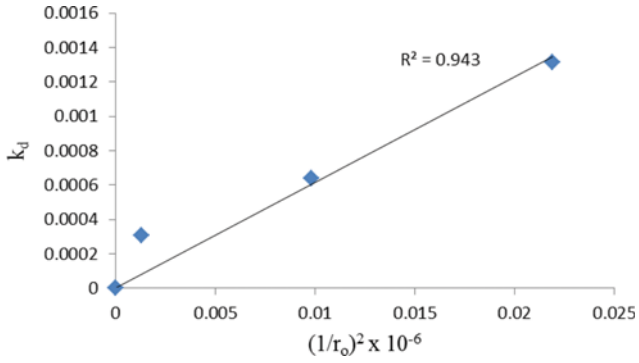

Fig. 12. Plot of k_d versus $(1/r_o)^2$.

supports the proposed diffusion controlled mechanism. Similar works examined in different media where copper ores dissolution are found to be diffusion controlled process include Ekmekyapar et al. [4]: 29.5 kJ/mol, Bingol et al. [14]: 15 kJ/mol, Liu et al. [16]: 26.75 kJ/mol and You-Cai et al. [27]: 32.3 kJ/mol.

To further support the proposed mechanism, the kinetic curves in Fig. 6 were also linearized by means of Eq. (6). The values of the rate constant k_d were then plotted against the reciprocal of the particle radii $(1/r_o)^2$ yielding a linear relationship with a correlation coefficient of 0.943.

The linear dependence of the rate constant on the square of

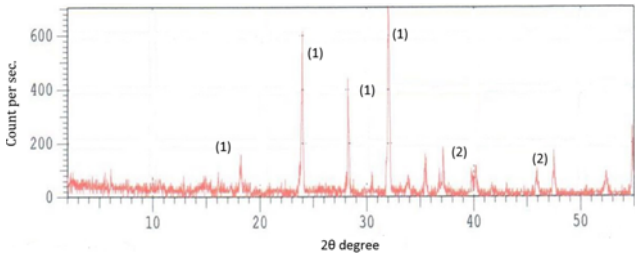

Fig. 13. X-Ray diffraction pattern of leached residual product, showing presence of (1) CuO (tenorite) {045-0937}, (2) $Fe_2O_3 \cdot H_2O$ (hematite) {013-0092} as identified with the Joint Committee on Powder Diffraction Standard file numbers.

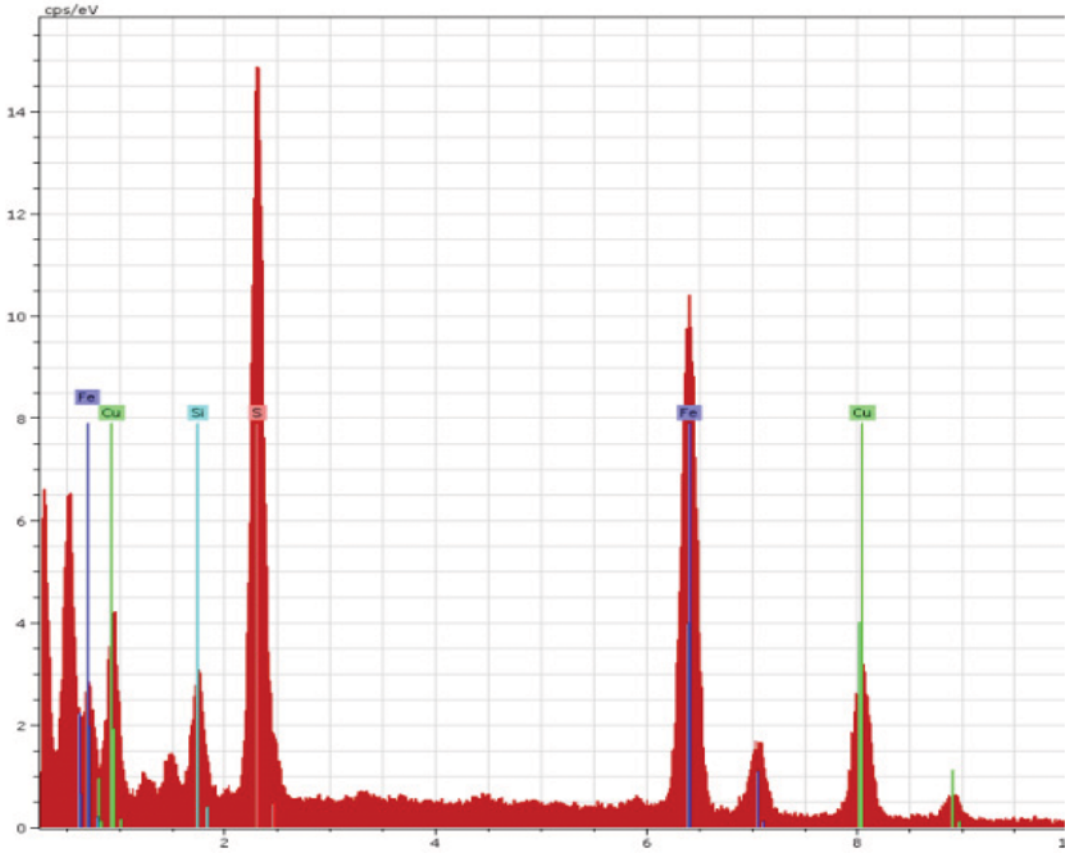

Fig. 14. EDS spectrum of ammonia/ammonium sulfate leached product.

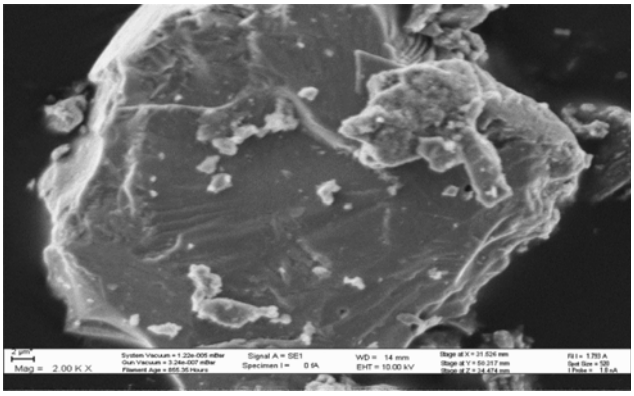

Fig. 15. SEM image of ammonia/ammonium sulfate leached product.

inverse of the particle size radius showed that the rate controlling step for the dissolution of the covellite ore occurred via diffusion control mechanism as shown in Fig. 12. However, the plot of k_d against $(1/r_o)$ did not give a perfect straight line.

3-2. Residual Product Analysis

The leached product formed after optimal leaching was analyzed by using XRD and SEM techniques. The basic mineralogical and morphological composition of results was compared to the raw ore. To determine the mineralogy of dissolved covellite ore, X-ray diffraction (XRD) analysis of the solid residue obtained after leaching process was performed with $[NH_3/(NH_4)_2SO_4]$ at optimum condition. The result of XRD analysis relating to leach residue is given in Fig. 13. It can be observed from Fig. 13 that the peaks of CuS (covellite) disappear, while traces of tenorite (CuO), and iron (Fe) remained in the leach residue when compared with XRD spectral in Fig. 1. This result shows that covellite ore can be leached by using ammonia-ammonium sulfate solutions.

The SEM images of leached residues with the diameter −90+75 μm at 75 °C by 0.5 mol/L ammonia/ammonium sulfate solution is presented in Fig. 15.

The SEM image (Fig. 15) and the SEM-EDS of the leached residue (Fig. 14) show occurrences of colloidal precipitates on the leached residue and well etched ore grains. EDS micro-analyses again showed an enrichment of copper, silicon, iron and sulfur on the covellite surface, and the presence of an oxidized compound in the zone was assumed to contain hematite. The EDS spectrum contains few traces of copper in the leached product: Cu (2.13%) with admixtures of other elements: Fe (46.81%), Si (3.60%) and S (20.29%) as compared to the raw ore containing Cu (33.76%), Fe (29.39%) and S (36.85%).

4. Conclusions

Based on the results of the characterization and dissolution studies undertaken, the following conclusions can be drawn:

1) The elemental analysis of the ore by energy dispersive X-ray fluorescence (EDXRF) showed that the covellite mineral used in this research contained 19.5% CuO, 36.86% Fe_2O_3 and 24.6% S as the major constituents. Other compounds detected occurring from low to trace level included 429% MnO, 0.33% CaO, 0.30% Eu_2O_3, 0.22% BaO and 0.21% K_2O. The XRD analysis confirmed the originality of the covellite ore, and it also revealed the presence of other associated minerals: chalcopyrite ($CuFeS_2$), $Cu_9(Fe, Ni)_9S_{16}$ (putoranite), $Fe(CO_3)$ (siderite) and C (graphite).

2) The dissolution rate of copper increases with increasing concentrations of ammonia-ammonium sulfate and reaction temperature, and with decreasing particle size. At optimal conditions (1.75 mol/L NH_4OH+0.5 mol/L $(NH_4)_2SO_4$, −90+75 μm, 75 °C, with moderate stirring) about 86.2% of copper ore was reacted within 120 minutes.

3) The dissolution process of covellite was found to be controlled by diffusion kinetics. The activation energy was found to be 37.37 kJ/mol and the reaction order with respect to the concentrations of ammonia-ammonium sulfate was determined to be 0.52. The EDS and phase analyses of the residues indicate that covellite is almost completely dissolved in ammonia-ammonium sulfate solution at optimal conditions. Finally, the result of post-leaching residue showed the presence of substantive of sulfur and iron as major constituents.

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