QUANTITATIVE LEACHING OF A NIGERIAN CHALCOPYRITE ORE BY NITRIC ACID

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ABSTRACT
Due to increasing uses of copper nitrate, $Cu(NO_3)_2$, as catalysts, textile and polishing agents for other metals, experiment on the leaching of a Nigerian chalcopyrite ore by nitric acid for possible production of copper nitrate was examined. The effects of acid concentration, temperature and particle size on the dissolution rates of chalcopyrite ore have been investigated. Distribution of elements, compounds present within the ore particle size -90 + 75 µm was initially determined by X-ray Fluorescence (XRF), X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) to provide basis for explaining the dissolution process. It was observed that dissolution rates were greatly affected by acid concentration, temperature and particle diameter. Kinetic data analysis showed that the dissolution mechanism followed diffusion as the rate controlling step. The reaction order was calculated to be 0.51 while the activation energy was deduced to be 29.99 kJmol^{-1} from the dissolution data. The X-ray diffraction analysis of the unleached residue at optimal leaching showed that it contains α-quartz (α-SiO_2) and Tin oxide (SnO_2).
Keywords: Chalcopyrite ore, Nitric Acid, Leaching, Dissolution Kinetics, Copper Nitrate.

INTRODUCTION

Chalcopyrite ($CuFeS_2$) is a sulphide mineral that derived from Greek words "chalkos", copper and pyrites known as "strike fire" (Szymanowski, 1996). It is the most common copper bearing mineral ever known, occur in igneous and metamorphic rocks and in any metalliferous vein (McGraw-Hill, 1987). Large, well shaped crystals of chalcopyrite are widely available and deposited across the globe such as England, Akita, Ugo in Japan, Zacatecas Mexico and in other places around the world. The French Greek mine in Chester co. Pennyslvania has produced huge crystal, many distorted and highly tarnished chalcopyrite (Rotuska and Chmielewski, 2008). However, chalcopyrite is often contaminated by a variety of other trace elements such as Co, Ni, Mn, Zn and Sn substituting for Cu, Fe, Se and As substitute for sulfur and trace amount of Ag, Au, Pb and Sb as reported. It is likely many of these elements are present in finely inter-grown mineral within the chalcopyrite ore (Louise, 2008).

Due to the decline in the world deposit of high grade ores, attention has been drawn to low-grade complex sulphide ore thereby given room to the ore processing by conventional hydrometallurgical alternatives. Hydrometallurgical processes are suitable for lean and complex ore, as processing of ores containing large amount of gangue at high temperature demands high energy and thus, creates problem of slag disposal and evolution of gaseous pollutants to the environment (Olubambi *et al.* 2006; Habashi, 2002; Ghosh and Ray, 1991). It has been used for copper recovery for more than 300 years. The most important development in copper hydrometallurgy, with respect to the growing number of its application as well as its future potential, has been solvent extraction. This has been the great achievement that revolutionized copper compound production all over the world and enabled to introduce hydrometallurgy for industrial scale (Szymanowski, 1996). It is evident that leaching is an important operation during solvent extraction of copper prior to its beneficiation (Baba *et al.* 2013).

During leaching process, different leaching media are applied (Ikiz, *et al.* 2006). These leachant include hydrochloric acid, sulfuric acid, ferric chloride, nitric acid, as well as other available oxidants. Thus, due to high oxidizing capacity, nitric acid often preferred among the aforementioned leachants. Therefore, the establishment of physicochemical conditions for leaching Nigerian chalcopyrite ore by nitric acid, aimed at predicting conditions for possible production of $Cu(NO_3)_2$ was the focus of this investigation. The $Cu(NO_3)_2$ is a valuable compound with varieties of application such as catalyst, textile and polishing agents for other metals as well as in the chemical voltaic cell reactions.

MATERIALS AND METHODS
Materials/Instrumentation
The chalcopyrite mineral used for this study was sourced from Akiri village, Awe Local Government of Nasarawa State, Nigeria. The ore was crushed, grounded and sieve to obtain particle size fractions: (-90 + 75µm, -112 + 90 and -300 + 112µm). All experiment were performed with particle sizes: -90 + 75µm unless otherwise stated.

Characterizations of chalcopyrite ore before and after leaching at optimal conditions were carried out using X-ray fluorescence (XRF, Philips model 120454/3), X-ray diffraction (XRD, Philip PW 1800) and Scanning electron microscopic techniques (JEOL JSM-6510). Nitric acid used was BDH analytical reagent grade and doubly distilled water was used in the preparation of all solutions.

Leaching Procedure

The solution was investigated in a 250ml glass reactor equipped with a mechanical stirrer. The reactor was filled with acid solution which was heated to the desired temperature on introduction of 10g/L of the ore to the reactor (Aydogan *et al.* 2005; Baba *et al.* 2009, 2012). The leaching of chalcopyrite ore with HNO_3 at different concentration ranges (0.1 – 8.42M) were examined at various time up to 120 minutes. The concentration of HNO_3 which gave the maximum dissolution (4M) was subsequently used for the optimization of other leaching parameters such as reaction temperature (*Experimental conditions:* HNO_3 concentration = 4M, Particle size = -90 + 75µm, Solid/liquid ratio = 10g/L by moderate stirring) and particle size (*Experimental conditions:* HNO_3 concentration = 4M, Temperature = 80^0C, Solid/liquid ratio = 10g/L by moderate stirring). Energy of activation, E_a, and other constants were determined from the Arrhenius plots. In all experiments, the fraction of the ore dissolved was evaluated from the initial difference in weight of the amount dissolved or undissolved at various time intervals up to 2 hours after oven drying at about 60^0C. The residue at optimal leaching (80^0C, 4M HNO_3 for 2 hours) was analyzed by XRD and SEM techniques.

RESULTS AND DISCUSSION

The elemental composition of the chalcopyrite ore under study examined by XRF technique showed that the ore contains 24.16% Cu, 36.53% Fe and 2.02% Mn as major elements. Other elements found in the ore include Sn, Mg, Pb and Ca. These were recorded at low to trace levels (Ayinla, 2012).

The ore phase characterized by X-ray diffractogram revealed the presence of typical lean copper which is composed by majority of oxide minerals. The phases were identified using Joint Committee on Powder Diffraction Standard File number (in curl brackets). The compounds present in the ore include: **(1)** $CuFeS_2$ (chalcopyrite) {24-0211}; **(2)** $Cu_{0.47}Fe_{0.58}S_2$ (Fukuchilite) {17-0137}, **(3)** Fe_2O_3 (hematite) {024-0072} and **(4)** FeS_2 (pyrite) → pyrohytite (Fe_7S_8) {22 – 1220}. These are the major compounds detected. Other phases include: **(5)** SnO_2 (cassiterite) {21 – 1250}; **(6)** SiO_2 (α-quartz) {05-0490}; **(7)** Galena (PbS); {05-0792}; **(8)** $CaCO_3.MgCO_3$ (dolomite) {05-0490} and **(9)** Hausmannite (Mn_3O_4) {24-07340}. It is important to note that the compounds **(5) to (9)** occurred in low to trace levels (Ayinla, 2012; Baba *et al.* 2013).

The effect of HNO_3 concentration on the fraction of chalcopyrite ore dissolved using particle size -90 + 75µm at 55^0C was investigated at HNO_3 concentration ranges 0.1M – 8.42M. The plot of fraction (α) dissolved as a function of leaching time is shown in Figure 1.
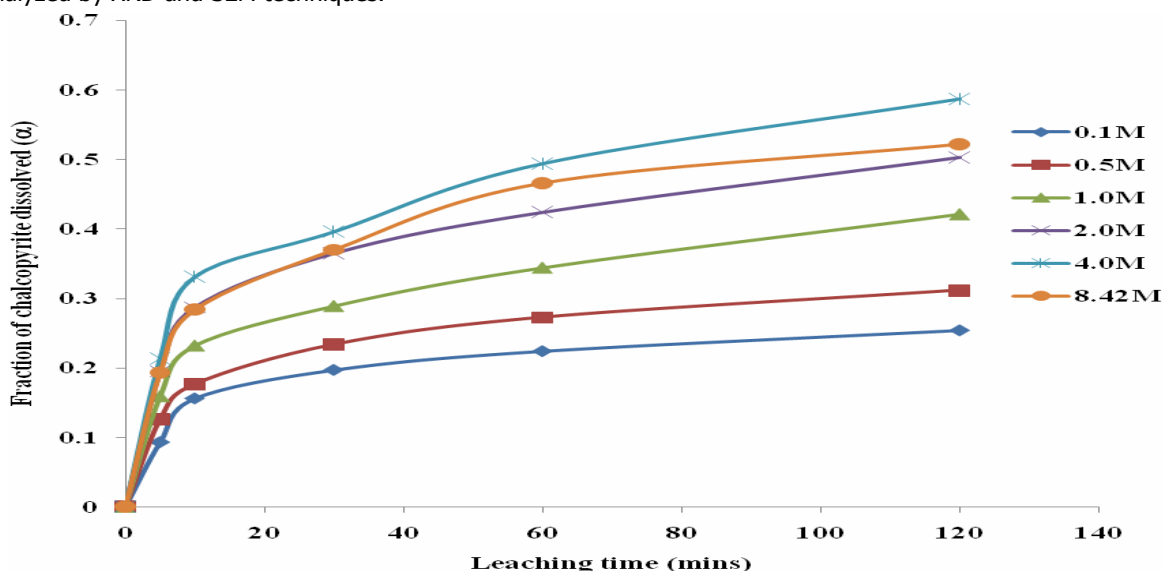

Figure 1: Effect of HNO$_3$ concentration on chalcopyrite ore dissolution.

As shown in Figure 1, the chalcopyrite dissolution increases gradually with leaching time and with increase in HNO_3 concentration. This result indicates that chalcopyrite dissolution is controlled by the hydrogen ion [H$^+$] concentration in the solution. It is important to note that the extent of increasing ore dissolution by HNO_3 as leachant could apparently be as a result of high oxidizing power of the leachant (Liu *et al.* 2010).

The effect of temperature on the rate of chalcopyrite ore dissolution was investigated using temperature range 27^0C–80^0C by 4M HNO_3 solution. The result of this investigated is presented in Figure 2.
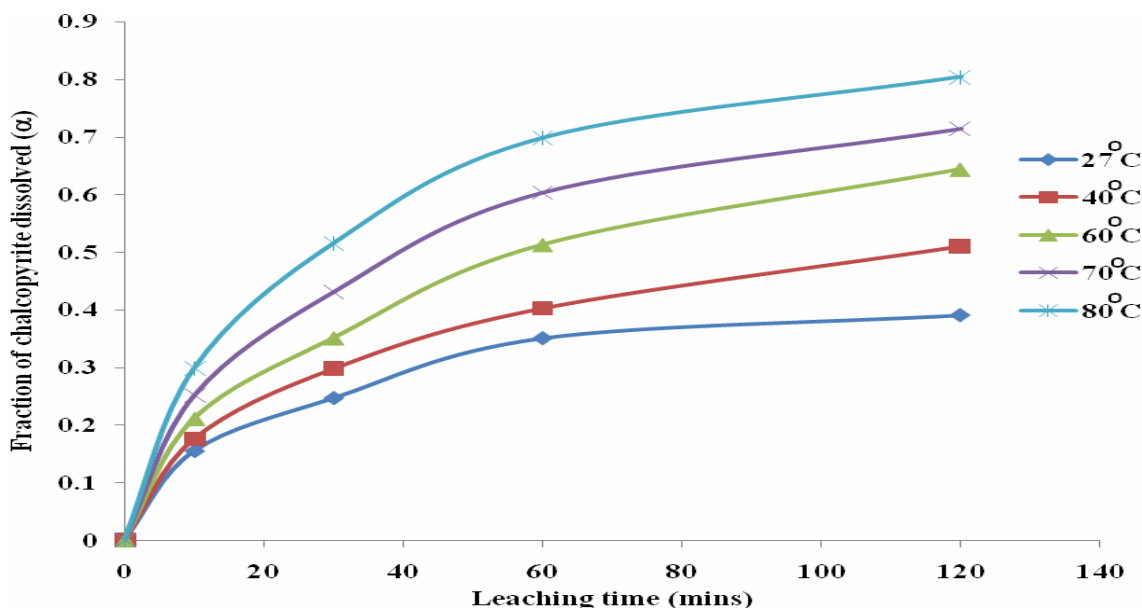
Figure 2 Effect of temperature on chalcopyrite leaching by 4M HNO$_3$ solution.

From the result in Figure 2, it is observed that increasing the temperature is accompanied by increase in chalcopyrite dissolution rate. At 80^{0}C, for example, about 80.5% of chalcopyrite ore was dissolved within 120 minutes. The result of other similar studies showed that chalcopyrite mineral is very active at high temperature, and the dissolution rate of the ore will be increased (Abouzeid, 1990). Though, in this study, the reaction temperature was particularly limited to 80^{0}C because of significant loss of acid solution through evaporation (Baba *et al.* 2009; Olanipekun, 1999).

The effect of particle size on the dissolution of chalcopyrite ore by 4M HNO$_3$ solution at 80^{0}C was examined using three particle sizes: -90 + 75 μm, -112 + 90 μm, and -300 + 112 μm. The result of this investigation is shown in Figure 3.
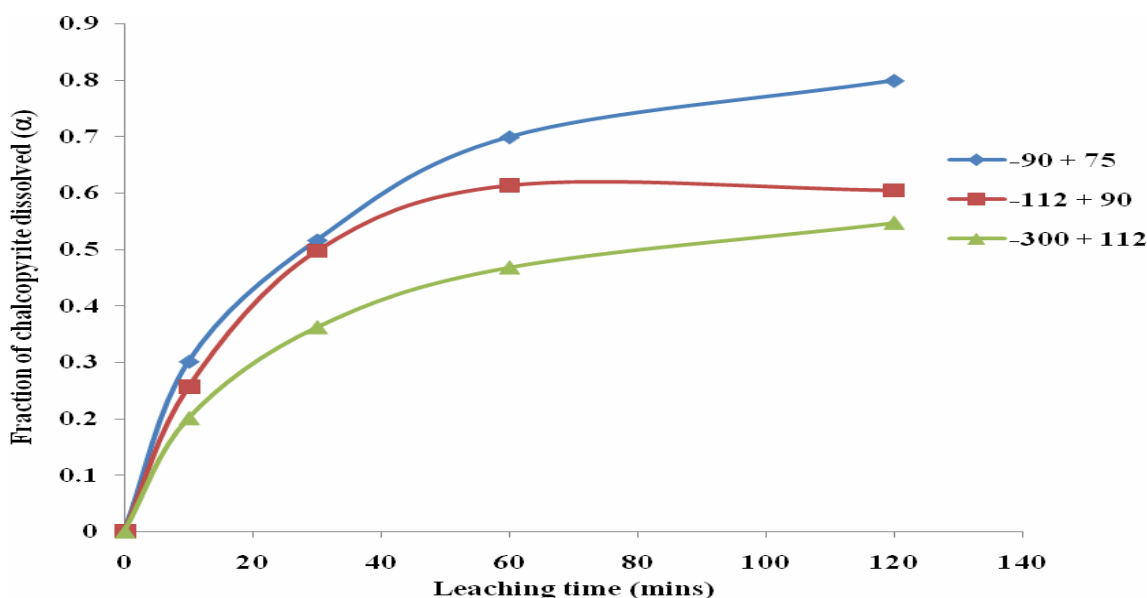
Figure 3: Effect of particle size on nitric acid chalcopyrite dissolution at various leaching time.

From Figure 3, while the dissolution of chalcopyrite with the samples of particle size -90 + 75μm was between 30 − 80% after 120 minutes, the dissolution decreased to about 20 − 55% for the particle size above -90 + 75μm. This may be attributed to increase in surface area for the finer size chalcopyrite ore (Baba *et al.* 2012; Baba *et al.* 2007; Aydogan *et al.* 2005).

DISCUSSION
Due to reduction in both the mass of solid and the particle size during leaching, the shrinking particle model is always applied to describe the leaching kinetics (Fabiano *et al.* 2010; Levenspiel 1972). Consequently, the dissolution mechanism of chalcopyrite ore is based on three main kinetic models.

These are the diffusion, surface reaction and the mixed kinetic model containing diffusion and surface reactions, which takes place simultaneously (Aydogan *et al.* 2005). If the reaction rate is controlled by diffusion through a product layer, the integrated rate equation (1) holds (Aydogan *et al.* 2005; Sohn and Wahworth 1979). Apparently, if the reaction is controlled by a surface reaction, then equation (2) is applicable.

$$1 - \frac{2}{3}\alpha - (1-\alpha)^{2/3} = \frac{K_C M_B C_A t}{\rho_b a r_0} = K_d t \qquad (1)$$

$$1 - (1-\alpha)^{1/3} = \frac{K_C M_B C_A t}{\rho_b a r_0} = K_r t \qquad (2),$$

where α is the fraction reacted, K_c is the kinetic constant, M_B is the molecular weight of the solid, C_A is the concentration of the dissolved lixiviant, A is the bulk of the solution, a is the stoichiometric coefficient of the reagent in the leaching reaction, r_0 is the initial radius of the solid particle, t is the reaction time, D is the diffusion coefficient in the porous product layer, ρ_b is density of the solid and K_d and K_s are rate constants (Ayinla, 2012; Baba *et al.* 2012, 2013; Baba and Adekola, 2010; Fabiano *et al.* 2010).

It was observed that of the two tested models, the one of equation (1) fitted all data expressed in Figs. 1 −3. According to equation (1), a plot of $1 − 2/3\alpha − (1 − \alpha)^{2/3}$ versus leaching time is a straight line with slope K_d when the process is diffusion controlled mechanism as shown in Figure 4.
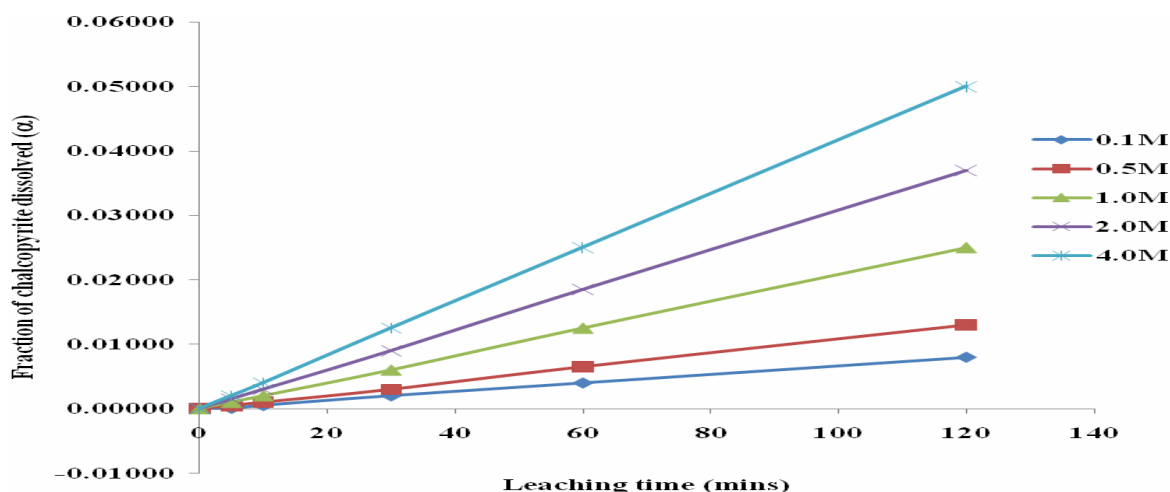

Figure 4: Plot of $1 - \frac{2}{3}\alpha - (1-\alpha)^{2/3}$ **versus leaching time at different HNO₃ concentration.**

Hence, the experimental rate constants, K_d, were evaluated from the slope of Figure 4. These values were used to plot ln K_d versus ln[HNO₃], as shown in figure 5.

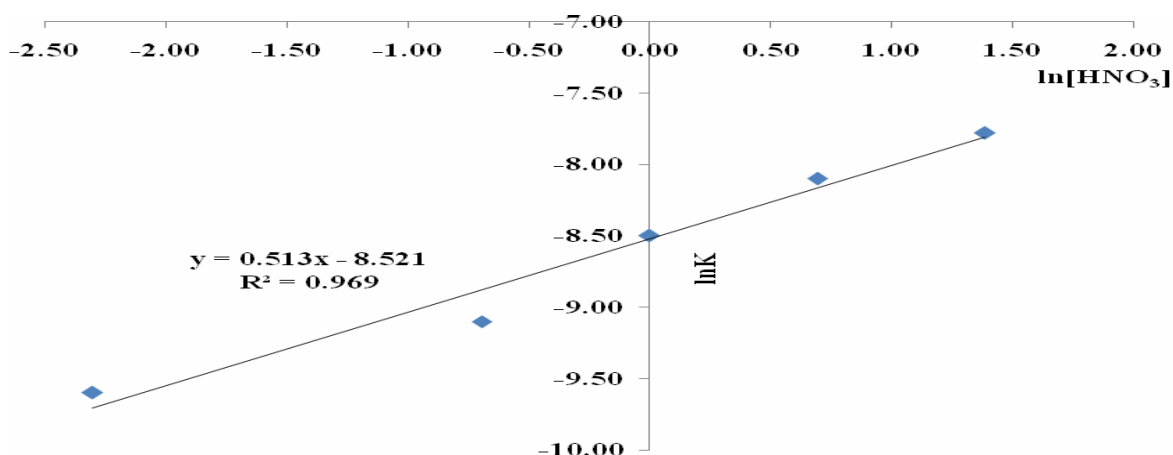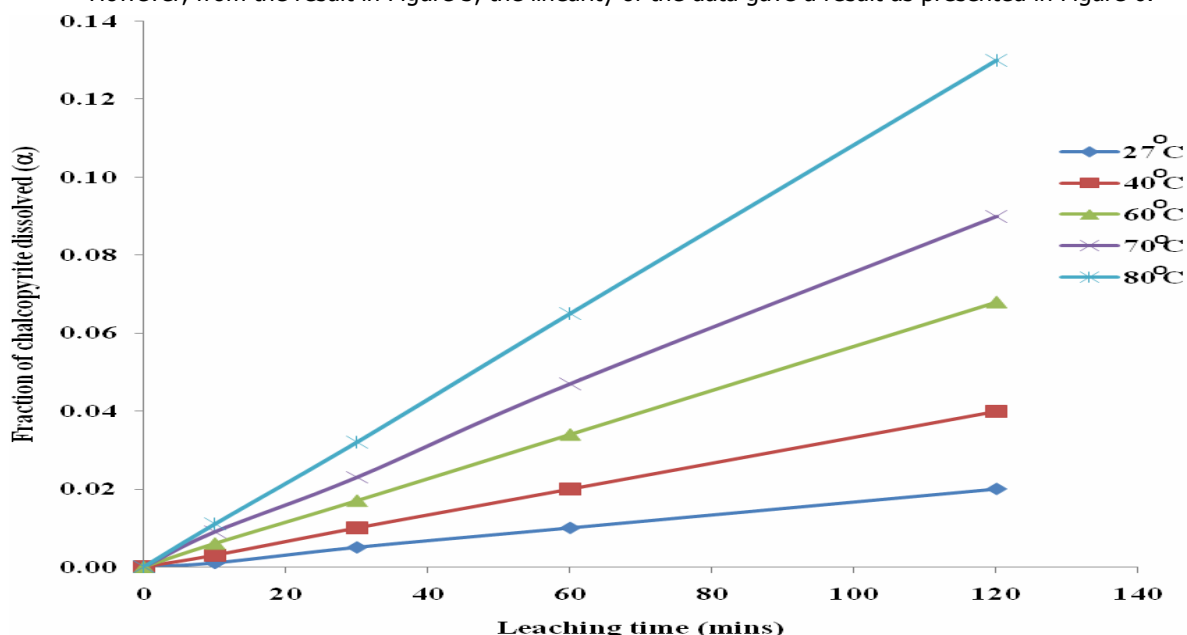**Figure 5: Plot of lnK versus ln[HNO₃]**

From the result in Figure 5, the slope of the straight line graph was calculated to be 0.51. This indicates that the reaction order is half order with respect to HNO_3 leaching for which its concentration $\leq$ 4M.

However, from the result in Figure 3, the linearity of the data gave a result as presented in Figure 6.

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

The apparent rate constants K_d were determined from the slopes of the straight lines in Figure 6 and were used to plot Arrhenius plot of Figure 7.

$$y = -3675x + 3.440$$
$$R^2 = 0.993$$
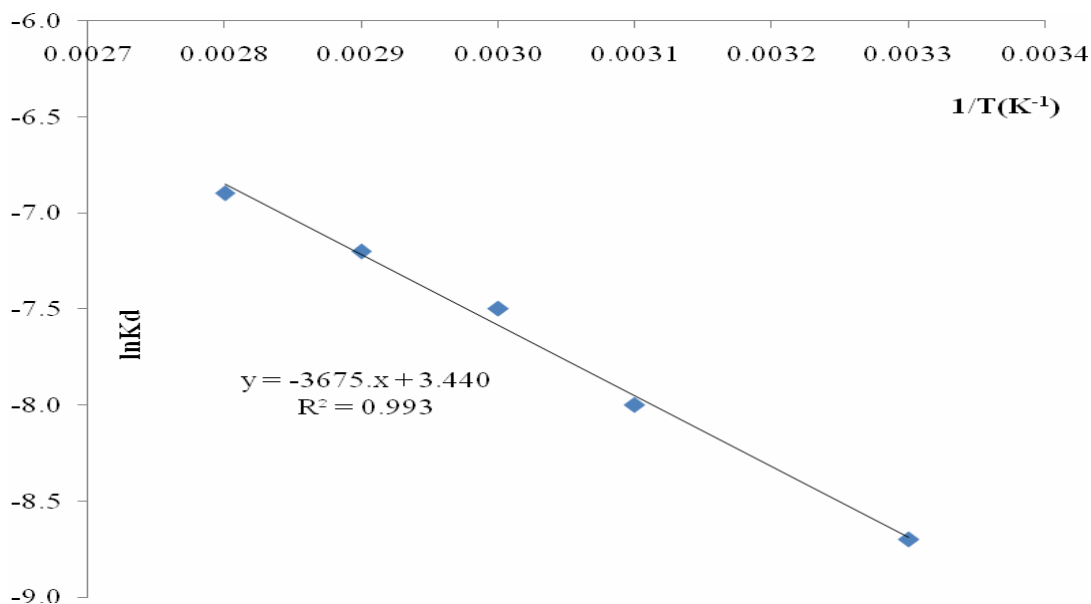
Figure 7: Plot of lnK$_d$ versus 1/T.

Figure 8 shows the Arrhenius plot, lnK$_d$ against the reciprocal of reaction temperature, from which the activation energy was calculated to be 29.93 kJmol^{-1}. The value suggests that the mechanism of dissolution via HNO_3 occurs through a diffusion control route.

To further support this assertion, the plot of the rate constant, K, versus inverse of square of particle radii $(1/r_0)^2$ on the particle diameter gave a linear relationship as presented in Figure 8. Hence, linearity of the plot in Figure 8 affirmed the rate determining step for the dissolution of chalcopyrite ore by HNO_3 media occur via diffusion control mechanism. Apparently, the plot of K versus $(1/r_0)$ was not linear.
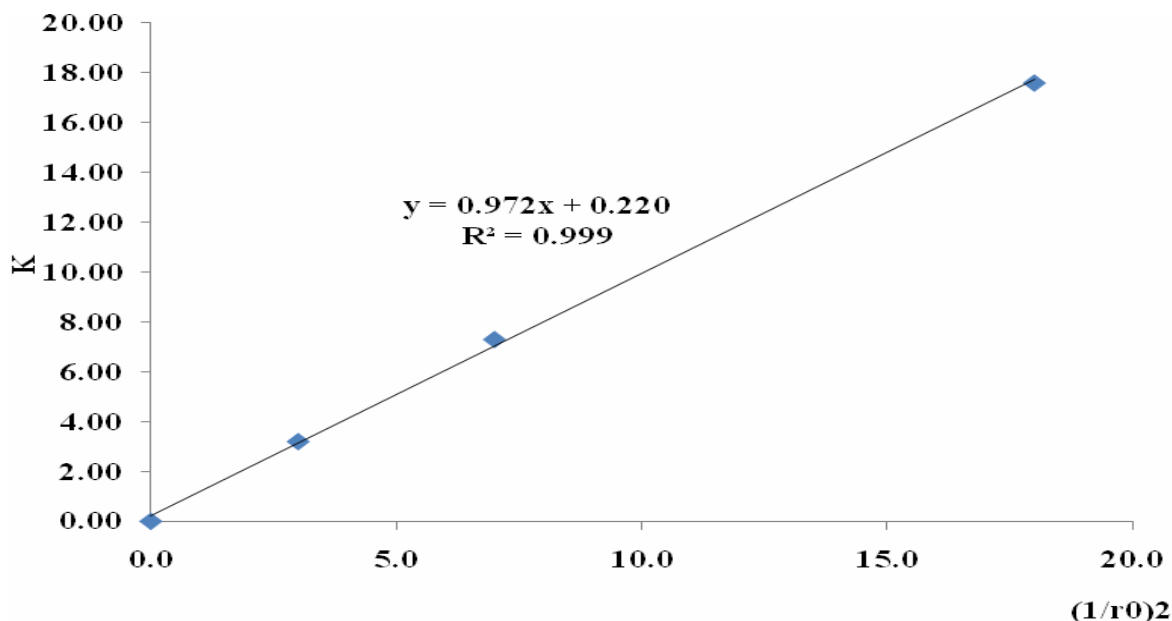
Figure 8: Plot of K versus $(1/r_0)^2$

The X-ray diffraction analysis of the solid residual product obtained from the leaching of 10g/L chalcopyrite ore at optimal condition by 4M HNO_3 at 80^0C are presented in Table 1.

Table 1: Retained peaks after optimal leaching

2-theta (deg)	d= $\overset{o}{A}$	Compound	JCPDS File Number
49.9150	1.8256	α-quartz (SiO_2)	05 – 0490
7.7162	1.5959	Tin oxide (SnO_2)	13 – 0111

Table 1 showed that the predominant peaks in the chalcopyrite ore ($CuFeS_2$), namely pyrite (FeS_2) and host of other iron compounds in the original sample were effectively leached at optimal conditions. However, the dominant mineral phases that formed the residual products are α-quartz (SiO_2) and tin oxide (SnO_2). Further investigation of change on chalcopyrite surface at 80^0C by 4M HNO_3 solution during leaching for 2 hours was also examined by SEM as depicted in figure 9.
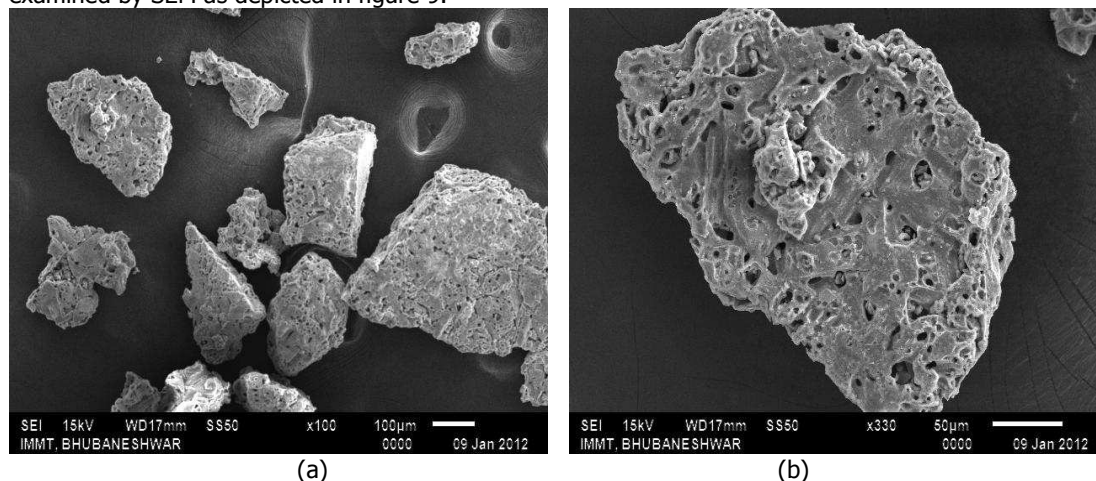

(a)

(b)

Figure 9: SEM Micrograph of leaching residue of chalcopyrite ore by 4M HNO_3 at 80^0C
(a) Image of leaching residue at 60 min (about 70% dissolution)
(b) Image of leaching residue at 120 min (about 81% dissolution)

From SEM in figure 9, it is evident that a greater reduction in the phase of the ore **(b)** comparing with the SEM of leaching at 60 minutes **(a)** based on the larger pore size observed. Furthermore, it is worthwhile to predict that the possible presence of pyrite on the surface of the ore may gave rise to sulphur layer formation, because of high copper recovery and may prevent the leaching of chalcopyrite ore. Therefore, the possible presence of pyrite (when unleached) may leads to greater permeability and the porosity of the sulphur layer formed which apparently may enhances chalcopyrite leaching (Javad-Koleini *et al.* 2010).

CONCLUSION

Based on the results established from the present study, it was found that leaching by 4M HNO_3 solution using 10g/L of -90 + 75μm particle size within 120 minutes by moderate stirring, the extent of the chalcopyrite ore reached 81.46%. Also, the reaction rate increases with increasing HNO_3 concentration, reaction temperature, and decrease in particle size. The result of dissolution study has been analyzed using shrinking core model and found that the reaction rate is controlled by diffusion of copper through the porous product layer. To this end, the reaction order with respect to HNO_3 concentration was found to be 0.51. The activation energy Ea, and Arrhenius constant (on plotting Figure 7 from the origin) gave 29.93 $kJmol^{-1}$ and 3.44 x 10^3 s^{-1}, respectively for the dissolution process. Finally, analysis of the residual product by X-ray diffraction data showed that about 19% of the initial solid material that form undissolved materials contained α–quatz (α-SiO_2) and Tin oxide (SnO_2).

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