

Hydrometallurgical application for treating a Nigerian chalcopyrite ore in chloride medium: Part I. Dissolution kinetics assessment

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Abstract: The dissolution kinetics of a Nigerian chalcopyrite ore in hydrochloric acid was studied in this article. Acid concentration, reaction temperature, and ore particle size were chosen as experimental parameters. The chemical and morphological studies of the ore before and after leaching at optimal conditions were carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM). It is revealed that increasing the acid concentration and system temperature and decreasing the ore particle size greatly enhances the dissolution rate. The dissolution kinetics was found to follow the shrinking core model for the diffusion control mechanism where the activation energy (E_a) of $32.92 \text{ kJ}\cdot\text{mol}^{-1}$ was obtained for the process and supported by morphological changes at a higher dissolution of 91.33%.

Keywords: chalcopyrite; hydrometallurgy; leaching; hydrochloric acid; dissolution; ore treatment

1. Introduction

There are between 150 and 180 copper minerals on the earth of which chalcopyrite (CuFeS_2) is the most common copper bearing mineral [1]. It is the most stable of the minerals because of its structural configuration (face-centered tetragonal lattice), and thus, the most refractory to hydrometallurgical processing [2]. Historically, copper sulphides including chalcopyrite have been smelted; however, since the early 1990s, a number of prospective leaching processes have been successfully demonstrated at the pilot scale [3].

Deposits of chalcopyrite ore, which may include bornite (Cu_5FeS_4), chalcocite (Cu_2S), and pyrite (FeS_2) have long been known in Nigeria, but they are only been mined and exploited in the past on a very small scale [4]. Substantial deposits and proven reserves are available in northern part of the country with those of Bauchi and Nassarawa States being of high grades [4]. In recent years, more and more attention has been focused on extraction

of oxidized copper ores due to depletion of higher grade copper sulphides [5-6].

At present, there are basically two main methods employed worldwide to process chalcopyrite for metal production. The most important one is the conventional pyrometallurgy operation comprising numerous types of shaft and flash technologies, which consist of crushing, grinding, flotation, smelting, refining, and electro-refining methods. These are applicable to sulphide flotation concentrates rather than ores and are economically feasible for copper rich feed and for large-scale operations. However, the hydrometallurgical method is applied to the rest of world primary copper production. This consists of crushing, leaching (non-oxidation leaching, atmospheric leaching, and pressure leaching), solvent extraction, and electro-winning [7]. Thus, the need to utilize small and complex deposits and the environmental restrictions imposed on sulphide smelters stimulated the development of alternative methods, especially hydrometallurgical routes that

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avoid production of obnoxious SO_2 as a pollutant [8-9]. Chloride systems in hydrometallurgy have been used for the treatment and recovery of precious metals including copper for a number of years, due to the fact that leaching can be carried out at ambient temperature compared to a sulphate process that requires elevated temperatures that are not suitable for ore heap leaching. Also, the stability of copper I oxidation state, which allows electro-deposition of copper via electron transfer that often leads to reduced energy consumption as well as formation of stable chloro-complexes, is the major considerable reasons for sulphide dissolution in chloride media, which is a subject of considerable interest [10-13].

Due to various interests that include environmental aspects and the possibility of increased exploitation of mixed and lower grade ores and relatively small isolated deposits, there has been a worldwide upsurge of interest in hydrometallurgical processing of chalcopyrite ore for production of high grade copper [14]. Thus, any proposal for an economically viable hydrometallurgical process for chalcopyrite ore treatment should take into account basic studies that elucidate the chemical and electrochemical aspect governing leaching as highlighted above [10-13, 15]. Therefore, the objective of the present investigation was to elucidate the leaching kinetics of chalcopyrite ore in hydrochloric acid (HCl) solution. There is practically few data in this area of study with respect to Nigeria chalcopyrite ore [16-17]. This study is therefore expected to provide useful information on kinetic parameters for leaching of the ore from Nigerian origin for its subsequent extraction.

2. Experimental

2.1. Ore samples/instrumentation

The chalcopyrite sample was obtained from an ore deposit at Akiri Village, Awe Local Government Area of Nasarawa State, Nigeria. It was crushed, ground, and sieved using the American Society for Testing and Materials (ASTM) standard sieve into three size fractions: $-90 + 75$, $-112 + 90$, and $-300 + 112 \mu\text{m}$. All experiments were performed with $-90 + 75 \mu\text{m}$ size, unless otherwise stated. The elemental analysis of the ore sample was carried out using an X-ray fluorescence (XRF) technique (Philip's model 120454/3). The mineralogical purity of the ore was examined using a PHILIP PW 1800 X-ray diffractometer (XRD) with $\text{Cu K}\alpha_1$ (0.154 nm) radiation, generated at 40 kV and 55 mA. Deionized water and British Drug Houses (BDH) reagent grade hydrochloric acid were used to prepare all solutions. The petrological feature and mineralogy of the ore was also investigated from thin and polished ore sections studied under petrological and reflecting (ore) microscopes.

2.2. Equipment and methods

Leaching experiments were carried out in a 250 mL

spherical glass reactor equipped with a mechanical stirrer. Typically, for each run, 100 mL HCl solution of predetermined molarity was charged to the reactor and heated to the required temperature, following the procedures developed by Liu *et al.* [5], Aydogan *et al.* [8], Baba and Adekola [9], and Ucar [10]. For every leaching experiment, the solution mixture was freshly prepared by dissolving $10 \text{ g}\cdot\text{L}^{-1}$ of the ore in the leachant at 55°C . According to previous experimental results, it was found that the effect of stirring speed could be neglected when it was larger than 360 r/min. All leaching experiments were carried out at the stirring speed of 400 r/min [14]. The concentration of HCl, which gave the maximum dissolution ($4.00 \text{ mol}\cdot\text{L}^{-1}$), was subsequently used for optimization of other leaching parameters including temperature and particle size. The activation energy (E_a) and constants were determined from the Arrhenius plots. The fraction of dissolved chalcopyrite was calculated from the initial differences in mass of the amount dissolved or undissolved at various intervals up to 120 min, after oven drying at 60°C for 12 h [9]. The postleaching residual products obtained at 80°C in $4.00 \text{ mol}\cdot\text{L}^{-1}$ HCl solution was then analyzed by XRD and scanning electron microscopy (SEM) for morphological studies.

3. Results and discussion

3.1. Ore characterization studies

3.1.1. Elemental analysis by XRF

The elemental chemical analysis of the $-90 + 75 \mu\text{m}$ ore fraction by XRF contain $24.16\text{wt}\% \pm 0.10\text{wt}\%$ Cu, $36.53\text{wt}\% \pm 0.94\text{wt}\%$ Fe and $2.02\text{wt}\% \pm 0.01\text{wt}\%$ Mn as the major elements. Other elements found in the ore include Sn ($0.069\text{wt}\% \pm 0.01\text{wt}\%$), Mg ($0.17\text{wt}\% \pm 0.3\text{wt}\%$), Pb ($0.12\text{wt}\% \pm 0.015\text{wt}\%$), and Ca ($1.081\text{wt}\% \pm 0.02\text{wt}\%$). Gangues, which include silica (SiO_2) and other impurities, constituted about 35.0wt%.

3.1.2. Phase analysis

Powdered X-ray diffraction of the Cu ores (Fig. 1) gave phase composition dominated by chalcopyrite (CuFeS_2) and pyrite (FeS_2) which may be a mixture of pyrothite (Fe_7S_8). The XRD data also showed the presence of minor abundance ($\leq 2\text{wt}\%$) of other associated compounds, including galena (PbS), cassiterite (SnO_2), hausmannite (Mn_3O_4), fukuchilite ($\text{Cu}_{0.47}\text{Fe}_{0.58}\text{S}_2$), and quartz (SiO_2).

3.1.3. Petrography and mineralogy

Microscopic studies of the ore (Fig. 2) also showed highly reflecting bright yellow to redish brown chalcopyrite (CuFeS_2) as the dominant phase. Other associated minerals include pleochroic pale yellow α -quartz (SiO_2), opaque pyrite (FeS_2), light blue fukuchilite, and dark gray to opaque lead sulphide galena (PbS).

3.1.4. SEM morphology

The SEM study of the raw chalcopyrite, as depicted in Fig. 3, showed a rectangular structure with perfect sets

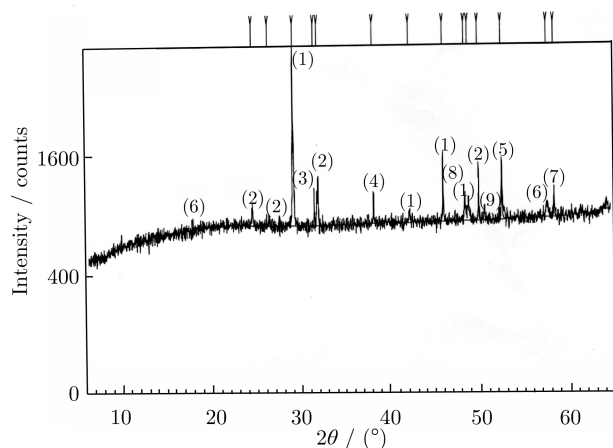


Fig. 1. XRD pattern of raw chalcopyrite ore, showing the identified compounds with their respective Joint Committee on Powder Diffraction Standard file numbers used in peaks attribution: (1) CuFeS_2 (chalcopyrite) {24-0211}; (2) $\text{Cu}_{0.47}\text{Fe}_{0.58}\text{S}_2$ (fukuchilite) {17-0137}; (3) Fe_2O_3 (hematite) {024-0072}; (4) FeS_2 (pyrite) $\rightarrow$ Fe_7S_8 (pyrrhotite) {22-1220}; (5) SnO_2 (cassiterite) {21-1250}; (6) SiO_2 (α -quartz) {05-0490}; (7) PbS (galena) {05-0792}; (8) $\text{CaCO}_3 \cdot \text{MgCO}_3$ (dolomite) {05-0490}; (9) Mn_3O_4 (hausmannite) {24-0734}.

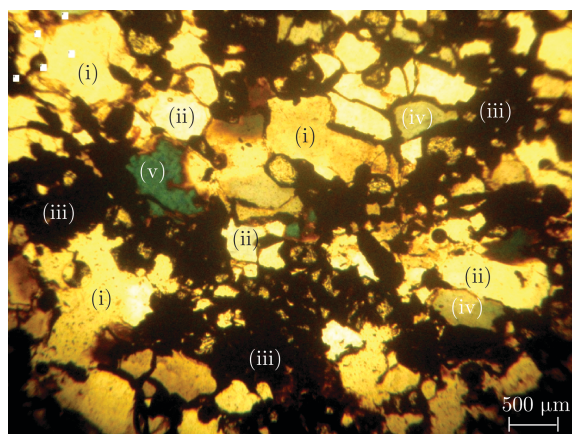


Fig. 2. Thin polished section photomicrograph of Cu ore: (i) chalcopyrite (CuFeS_2), (ii) α -quartz (SiO_2), (iii) pyrite (FeS_2), (iv) galena (PbS), and (v) fukuchilite ($\text{Cu}_{0.47}\text{Fe}_{0.58}\text{S}_2$).

of cleavage plane particles on the surface and edge of the particles could easily be found in the image of the particles prior to leaching.

3.2. Leaching operation studies

3.2.1. Effect of HCl concentration

The effect of HCl concentration ($0.10\text{--}8.42\text{ mol}\cdot\text{L}^{-1}$) on chalcopyrite ore dissolution was investigated at 55°C using $-75 + 90\text{ }\mu\text{m}$ particle size fraction. The fraction of the ore dissolved is plotted against leaching time for the different HCl concentrations, as depicted in Fig. 4.

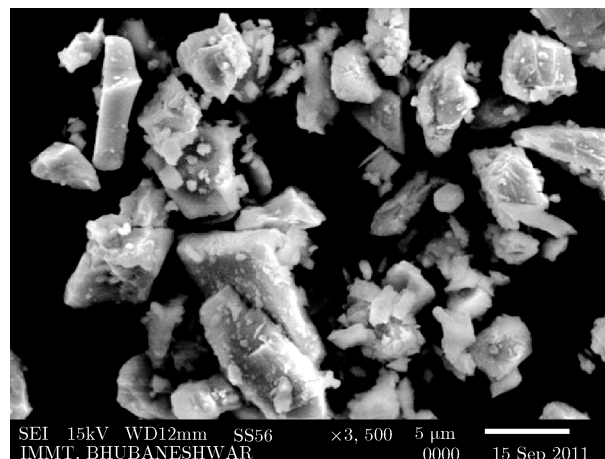


Fig. 3. SEM image of the chalcopyrite raw ore.

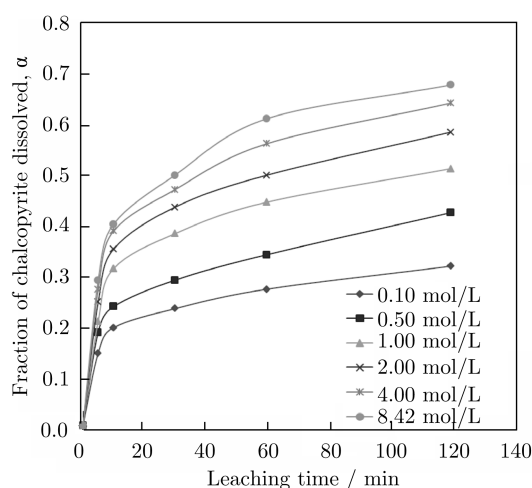


Fig. 4. Effect of HCl concentration on chalcopyrite ore dissolution at various leaching time.

In Fig. 4, it is evident that increasing the HCl concentration led to increased ore dissolution because of either greater contact with the solid or improved diffusional characteristics of the solution to the inner core as the concentration increases, thus increasing the leaching rate. This may result from the formation of intermediate mixed ligands, e.g., $\text{Cu}(\text{OH})\text{Cl}$ and $\text{Cu}(\text{Cl}(\text{OH}_3))$ complexes on mineral surfaces, which are conducive to ligand-promoted dissolution [18–20]. Increased leaching rate with increasing HCl concentration (Fig. 4) is effective up until $4.00\text{ mol}\cdot\text{L}^{-1}$ HCl solution. The reason for this observation could be attributed to possible precipitation phenomena [9].

3.2.2. Effect of temperature

The effect of temperature on the rate of chalcopyrite ore dissolution was studied over the temperature ranges of $27\text{--}80^\circ\text{C}$, as shown in Fig. 5. It can be seen from Fig. 5 that increasing temperature improves the chalcopyrite ore dissolution rate. This observation can be attributed to the fact that particles only react when they collide effec-

tively with increasing dissolution temperature. This is in line with the fact that when a substance is heated, particles gain more kinetic energy and collides more frequently, thus, speeding the rate of reaction. Results of other similar studies affirmed that increasing the temperature of the system during dissolution increases the amount of the ore or material dissolved at various leaching time [5, 9]. Thus, high temperature enhances the breaking down of the bond in chalcopyrite crystal lattices during dissolution [15]. However, tests at higher temperatures ($>80^{\circ}\text{C}$) would be less suitable due to increase the loss of HCl vapor [21].

3.2.3. Effect of particle size

The effect of particle size on chalcopyrite ore dissolution was studied in $4.00\text{ mol}\cdot\text{L}^{-1}$ HCl solution at 80°C , using the three particle size fractions: $-90 + 75$, $-112 + 90$, and $-300 + 112\text{ }\mu\text{m}$. As shown in Fig. 6, the rate of chalcopyrite dissolution increases with decreasing particle diameter. This could be attributed to the increase in particle number per amount of solid when the particle size

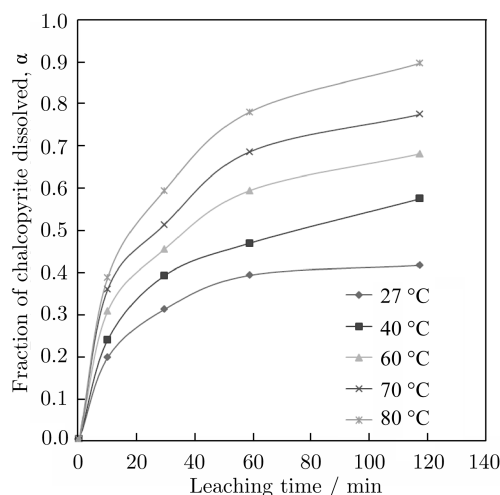


Fig. 5. Effect of temperature on chalcopyrite ore dissolution in $4.00\text{ mol}\cdot\text{L}^{-1}$ HCl solution.

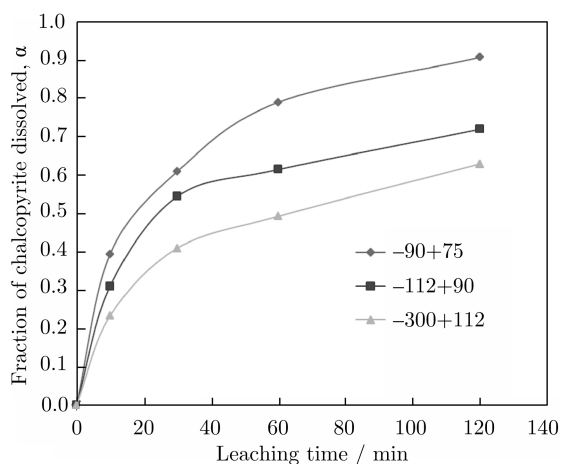


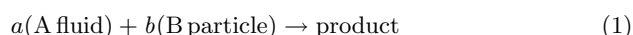
Fig. 6. Effect of particle size on hydrochloric acid chalcopyrite dissolution.

decreases and correspondingly the surface area increase, which causes better exposure of chalcopyrite ores to the solution [5]. Therefore, the lower dissolution rates at larger particle sizes could also be attributed to the decrease in surface area of the reacting ore. At larger particle sizes, less metal content is exposed to the reacting solution, thereby reducing contact between the leaching reagent (HCl solution) and the metal content of the ore [17].

3.3. Discussion

3.3.1. Dissolution kinetics model

Understanding the mechanism of chalcopyrite dissolution in HCl solution is one of the aims of the present study. A heterogeneous reaction (solid-liquid reaction) can be considered by the following equation [21-22]:



The most important model suggested for the derivation of the rate expression of noncatalytic fluid-solid reaction is the shrinking core model and the progressive conversion model. According to the shrinking core model, the reaction is thought to take place on the outer surface of the solid, and this surface shrinks toward the center of the solid as the reaction proceeds, leaving an inert solid layer, called "ash layer", around the core of the reacted ore [5, 23]. Therefore, for this study, the following mathematical models with the assumption of a shrinking core/constant particle model have been considered:

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3} = \frac{K_c M_B C_A t}{\rho_B a r_0} = K_d t \quad (2)$$

$$1 - (1 - \alpha)^{1/3} = \frac{K_c M_B C_A t}{\rho_B \text{ox} B a r_0} = K_r t \quad (3)$$

$$1 - (1 - \alpha)^{1/3} + \frac{y}{6} \left[(1 - \alpha)^{1/3} + 1 - 2(1 - \alpha) \right]^{2/3} = K_m t \quad (4)$$

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 stoichiometric coefficient of reaction 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 , K_r , and K_m are rate constants, and y in Eq. (4) is assumed to be 1 [9-10].

If the reaction rate of the particle is controlled by diffusion of the fluid through the product layer, the model can be expressed by Eq. (2). However, if the reaction is controlled by surface reaction, then Eq. (3) can be employed or by mixed controlled process (chemically and diffusion controlled reactions), and the model Eq (4) is applicable.

The three kinetic models (Eqs. (2)-(4)) were tested for understanding the dissolution mechanism of the chalcopyrite ore by HCl solution. On applying Eqs. (2)-(4) to dissolution data in Figs. 4-6, it was found that, of all the

three tested models, the model Eq. (2) fitted the dissolution data with the average correlation coefficient (R^2) $\approx$ 0.954. Consequently, all the kinetic data were expressed using Eq. (2). The results indicate that the linear relationship between $1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3}$ and leaching time (t) is significant and thus suggests that chalcopyrite dissolution is controlled by diffusion reaction. Consequently, experimental data in Fig. 4 were also found to fit the model Eq. (2) as depicted in Fig. 7.

The experimental rate constant, K_d , was determined from the slopes in Fig. 7, and the plot of $\ln K_d$ versus $\ln[\text{HCl}]$ was made, as shown in Fig. 8.

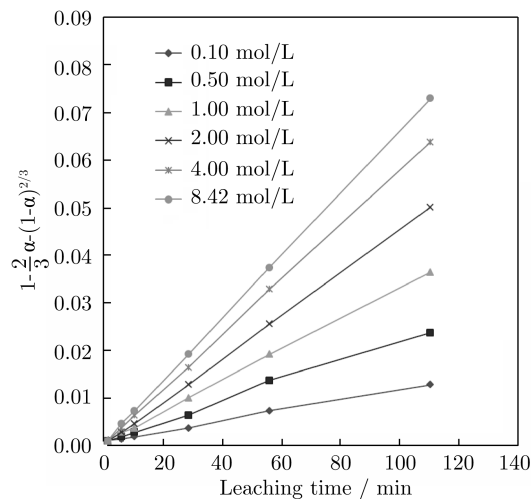


Fig. 7. Plot of $1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3}$ versus leaching time at different HCl concentrations.

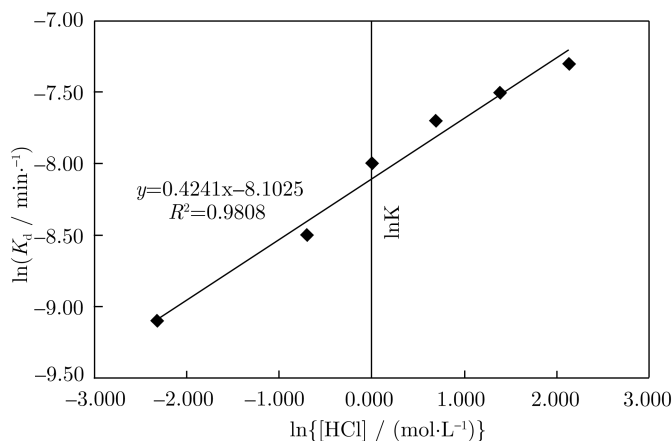


Fig. 8. Plot of $\ln K_d$ versus $\ln[\text{HCl}]$.

The slope of the resulting plot in Fig. 8 gave 0.42, which indicates that the reaction order is 0.42 with respect to $[\text{H}^+]$ ion concentration. This shows that the studied dissolution reaction is the 0.42-order mechanism. In addition, the linearization of data in Fig. 5 was done using Eq. (2). This is represented in Fig. 9.

The apparent rate constant, K_d , was calculated from

the slopes of straight lines obtained. These values and their correlation coefficients (R^2) were given in Table 1.

The apparent rate constant (K_d) values were used in constructing the Arrhenius plot (Fig. 10). From the Arrhenius equation (Eq. (5)), the determination of activation energy for the dissolution process was evaluated.

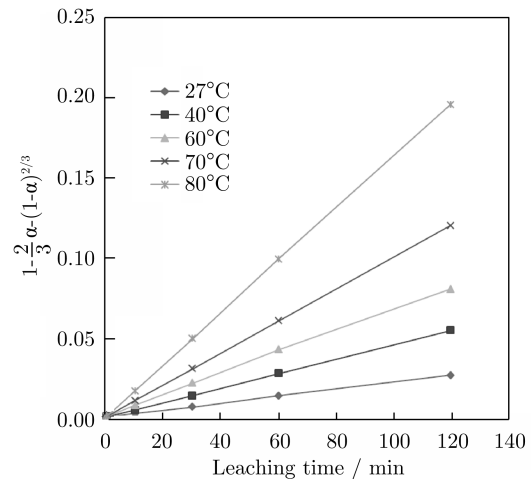


Fig. 9. Plot of $1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3}$ versus leaching time at different temperatures.

Table 1. Rate constant (K_d) with their correlation coefficient values for chalcopyrite ore dissolution at different temperatures in 4.00 mol·L⁻¹ HCl solution

Temperature / °C	Apparent rate constant, K_d / min ⁻¹	Correlation coefficient (R^2)
28	2.1×10^{-4}	0.9875
40	4.5×10^{-4}	0.9883
60	7.0×10^{-4}	0.9974
70	4.4×10^{-3}	0.9988
80	1.6×10^{-3}	0.9934

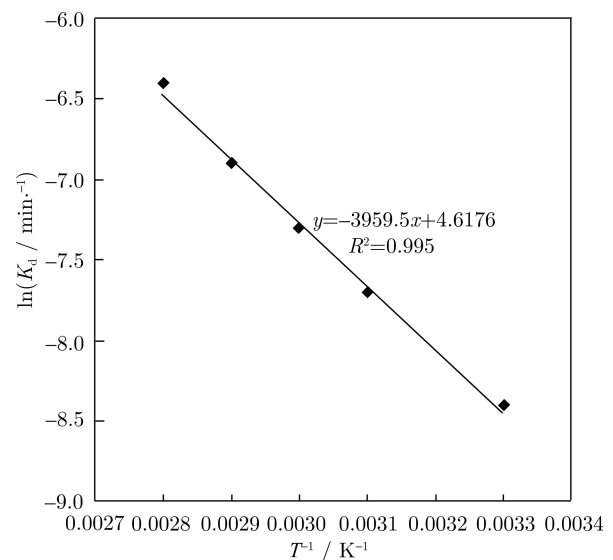


Fig. 10. Plot of $\ln K_d$ versus $1/T$.

$$K_d = A \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

where A is the frequency factor, R is the universal gas constant, and T is the absolute temperature.

From the Arrhenius relation in Fig. 10, the value of activation energy was calculated as $31.6 \text{ kJ}\cdot\text{mol}^{-1}$. This value clearly confirms that the dissolution process is of diffusion control through the ash layer around the unreacted shrinking core. Some of the reported activation energies, E_a , for chalcopyrite ore dissolution in chloride media are summarized in Table 2.

In Table 2, it is evident that different activation energies on chalcopyrite leaching were reported at different locations. The wide range of the reported activation energies are likely from differences in experimental design, leach solutions, preparation of starting minerals composition, etc. [19]. Therefore, the calculated value of activation energy obtained in this study affirmed the thermodynamic feasibility as compared to those of Turkey, Australia, China, etc.

3.3.2. Composition of the residual products

The mineralogical examination of the product formed after optimal leaching was investigated using an XRD technique. The result of the dominant peak observed is presented in Table 3.

The data and results of X-ray diffraction phases pre-

sented in Table 3 showed that the concentrate undergoes a number of transformations caused by oxidation of sulphides and interaction of solid substances among themselves. The basic mineralogical compositions of result samples were compared to the original raw ore. The results shown in Table 3 affirmed that the substantial quantity of the chalcopyrite ore was readily dissolved at optimal conditions of $4.00 \text{ mol}\cdot\text{L}^{-1}$ HCl solution at 80°C within 2 h. However, it can be seen in Table 3 that quartz with a mixture of cristobalite, elemental sulphur, and few traces of tin oxide and fukuchilite ($\leq 1\%$) were essentially unleached. Also, the SEM image of leached residues at optimal conditions of the diameter $-90 + 75 \mu\text{m}$ and $4.00 \text{ mol}\cdot\text{L}^{-1}$ HCl solution at 80°C for 2 h are presented in Fig. 11.

Chalcopyrite ore exist as a single particle on the surface and could easily be found in the image of the particle after 60 min leaching (Fig. 11(a)), while being scarcely found in the image of the leached residue after 120 min leaching (Fig. 11(b)). Copper minerals that still have not been leached exist in the inner of the ore particle, and these minerals as well as gangue are found to contain high content of silica. Therefore, it is evident that smooth and nearly rectangular grains of the ore (Fig. 3) are completely transformed to porous and wave-like clusters of particles after optimal leaching, leading to about 91.33% dissolution (Fig. 11(b)).

Table 2. Some reported activation energies for chalcopyrite ore dissolution in chloride media

Reference	Ore origin	Activation energy, E_a / ($\text{kJ}\cdot\text{mol}^{-1}$)	Reaction order	Proposed mechanism
[24]	Kastamonu Kure, Turkey	37.9	ND	Diffusion control
[25]	Murdoch, Australia	75.0	ND	Chemical control
[26]	Catalonian Coastal range, Spain	35.0	0.16	Diffusion control
[27]	Nishikhal and Sandur, India	70.6	4.6	Chemical control
[28]	China	64.0	ND	Chemical control
This study	Akiri, Nigeria	31.6	0.42	Diffusion control

Note: ND = Not detected.

Table 3. XRD analysis of leach residue (HCl) after optimal leaching

2θ / ($^\circ$)	d / nm	Compound	JCPDS file number
29.4500	0.30304	Sulphur (S°)	09-2146
48.6770	0.18690	α -quartz (SiO_2)	05-0490
49.1079	0.18536	Cristobalite (SiO_2)	27-0605
53.4032	0.17141	Sulphur (S°)	09-2146
57.8660	0.15922	*Tin oxide (SnO_2)	13-0111
58.6800	0.15720	*Fukuchilite ($\text{Cu}_{0.47}\text{Fe}_{0.58}\text{S}_2$)	17-0137

Note: * For fukuchilite ($\text{Cu}_{0.47}\text{Fe}_{0.58}\text{S}_2$) and tin oxide (SnO_2), intensities reduce sharply ($\leq 1\%$).

4. Conclusions

(1) Elemental analysis by an X-ray fluorescence technique showed that the chalcopyrite mineral used in this study exists mainly as CuFeS_2 with metals, such as Cu, Fe, and Mn as the major elements. Other metals de-

tected at traces to low levels include Sn, Mg, Pb, and Ca. The XRD analysis confirmed the originality of the chalcopyrite ore, and it also revealed the presence of other associated minerals including FeS_2 (pyrite), PbS (galena), Mn_3O_4 (hausmannite), and $\text{Cu}_{0.47}\text{Fe}_{0.58}\text{S}_2$ (fukuchilite).

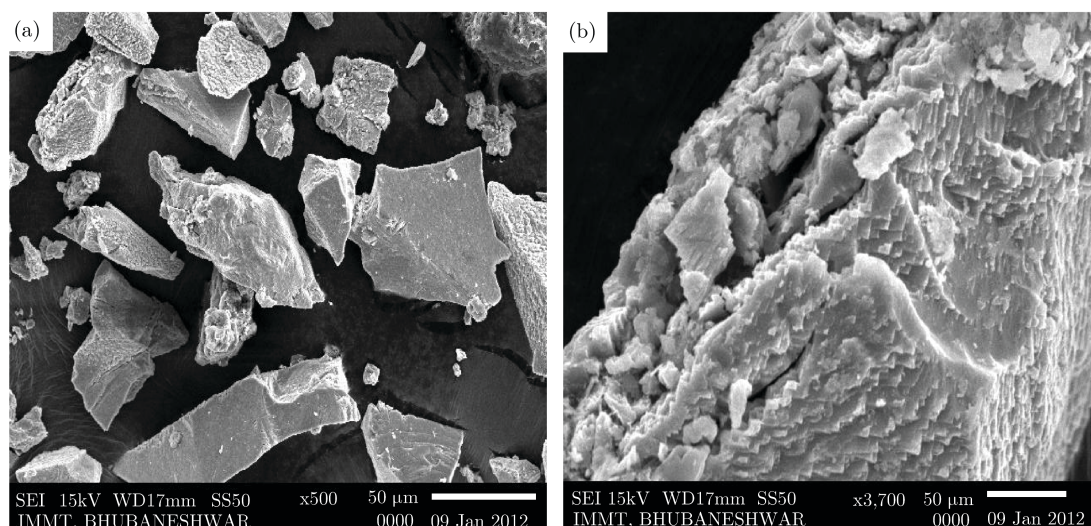


Fig. 11. SEM images of leached residue with diameter of $-90 + 75 \mu\text{m}$ at 80°C : (a) after 60 min leaching (about 79.83% dissolution); (b) after 120 min leaching (about 91.33% dissolution).

(2) HCl concentration, temperature, and particle size have significant influence on chalcopyrite ore dissolution. The leaching rate increases with increasing HCl concentration and temperature and with decreasing particle diameter. Using 4.00 mol.L^{-1} HCl solution at a 80°C with the particle diameter of $-90 + 75 \mu\text{m}$, about 91.33% of the 10 g.L^{-1} chalcopyrite ore was dissolved within 120 min.

(3) The results of leaching investigations indicated that the shrinking core model for spherical particles is applicable. The reaction mechanism of dissolution is controlled by diffusion through the ash layer around the shrinking unreacted core, which is supported by the calculated activation energy and reaction order of 31.6 kJ.mol^{-1} and 0.42, respectively.

(4) The post-leaching residues as confirmed by XRD are made up of α -quartz ($\alpha\text{-SiO}_2$), elemental sulphur (S^0), and traces of fukuchilite ($\text{Cu}_{0.47}\text{Fe}_{0.58}\text{S}_2$) and tin oxide (SnO_2).

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