ASSESSMENT OF A NIGERIAN CHALCOPYRITE ORE DISSOLUTION IN SULFURIC ACID MEDIUM

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ABSTRACT. This paper presents a study of dissolution kinetics of a Nigerian chalcopyrite ore in sulfuric acid lixiviant. The effects of acid concentration, temperature and particle diameter on the dissolution rates of chalcopyrite ore have been examined. The dissolution rates are significantly influenced by increase in temperature, hydrogen ion concentration [H^+], and decrease in particle diameter. The experimental data for the dissolution rate have been analyzed with the shrinking core model which shows the rate controlling step for the dissolution of chalcopyrite ore occurs via surface chemical solution. With 4 M H_2SO_4 solution, about 91.6% of 10 g/L chalcopyrite ore at 80 ºC was dissolved within 120 min using -90+75 μm particle diameter. The reaction order with respect to hydrogen ion concentration was found to be 0.57 with correlation coefficient 0.968. The calculated activation energy, (Ea) value of 44.9 kJ/mol for the dissolution process was established. However, the SEM morphology of the residues from leaching process showed that about 8.4% of the initial solid material contained admixtures of Fukuchilite ($Cu_{0.42}Fe_{0.58}S_2$), and elemental sulphur (S^o) and are formed around the shrinking core of the unreacted material.

KEY WORDS: Chalcopyrite, Sulfuric acid, Dissolution kinetics

INTRODUCTION

Chalcopyrite ($CuFeS_2$), the principal copper mineral that produces copper from sulfide ores account for about 70% of the copper reserves in the world [1]. The ore is often associated with other viable sulfide minerals, such as galena (PbS), pyrite (FeS_2) and host of others which are generally separated from each other by froth flotation methods [2]. Apparently, 70% world production of copper is produced from this mineral through flotation process followed by a pyrometallurgical method [3, 4]. The percentage of copper consumption worldwide has grown by about one or two percent per year since 1980 and has been projected to grow continually at this rate, due to the growth and increased in world trade [5]. However, the increased use of copper due to its electrical conductivity, corrosion resistance, thermal conductivity and new applications has gradually led to a decrease in exploitable ore reserves, in which more efficient mining and extraction will ensure the continued availability of copper for future use [2, 6].

In recent years, more and more attention have been focused on the extraction of oxidized copper ores due to the depletion of higher grade copper sulfides [7]. As there are growing public awareness of the copper mining industry due to emission of obnoxious pollutants such as sulfur dioxide (SO_2) from a named pyrometallurgical process, there has been growing worldwide interest in hydrometallurgical processes for the industrial copper production [1, 8, 9]. The

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hydrometallurgical treatment of copper sulfide concentrate is increasingly establishing itself as a viable route for the extraction of copper and recovery of associated precious metal values. This is attributed to the merits of this route that include; suitability for low-grade and complex ores, high recoveries competitive economics, and other operational feature [10]. Also, the conversion of sulfur in the raw ore to elemental sulfur - while avoiding the release of SO_2 to the atmosphere is another merit of hydrometallurgical method with leaching as important operational unit [11, 12].

From the literature, several leaching agents including oxidative, non-oxidative or both have been extensively studied [13-18]. However, due to relatively cheap and plentiful material resulting from the sulfide value of the ore being processed, the use of sulfuric acid was constituted with the following stoichiometry and was adopted in this study [19]:

$$CuFeS_2 + 4H_2SO_4 \rightarrow CuSO_4 + FeSO_4 + 2S^o + SO_2 + 4H_2O \qquad (1)$$

Hence, the present study is to propose the physico-chemical conditions for the dissolution and possible beneficiation of the copper leach liquor to produce copper sulfate pentahydrate ($CuSO_4.5H_2O$) of industrial value. The $CuSO_4.5H_2O$ crystal is an important compound with many diverse applications such as fungicide, insecticide, wood preservatives, dyestuff preparation, electrolyte, varnish in paint making, etc.

EXPERIMENTAL

Material and analysis

The chalcopyrite ore sample used for this investigation was sourced from Akiri, (latitude: 8° 21' 59'' N; longitude: 9° 21'' 14' E), Awe Local Government Area of Nassarawa State, Nigeria. The sample was crushed, ground and sieved into different size fractions: (-90+75, -112+90, -300+112 μm). All experiments were performed with particle size -90+75 μm, unless otherwise stated. In the leaching experiments, sulphuric acid with a purity of approximately 98% was used in this work and deionized water was used in the preparation of all solutions.

Chalcopyrite ore characterization

The X-ray fluorescence (XRF) - Philips model 12045B4/3 was used for the elemental analysis of chalcopyrite ore. The mineralogical purity of the ore was investigated using Philips PW 1800 X-ray diffractometer (XRD) with CuKα (1.5 Å) radiation, generated at 40 kV and 55 mA. The cabinet houses a high speed, high precision Gonimeter; high efficiency generator (X-ray) and an automatic sample loading facility.

Leaching procedure

Leaching experiments were performed in a 250 mL glass reactor with a mechanical stirrer. The reactor was filled with 100 mL of H_2SO_4 acid solution which was heated to the desired temperature on introduction of 10 g/L chalcopyrite ore [20]. The leaching of chalcopyrite ore with H_2SO_4 solution at different concentrations was done as described previously [21, 22]. The concentration of H_2SO_4 which gave the maximum dissolution was subsequently used for the optimization of other leaching parameters including temperature, and particle size. Energy of activation, Ea, and constants were determined from the Arrhenius plots. In all experiments, the fraction of the ore dissolved, were evaluated from the initial difference in weight of the amount dissolved or undissolved at various time intervals up to 120 min, after oven-dried at about 60 ºC. The post leaching residual product at 80 ºC in 4 M H_2SO_4 solution was then analyzed by X-ray diffraction and scanning electron micrographic techniques for better understanding of the dissolution process.

RESULTS AND DISCUSSION

Raw ore characterization results

The elemental composition of the ore by XRF has been earlier reported [23]. The ore contains $24.16 \pm 0.01\%$ Cu, $36.53 \pm 0.04\%$ Fe, $2.02 \pm 0.01\%$ Mn as the major elements. Other elements found in the ore include: Sn ($0.069 \pm 0.01\%$), Mg ($0.17 \pm 0.3\%$), Pb ($0.12 \pm 0.01\%$) and Ca ($0.08 \pm 0.02\%$). X-ray diffraction analysis reveals the presence of the compounds such as chalcopyrite ($CuFeS_2$), pyrite (FeS_2) which may be a mixture of pyrottrite (Fe_7S_8). The XRD data also identified the presence of other associated compounds including silica (SiO_2), Galena (PbS), siderite (SnO_2), Hausmanite (Mn_3O_4) and Fukuchilite ($Cu_{0.47}Fe_{0.58}S_2$). These compounds occurred from low to trace levels ($\leq 5\%$). The SEM image of raw ore gave a rectangular structure with perfect sets of cleavage plane particles on the surface and edge of the particles could easily be found in the image of the particles before leaching [24].

Effect of H₂SO₄ concentration

According to Habashi [25], the rate of leaching process is expectedly to increase with increasing concentration of leaching agent. However, in this study, the statement is valid only for the conditions where the concentration of sulphuric acid (H_2SO_4) increases from 0.1 - 4.0 M. At higher concentration of sulphuric acid, the dissolution of the ore decreased, most probably due to the decrease in the reactivity of sulfuric acid at higher acid concentration, causing possible precipitation phenomena [26, 27]. It can be seen in Figure 1, that increasing the acid concentration from 0.1-8.4 M, at a temperature of 55 °C and leaching time varied from 0 to 120 min, there is decreased in the ore dissolution from 58.1% to 48.2% with 4.0 M to 8.4 M H_2SO_4 solutions, respectively. Hence, 4.0 M H_2SO_4 solution is considered for the optimization of other parameters such as temperature and particle size variation.
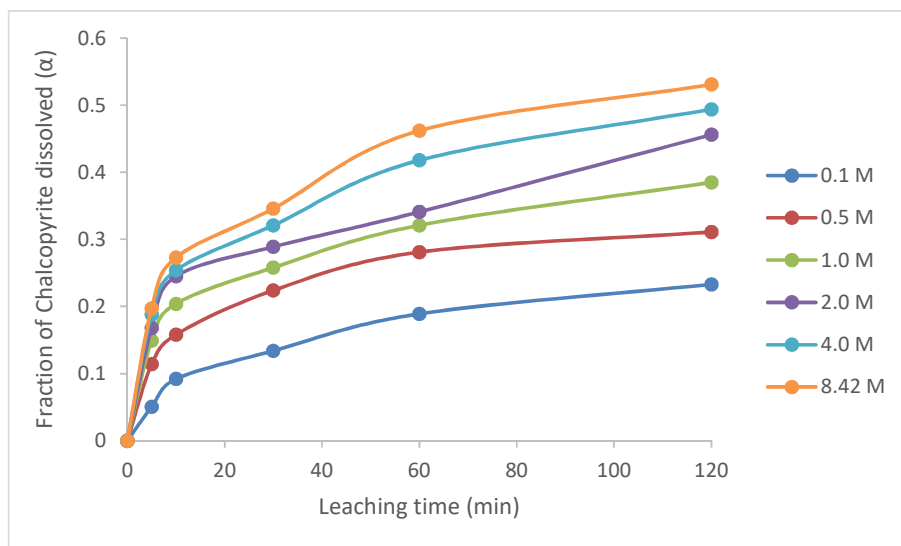

Figure 1. Effect of H_2SO_4 concentration on chalcopyrite dissolution. Experimental conditions: H_2SO_4 concentration = 0.1–8.4 M, temperature = 55 °C, particle size = -90+75 μm, solid/liquid ratio = 10 g/L with moderate stirring.

Effect of temperature

The dissolution rate of copper as a function of temperature between 120 min leaching time using particle size diameter -90+75 μm by 4.0 M H_2SO_4 solution is summarized in Figure 2. It was observed that the dissolution of the ore increases from 53.1% to 91.3% as the temperature increased from 55 °C to 80 °C. It is apparently clear that the rate of ore dissolution depends on increasing reaction temperature. However, temperature beyond 80 °C was not considered in this study because of severe loss of acid reagent through evaporation [28].
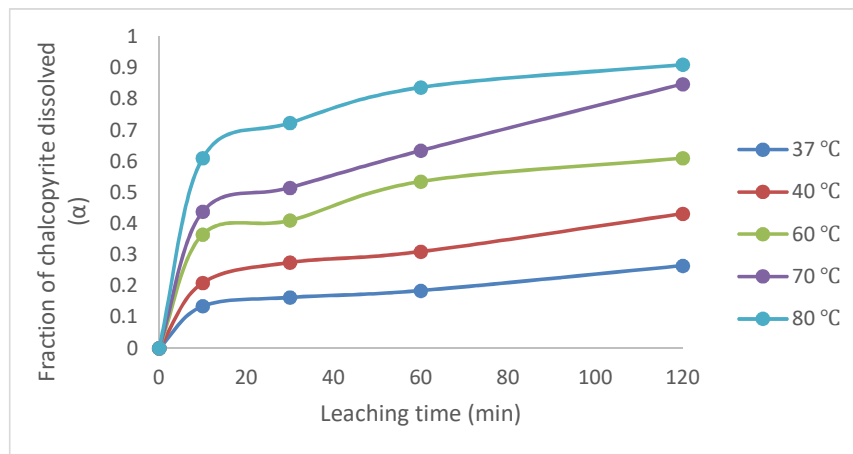

Figure 2. Effect of temperature on chalcopyrite dissolution by 4 M H_2SO_4 at various contact time. Experimental conditions: H_2SO_4 concentration = 4 M, temperature = 28–80 °C, particle size = -90+75 μm, solid/liquid ratio = 10 g/L with moderate stirring.
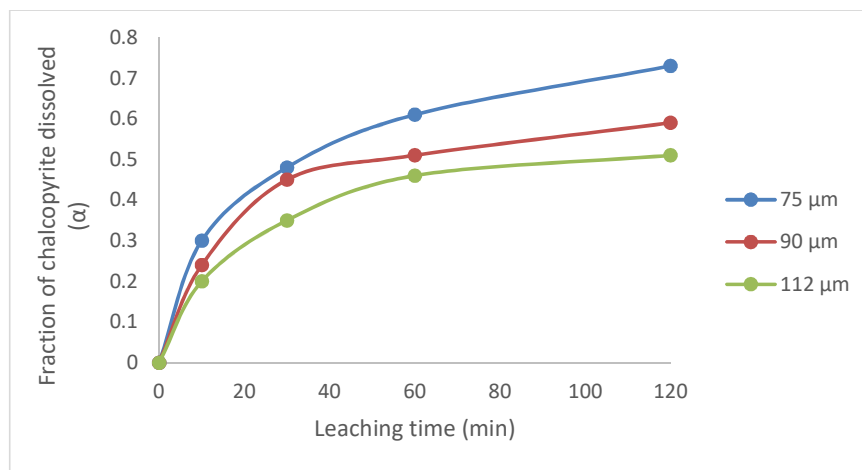

Figure 3. Effect of particle size on chalcopyrite dissolution at various contact time. Experimental conditions: H_2SO_4 concentration = 4 M, temperature = 80 °C, solid/liquid ratio = 10 g/L with moderate stirring.

Effect of particle size

The effect of particle size on the dissolution of chalcopyrite ore was studied using three different particle sizes (-90+75, -112+75, -300+112 μm) by 4 M H_2SO_4 solution at 80 °C with moderate stirring. The results shown in Figure 3 revealed that the leaching efficiencies of the ore increases with decreasing particle size. This is in agreement with the findings of [29, 30]. From Figure 3, it is obvious that the fraction with smallest particle size has the highest dissolution due to its high surface area as compared to other particle fractions investigated.
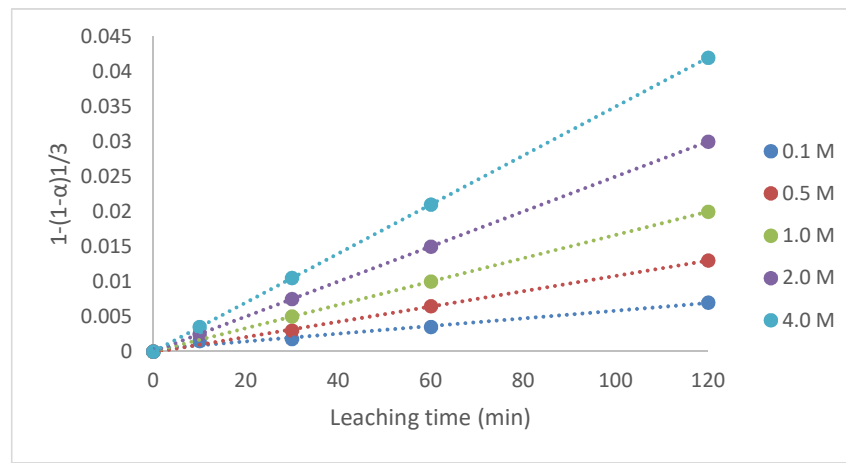

Figure 4. Plot of $1-(1-\alpha)^{1/3}$ versus leaching time at different H_2SO_4 concentrations. Experimental conditions: Same as in Figure 2.

Dissolution kinetic analysis

The dissolution process of the chalcopyrite ore leaching is a typical fluid solid reaction that is best described with the shrinking core model [31-33]. According to this model, the reaction takes place on the outer surface of the ore, and this surface shrinks towards the center of the solid as the reaction proceeds. If the reaction rate is controlled by diffusion through a product layer, the kinetic equation would follow the following stoichiometry:

$$1 - 2/3\, \alpha - (1-\alpha)^{2/3} = \frac{K_C M_B C_A}{\rho b a r_o^2} t = k_d \tag{2}$$

However, if the reaction is controlled by a chemical reaction, the kinetics equation is:

$$1 - (1-\alpha)^{1/3} = \frac{K_C M_B C_A}{\rho b a r_o} t = k_r \tag{3}$$

α is the fraction reacted, k_r is the kinetic constant, M_B is the molecular weight of the solid, C_A is the concentration of the dissolved leachant, A is the bulk of the solution, a is the stoichiometric coefficient of the reagent in the leaching reaction, r_o is the initial radius of the solid particle, t is reaction time, D is the diffusion coefficient in the porous product layer, ρb is density of the solid and k_d and k_r are reaction rate constants for the diffusion and chemical dissolution mechanisms, respectively. Therefore, equations (2) and (3) revealed that if the diffusion through the product

layer or the chemical reaction controls the leaching rate, there must be a linear relationship between the left side of the equation and time in each case. The results of the leaching investigations with respect to H_2SO_4 concentration variations showed that the leaching data in Figure 1 fitted equation 3 and was used to obtain the plot (Figure 4).

The experimental rate constants, k_d, were determined from the slopes in Figure 4 and the plot of ln k_d versus ln[H_2SO_4] were made as shown in Figure 5.
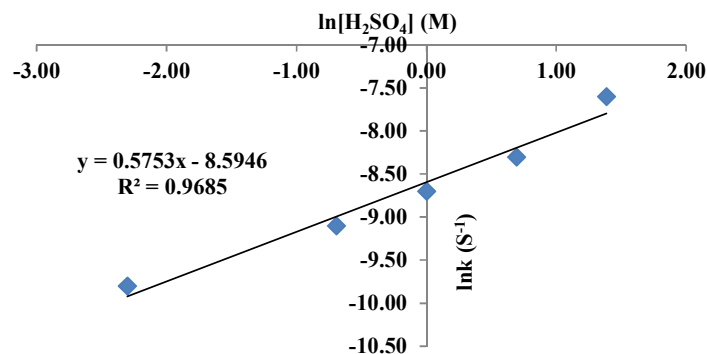

Figure 5. Plot of lnk versus ln[H_2SO_4].

As seen in Figure 5, the slope of the resulting plot indicates that the reaction order with respect to H^+ ion is 0.57 at the defined H_2SO_4 concentration $\leq$ 4 M. This value indicates that the ore dissolution by H_2SO_4 media may occur through first order process. Also, the linearization of the data in Figure 2 gave the Arrhenius plot as summarized in Figure 6.
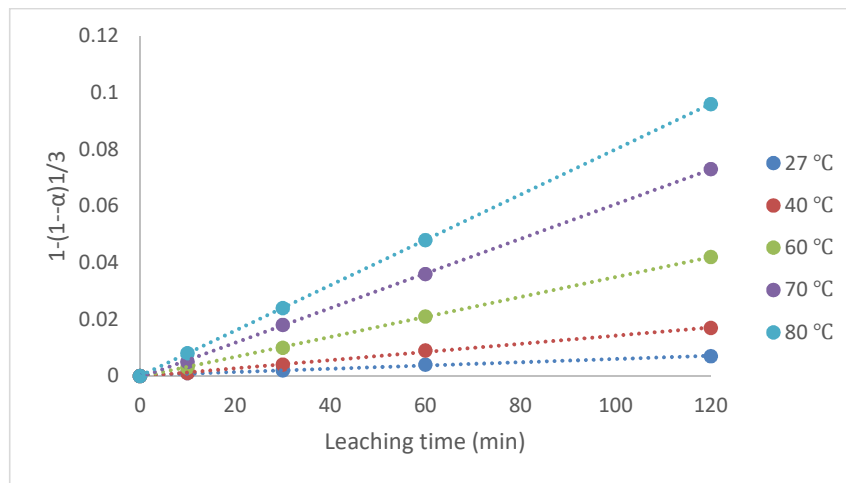

Figure 6. Plot of $1-(1-\alpha)^{1/3}$ versus leaching time at different temperatures. Experimental conditions: Same as in Figure 2.

The apparent rate constant k_d was calculated from the slopes of the straight lines obtained from Figure 6 and used to plot Arrhenius plot consistent with the following relation:

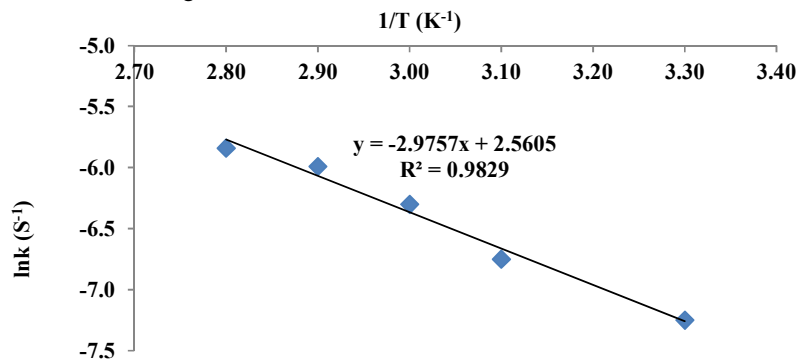$$\ln k_r = \ln A - Ea/RT \tag{4}$$

as summarized in Figure 7:

Figure 7. Plot of lnk versus 1/T. Experimental conditions: Same as in Figure 2.

From the Arrhenius relation in Figure 7, the activation energy was calculated to be 44.9 kJ/mol clearly supports chemical reaction control for the dissolution process.

Characterization of solid leaching residue

Characterization of solid residues after optimal leaching process was done using X-ray powder diffraction (XRD) and SEM analyses. The solid residues obtained at 80 ºC under following optimum conditions: 4.0 M H_2SO_4, 10 g/L solid-liquid ratio with moderate stirring and particle diameter -90+75 µm showed that the undissolved solid as identified by XRD consist of the following associated copper mineral phases: Fukuchilite ($Cu_{0.42}Fe_{0.58}S_2$) and sulfur (S^o) (Table 1). These minerals including chalcopyrite were found to occur from low to trace levels ($\leq$ 5%).
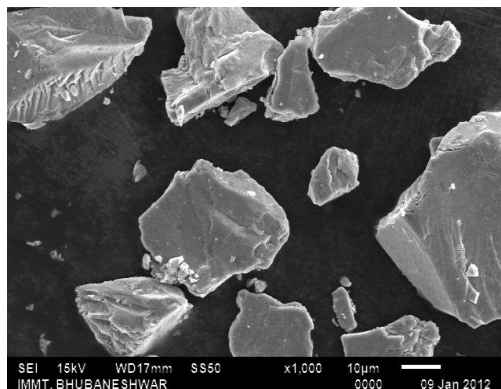

Figure 8. SEM morphology of the leached solid residual showing possible undissolved sulfurite species (Fuchucilite and other varieties).

Table 1. XRD data of prominent peaks in leached product at optimal leaching conditions.

2-theta (deg)	d = Å	Compound	JCPDS File Number
29.3280	3.04278	Chalcopyrite ($CuFeS_2$)	24 – 0211
49.9900	1.85780	Fukuchilite ($Cu_3Fe_8S_2$)	17 – 0138
58.5060	1.57630	Sulfur (S^0)	05 – 0661

The SEM image of chalcopyrite leached residue (Figure 8) showed that the unleached product at optimal leaching gave erosive crystal deposited around the ore surface forming the sulfurite species (*Fuchucilite* and other varieties), which apparently affect the dissolution efficiency during chalcopyrite leaching with H_2SO_4 leachant.

CONCLUSION

The kinetics leaching of chalcopyrite ore dissolution by sulfuric acid solution was investigated. The effect of leaching parameters such as acid concentration, temperature and particle size on the extent of the ore dissolution was examined. The results obtained during the dissolution process shows that the dissolution rate increases with increase in acid concentration, temperature and decrease in particle diameter. In 4 M H_2SO_4 solution and temperature of 80 °C, dissolution of the initial 10 g/L of the ore reached 91.3% during 120 min leaching using -90+75 μm particle diameter. The estimated activation energy of 44.9 kJ/mol supported the proposed surface chemical reaction for the dissolution process. The residual product constituting about 10% examined by XRD indicates the presence of unleached sulfurite species such as Fukuchilite and other mineral phases which are found to occur from low to trace levels (≤5%). Further purification of the product at optimal leaching for possible production of copper sulphate pentahydrate ($CuSO_4.5H_2O$) crystal for industrial value is still on in our laboratory.

ACKNOWLEDGEMENT

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