

Characterization and kinetic study on ammonia leaching of complex copper ore

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Abstract: Ammonia leaching kinetics of a complex Cu-ore assaying 8.8% Cu and 36.1% Fe was examined. Mineralogical characterization indicated that the major phase of the ore was siderite with chalcopyrite as the major sulfide mineral. The effects of parameters such as agitation, temperature, NH₃ concentration, particle size and oxygen partial pressure (p_{O_2}) were investigated. Under the standard leaching conditions of 125–212 μm particle size, 120 °C, 1.29 mol/L NH₃ and 202 kPa of p_{O_2} , about 83% Cu could be selectively extracted in 2.5 h. However, when using higher NH₃ concentration and lower particle size, more than 95% extraction was achieved. The leaching process was found to be surface reaction controlling. The estimated activation energy was (37.6±1.9) kJ/mol and empirical orders of reaction with respect to p_{O_2} and [NH₃] were about 0.2 and 1, respectively.

Key words: ammonia leaching; chalcopyrite; siderite; leaching kinetics

1 Introduction

Chalcopyrite (CuFeS₂) has been the chief copper sulfide mineral studied for copper extraction from sulfide ores. This is mainly due to two reasons: 1) it is the most abundant source of sulfide copper in the earth's crust; and 2) it is one of the most refractory sulfide copper minerals [1]. At present, about 70% of the world's copper production is carried out from chalcopyrite ore through flotation followed by the pyrometallurgical route [2,3]. However, due to environmental regulations and the requirement of high-grade ores for the pyrometallurgical processing route, the hydrometallurgical methods are becoming more popular.

In recent years, much attention has been focused on the leaching of copper sulfide ores/concentrates in sulfate medium [1,4–6]. In acidic sulfate media, sulfide sulfur transforms to elemental sulfur under oxidizing conditions as can be seen from E_h -pH stability diagram [7] unless extreme high temperature and oxygen pressure are imposed [8]. Formation of elemental sulfur may impede the process kinetics by forming passivating layer on the unreacted particles. Other drawback is the contamination of leaching liquor with iron due to simultaneous dissolution and stability of copper and iron ions.

On the contrary, chalcopyrite leaching in aqueous

ammonia leads to the formation of SO₄²⁻ instead of S⁰ due to high pH of ammoniacal media. In general, the major advantage of ammonia leaching process lies in its selectivity towards copper since ammonia forms soluble ammine complex with Cu ions and iron is completely rejected as iron oxides. Aqueous ammonia as a leaching agent is fairly non-corrosive and leaching reactions occur in relatively mild conditions [9]. The best known application of direct reaction of ammonia and sulfide minerals is the process pioneered by the Sheritt–Gordon Co. for treating nickel sulfide concentrates [10]. The applications of ammonia leaching process for different sulfide minerals were widely investigated [11–14].

REILLY and SCOTT [9] investigated the leaching kinetics of chalcopyrite in NH₃ medium and proposed an electrochemical surface reaction model with cathodic reduction of oxygen on the solid surface as the rate determining step. The activation energy for the reaction was estimated to be 74.1 kJ/mol. BECKSTEAD and MILLER [15] proposed that the catalytic electrochemical surface reaction by cupric ions was the rate-controlling factor during oxidizing ammonia leaching of chalcopyrite concentrate. The estimated activation energy of 41.84 kJ/mol further supported the surface chemical reaction control mechanism.

Using statistical experimental design, BELL et al [16] demonstrated that temperature and ammonium salt

concentration as well as the interaction between these two factors greatly influences the in situ leaching of chalcopyrite in ammoniacal solutions. Particularly, the dissociation of NH_4OH into H_2O and NH_3 was found to be a crucial step since ammonia is known to be an active contributor to the Cu leaching reaction.

Besides copper sulphide, $\text{NH}_3/\text{NH}_4^+$ leaching was used for other copper minerals such malachite, low-grade mixed Cu ore, tenorite [17–19].

The reported studies on chalcopyrite leaching in ammonia solutions were based on either high-grade chalcopyrite (26.5% Cu) concentrate [9] or nearly pure (97% CuFeS_2) concentrate [15]. Moreover, previous studies on copper recovery by ammonia leaching were carried out with sulphide concentrates or oxide ores but this route was never tested for a complex Cu ore which has neither sulfide nor oxide as the major matrix. Hence in the present study, such a complex Cu ore was selected and after mineralogical characterization, ammonia leaching kinetics was studied. Main influencing factors such as temperature, ammonia concentration, particle size, oxygen partial pressure (p_{O_2}) were examined and the rate controlling step was determined. Ore sample and typical leach residues were characterized for better understanding of the process.

2 Experimental

The ore sample from Kokona District, Nasarawa State, Nigeria was obtained from the Department of Geology and Mineral Sciences, University of Ilorin, Nigeria. The bulk ore samples were ground and sieved into different narrow size fractions: 75–90, 90–125, 125–212 and 212–425 μm . Experiments were mostly performed with the 125–212 μm fraction, unless otherwise stated. The elemental analysis of the ore (125–212 μm fraction) is given in Table 1. Copper and iron contents of the various size fractions are given in Table 2 which indicates within the size fractions studied Cu and Fe contents do not vary widely. Analytic grade

Table 1 Chemical composition of ore (125–212 μm size fraction)

w(Cu)/ %	w(Fe)/ %	w(Mg)/ %	w(Ca)/ %	w(Mn)/ %	w(S)/ %	Acid Insol/%	LOI/ %
8.8	36.1	2.8	0.3	0.15	7.2	3.8	25

Table 2 Cu and Fe contents of ore at various size fractions

Size fraction	w(Cu)/%	w(Fe)/%
212–425 μm	7.35	34.60
125–212 μm	8.77	36.07
90–125 μm	8.23	34.00
75–90 μm	8.42	33.42

NH_3 and distilled water were used in the preparation of the leaching media.

The mineralogical phase identification of the ore sample was carried out using Philips X-ray diffractometer (PW 3050/60 X'pert-Pro) with $\text{Mo K}_{\alpha 1}$ radiation generated at 30 mA and 40 kV. X-ray diffraction pattern of the ground ore is shown in Fig. 1. XRD pattern confirms the presence of siderite (FeCO_3) as a dominant iron bearing phase and chalcopyrite as the main copper-bearing phase.

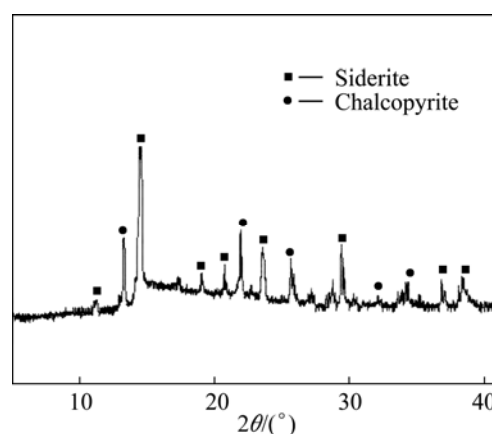


Fig. 1 X-ray diffraction pattern of Cu-ore sample

Leaching experiments were carried out in PARR[®] 2 L capacity stainless steel autoclave. For each experiment, 500 mL of aqueous ammonia solution of predetermined molarity and 10 g ore were mixed in the reactor vessel making 20 g/L slurry density (S/L ratio). Reactor contents were initially heated with mild agitation during heating stage and on attaining the set temperature, oxygen was introduced and full agitation was placed. The reaction time was counted from this point. Samples were collected at an interval of 0.5 h. When total pressure dropped, gas inlet valve was opened and oxygen was introduced to maintain the total pressure constant. Samples were filtered and analyzed for copper by EDTA titration using Fast Sulphon Black F indicator. Some of the selected leached residues were collected after filtration, thoroughly washed with dilute $\text{NH}_3-(\text{NH}_4)_2\text{SO}_4$ solution and oven dried at about 80 °C prior to characterization.

Fraction of copper extraction (α) was calculated using the following expression:

$$\alpha = \frac{\rho(\text{Cu})}{w(\text{Cu})\rho_L}$$

where $\rho(\text{Cu})$ is Cu concentration in leach liquor (g/L), $w(\text{Cu})$ is mass fraction of Cu in the ore and ρ_L is solid loading or solid-liquid ratio (g/L)

3 Results and discussion

3.1 Material characterization

The optical microscopy of a polished bulk sample was carried out in Leitz optical microscope under reflected light. In the photomicrograph (Fig. 2), chalcopyrite (C) and siderite (S) phases are observed as separate grains.

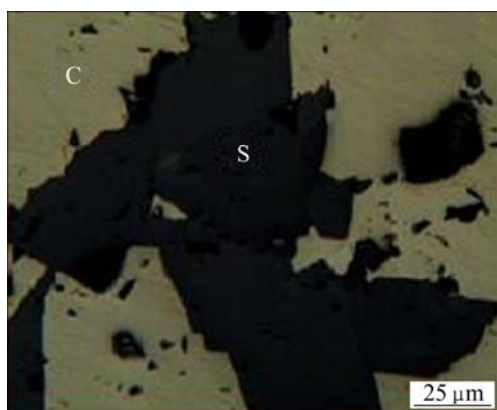
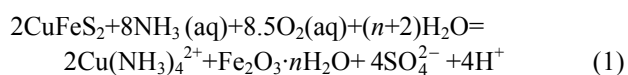


Fig. 2 Photomicrograph of polished bulk sample (S—Siderite; C—Chalcopyrite)

Quantitative estimation of elemental concentration of the chalcopyrite along with other copper sulfide phases in the polished section was carried out using ZEISS SUPRA–55 VP field emission scanning electron microscope (FESEM). The sample was subjected to elemental mapping by FESEM (Fig. 3). The point analysis of some of the grains was also carried out (Table 3). The FESEM images of the polished section of a bulk sample in combination with point analysis indicate that chalcopyrite contains 29.9%–32.2% Cu; 36.4%–43.8% S and 26.3%–32.9% Fe. Rarely, chalcocite was also recorded in the sample. Microscopic as well as FESEM studies further indicate that the samples are fresh.

3.2 Leaching reactions

Chalcopyrite oxidation reaction can be represented by the following equation [20]:



H^+ generated by the above reaction is neutralized by ammonia as follows:

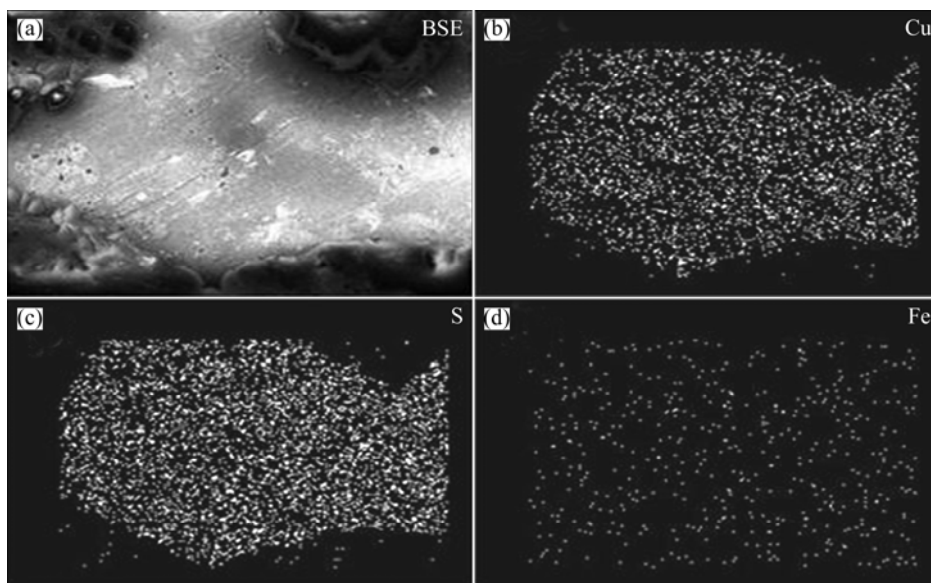


Fig. 3 Elemental mapping of chalcopyrite for its Cu, S and Fe components

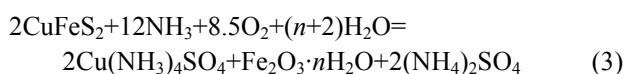
Table 3 Quantitative chemical analysis of copper sulfide phases under FESEM

Phase	Grain No.	w(Cu)/%	w(S)/%	w(Fe)/%	Total/%
Chalcopyrite	1	31.7	39.6	28.7	100
	2	29.9	43.8	26.3	100
	3	32.2	41.1	26.7	100
	4	30.0	41.8	28.2	100
	5	30.7	41.6	27.7	100
	6	31.5	40.7	27.8	100
	7	30.7	36.4	32.9	100
Chalcocite	1	23.5	76.5	ND*	100

* Not detected (ND)



Overall reaction for the leaching can be written as follows:



Generation of NH_4^+ ion as per reaction (2) decreases the solution pH which is initially very high (above 11) by buffering action as given in Eq. (4) and helps to maintain pH in the stable region of copper ammine complex.



The siderite phase (FeCO_3) does not take part in the leaching reaction and remains mostly unaltered.

The main parameters in the present investigation are degree of agitation, concentration of ammonia, partial pressure of oxygen, temperature and particle sizes. Standard leaching conditions are (unless otherwise stated): 120 °C, 125–212 μm , p_{O_2} =203 kPa, 1.29 mol/L NH_3 and solid–liquid ratio 20 g/L. The results observed are indicated and discussed below.

3.3 Influence of agitation

The influence of agitation on the Cu extraction from the ore was studied in the range of 150–650 r/min at 120 °C. It was observed that the stirring speed had a significant effect on the copper dissolution up to about 450 r/min. Above 550 r/min, however, agitation had no further effect on the dissolution rate. Therefore, the stirring speed was maintained at 600 r/min for further studies and considered to be appropriate to eliminate the effect of this variable.

3.4 Influence of ammonia concentration

The effect of ammonia concentration on the extent of copper extraction was studied in the range of 0.65–1.94 mol/L. Figure 4 shows the dissolution data as a function of ammonia concentration at various time of leaching.

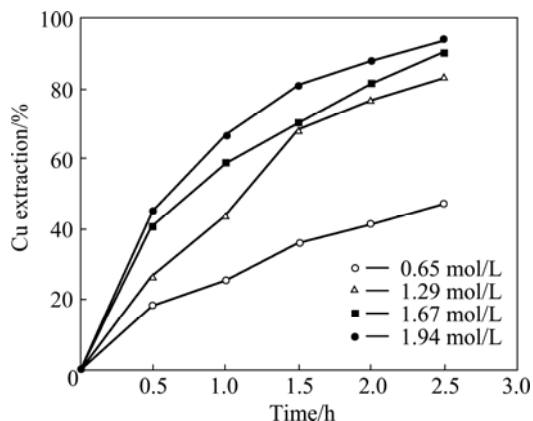


Fig. 4 Effect of NH_3 concentration on Cu extraction (120 °C, p_{O_2} =203 kPa, 125–212 μm particle size)

From Fig. 4, it can be seen that by increasing total ammonia concentration from 0.65 to 1.94 mol/L, copper extraction increases from 47% to 95% in 2.5 h leaching time. The reddish brown leach residue obtained at 1.94 mol/L ammonia (after 95% Cu extraction) indicates that iron component of chalcopyrite phase had been primarily oxidized to hematite. This observation is supported by XRD patterns. The initial pH values were 11.45 (0.65 mol/L), 11.65 (1.29 mol/L), 11.7 (1.67 mol/L) and 11.8 (1.94 mol/L). Although initial pH values were very high, with the progress of oxidation reaction pH decreased and the corresponding end pH values were 10.1, 10.45, 10.33 and 10.25 respectively and within the stable region of ammine complex. The decrease in pH was due to the generation of SO_4^{2-} and H^+ through oxidation reaction and simultaneous neutralization of H^+ ion as explained in Section 3.2. The decrease in pH is related to the initial ammonia concentration and amount of S to SO_4^{2-} oxidation reaction.

3.5 Influence of leaching temperature

The effect of leaching temperature on chalcopyrite dissolution was studied in the range of 90–130 °C under standard conditions of 1.29 mol/L NH_3 , 125–212 μm size and 203 kPa oxygen pressure. As shown in Fig. 5, increasing the leaching temperature significantly increases the leaching rate. Copper extraction after 2.5 h increased from 45% to 92% by increasing the leaching temperature from 90 °C to 130 °C.

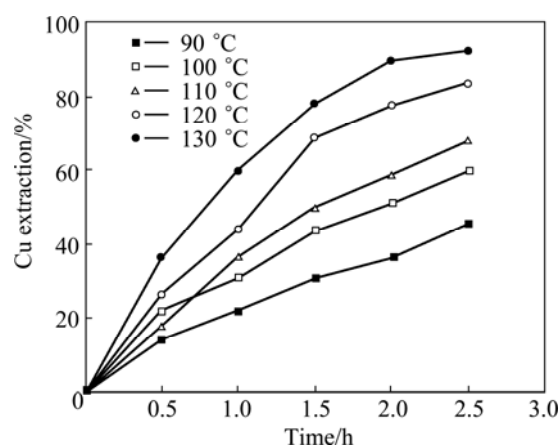


Fig. 5 Effect of temperature on Cu extraction (1.29 mol/L NH_3 , p_{O_2} =203 kPa, 125–212 μm particle size)

3.6 Influence of oxygen partial pressure

The effect of oxygen partial pressure on the rate of copper dissolution was examined by varying p_{O_2} in the range of 50.6–304 kPa in 1.29 mol/L ammonia solution at 120 °C. The results are presented in Fig. 6. From Fig. 6, it is observed that without introduction of oxygen in the system copper dissolution was only about 20% in 1.5 h which remained constant up to 2.5 h. This extraction

might be due to already present oxygen inside reactor from the start. By maintaining oxygen partial pressure to only 50.6 kPa, it was possible to achieve 72% Cu extraction and further increase in partial pressure to 203 kPa increased the extraction to 83%. However, increasing oxygen partial pressure beyond 203 kPa has no effect on improving the copper extraction. These results are in agreement with the observation made by BECKSTEAD and MILLER [15] who concluded that due to surface saturation by oxygen, leaching is not affected by oxygen partial pressure after a certain pressure. Dissolved oxygen adsorbs on the ore particle surface before reacting with it. In the present investigation, a low slurry density of 20 g/L may result in the surface saturation after about 203 kPa oxygen partial pressure, hence, the rate of reaction becomes insensitive to oxygen partial pressure above 203 kPa.

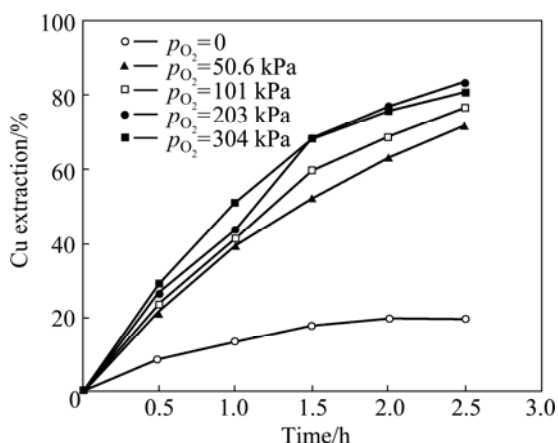


Fig. 6 Effect of O_2 partial pressure (p_{O_2}) on Cu extraction (1.29 mol/L NH_3 , 120 °C, 125–212 μm particles)

3.7 Influence of particle size

To determine the effect of particle size on the rate of copper dissolution, experiments were performed using four different size fractions in the range of 75–425 μm . The results of the investigation are illustrated in Fig. 7. As seen from Fig. 7, the rate of copper dissolution increases sharply as the size of the ore particle decreases. Nearly 100% copper dissolution was achieved with 75–90 μm and 90–125 μm particle sizes. Conversely, only 51% Cu extraction was obtained with 212–425 μm size. The reason for this could be due to the increase in the interfacial area of reaction as the solid particles become smaller [21,22].

3.8 Characterization of leach residues

Residues from several leaching experiments at various levels of copper extraction were examined using XRD and SEM. XRD pattern of a typical leach residue with >90% copper recovery is shown in Fig. 8. It is

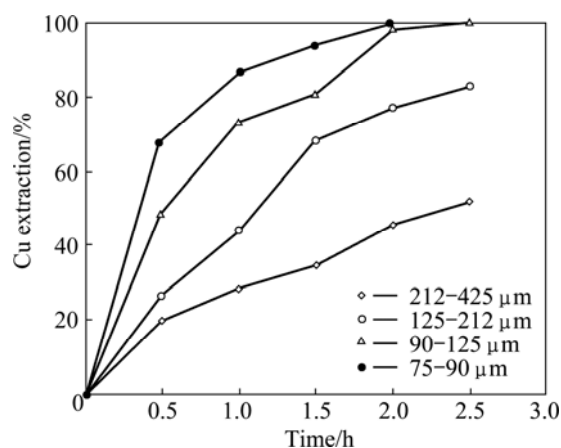


Fig. 7 Effect of particle size on Cu extraction (1.29 mol/L NH_3 , 120 °C, $p_{O_2}=203$ kPa)

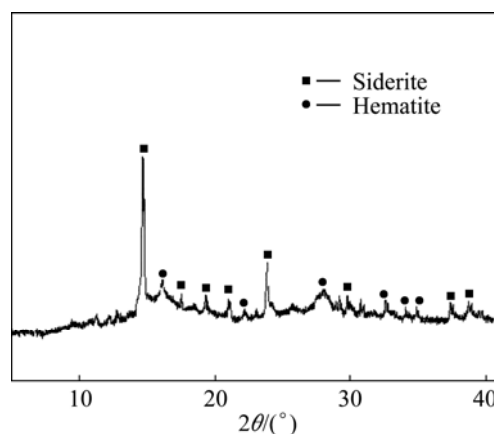


Fig. 8 XRD pattern of a typical leach residue (Cu extraction of 94%)

observed that all the chalcopyrite peaks disappeared and hematite phase appeared as a result of chalcopyrite oxidation in alkaline media. As expected, the siderite peaks remains nearly unaltered.

The morphologies of the ground ore and typical leached residues were examined by JEOL JSM–6510 scanning electron microscope. SEM image of the ore particles (Fig. 9(a)) clearly shows the morphological features of carbonate minerals. The grains show perfectly three sets of cleavage planes. In this case, it is siderite as revealed by XRD. Depending upon the level of copper extraction, hematite phase abundance in the leached residue is visible. Figure 9(b) shows small amount of hematite particles on the siderite surface for copper recovery of 22%. When the copper recovery increases to 63% (Fig. 9(c)), hematite particles are visible as separated grains besides on the surface of the siderite grains. In the case of residue with 95% copper extraction, siderite grains are nearly covered with hematite particles (Fig. 9(d)).

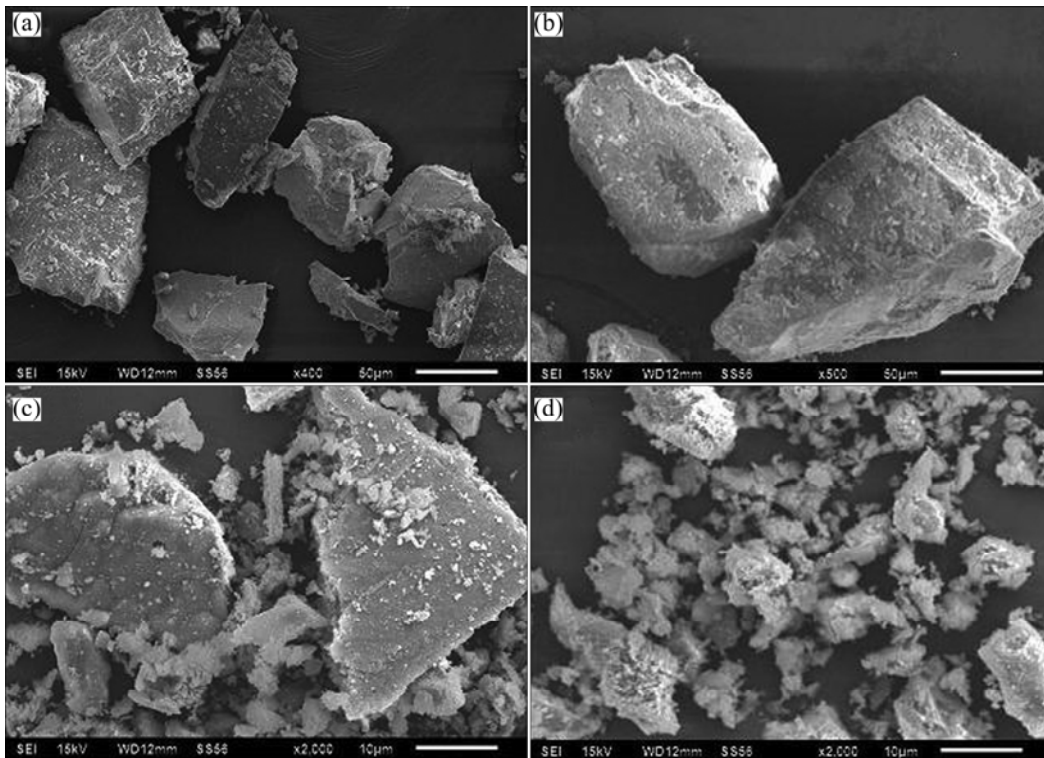


Fig. 9 SEM images of original ore (a), 22% Cu leached residue (b), 63% Cu leached residue (c) and 95% Cu leached residue (d)

3.9 Kinetic analysis

One of the major objectives of this study is the basic understanding of the mechanism of copper dissolution kinetics from the chalcopyrite containing complex Cu ore in ammonia solution.

Leaching is a fluid–solid heterogeneous reaction and can be represented as follows:



For the above reaction system, the following main steps are considered to occur in succession during the reaction:

- 1) Diffusion of fluid reactants from bulk liquid to fluid film;
- 2) Diffusion of reactants across the fluid film to the particle surface;
- 3) Diffusion of reactants across the product layer to the unreacted core;
- 4) Reaction on the unreacted core surface between fluid reactant and solid.

Each of the above steps offers a resistance to the overall reaction. The step with the largest resistance i.e. the slowest step becomes the rate controlling. Steps 1 and 2 are dependent on the hydrodynamics or mixing effects inside the reactor and can be enhanced by increasing the speed of rotation of the impeller or by improving the reactor design to promote better mixing. It can be assumed that the bulk diffusion is not rate controlling when the mixing is high enough to maintain

all the particles in suspension. In the case of a chalcopyrite leaching, insoluble layer of iron oxides may form a diffusion barrier for the reactants to reach the unreacted core. Diffusion across the product layer is mainly dependent on the thickness and porosity of the layer. For a particle reacting under shrinking core mode, the integrated rate equations for three different rate controlling mechanisms can be written as follows [23,24].

1) Film diffusion:

$$\alpha = k_f t \quad (6)$$

$$k_f = \frac{3bk_c c_A}{\rho_s r_0} \quad (7)$$

2) Product layer diffusion:

$$1 - \alpha - (1 - \alpha)^{\frac{2}{3}} = k_d t \quad (8)$$

$$k_d = \frac{2bD_e c_A}{\rho_s r_0^2} \quad (9)$$

3) Surface reaction:

$$1 - (1 - \alpha)^{\frac{1}{3}} = k_r t \quad (10)$$

$$k_r = \frac{bk_s c_A}{\rho_s r_0} \quad (11)$$

To determine the rate controlling mechanism and kinetic parameters, the experimental conversion data were analyzed on the basis of shrinking core models.

From the shape of time vs conversion plots (Figs. 4–7), it shows that film diffusion is not a rate-controlling step in the present investigation. Hence, the experimental time vs conversion data were tested with the model Eqs. (8) and (10). The best fit plots with coefficient of determination (R^2) more than 0.97 were obtained with the surface reaction controlling mechanism, i.e. model Eq. (10).

Application of Eq. (10) to the experimental data at different temperatures yielded linear relationship, which suggests that the dissolution rate of chalcopyrite ore is controlled by the surface chemical reaction (Fig. 10).

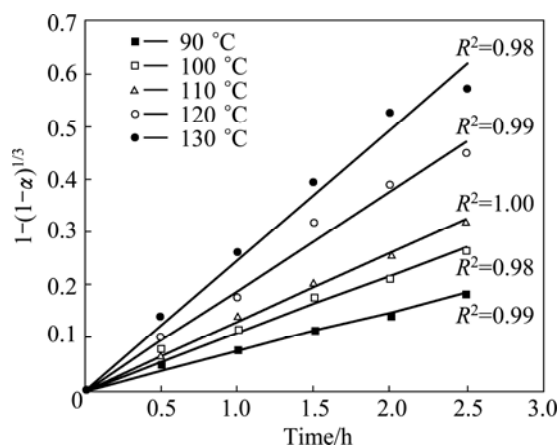


Fig. 10 Plots of $1-(1-\alpha)^{1/3}$ vs time at various temperatures (Data correspond to Fig. 5)

Arrhenius equation $k_r = A \exp[-E_a/(RT)]$ was used to estimate the activation energy for the process. Apparent reaction rate constants calculated from the slopes of Fig. 10 were used in the Arrhenius plot, i.e. $\ln k_r$ vs $1/T$ plot (Fig. 11). The estimated activation energy from the slope was (37.6 ± 1.9) kJ/mol. The obtained activation energy value further supports surface reaction controlling model because diffusion controlling reactions generally have activation energies in the range of 4.2–12.5 kJ/mol

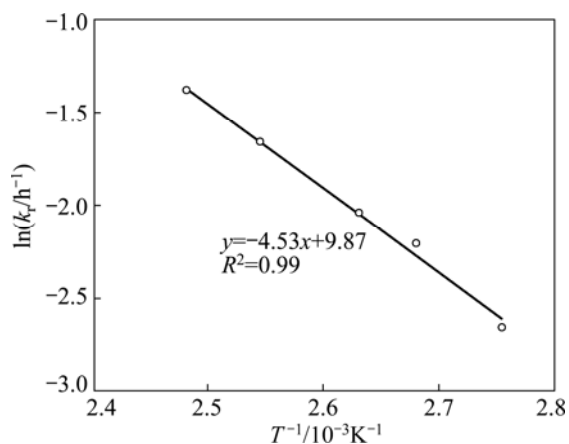


Fig. 11 Arrhenius plot for Cu ore leaching (Conditions: 1.29 mol/L NH_3 , $p_{\text{O}_2} = 203$ kPa, 125–212 μm particles)

[24]. Surface reaction controlled leaching with activation energy lower than 40 kJ/mol has been reported in several studies [25,26]. Low value of apparent activation energy can be associated with a reaction mechanism involving adsorption of reactants followed by chemical reaction itself [26]. In the present study, dissolved O_2 may first be adsorbed on the ore surface followed by oxidation reaction of chalcopyrite.

Also, applying Eq. (10) to the kinetic data in Fig. 6 at different p_{O_2} , chemical reaction rate constants were calculated from the slopes. In order to determine the reaction order with respect to oxygen partial pressures, $\ln k_r$ vs $\ln p_{\text{O}_2}$ plot was made as shown in Fig. 12. In this figure, two slopes exist. Empirical order with respect to oxygen pressure (50.6–203 kPa) is 0.22 ± 0.02 . However, at higher oxygen partial pressure (>203 kPa), the rate becomes independent of oxygen pressure variation and order approaches zero.

The surface chemical reaction model fitted well with the dissolution data at various ammonia concentrations. Apparent rate constants at various NH_3 concentrations were determined from $1-(1-\alpha)^{1/3}$ vs t plots. From the plot of $\ln k_r$ vs $\ln [\text{NH}_3]$, reaction order with respect to ammonia concentration is found to be 1.04 ± 0.08 (Fig. 13).

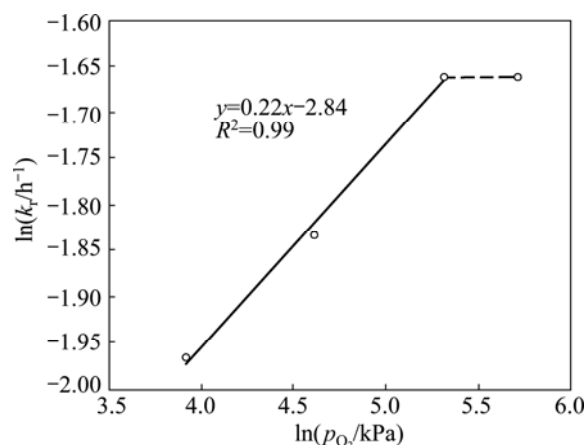


Fig. 12 Plot of $\ln k_r$ vs $\ln p_{\text{O}_2}$ to estimate reaction order

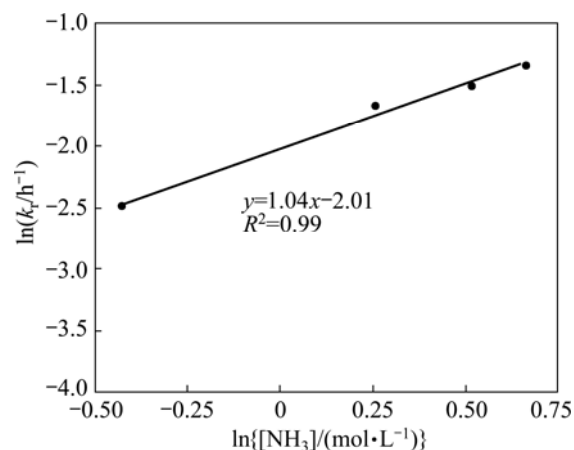


Fig. 13 $\ln k_r$ vs $\ln [\text{NH}_3]$ plot to estimate reaction order

In order to calculate the average particle radius, geometric average was calculated as follows:

$$r_0 = \frac{\sqrt{(f_1 f_2)}}{2} \quad (12)$$

The apparent rate constant (k_r) values calculated from $1-(1-\alpha)^{1/3}$ vs time plots for different particle sizes were plotted against inverse of initial particle radii (Fig. 14). The linear dependence of the rate constant on the inverse of particle radius and passing through the origin further supports that the surface chemical reaction is the rate controlling step here.

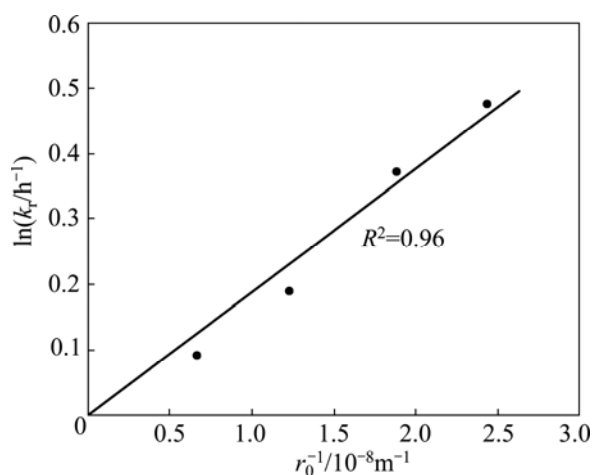


Fig. 14 Apparent rate constant vs inverse of particle radius plot

4 Conclusions

Mineralogical characterization of the copper ore sample reveals that siderite is the major phase and chalcopyrite is the main sulfide mineral. Ammoniacal leaching using O_2 gas under pressure is a feasible treatment route for this ore for selective dissolution of copper. Copper leaching rate is strongly influenced by temperature, NH_3 concentration and particle size whereas oxygen partial pressure has moderate influence up to about 203 kPa. Under standard leaching conditions of 1.29 mol/L NH_3 , 120 °C, 125–212 μm particle size and 203 kPa O_2 partial pressure, it is possible to achieve 83% copper recovery in 2.5 h. However, under higher ammonia concentration and lower particle sizes >95%, Cu extraction is feasible. The leaching process is surface reaction controlling one and precipitation of hematite does not alter the reaction mechanism. Empirical orders of reaction with respect to O_2 partial pressure and NH_3 concentration are about 0.2 and 1, respectively. The linear plot of rate constant vs inverse of particle radius passing through the origin coupled with activation energy value of (37.6 ± 1.9) kJ/mol further supports the surface reaction rate controlling mechanism.

Nomenclature

A	Pre-exponential factor in Arrhenius equation;
b	Stoichiometric coefficient in Eq. (5);
c_A	Concentration of fluid reactant (mol/m^3);
D_e	Effective diffusivity (m^2/s);
E_a	Activation energy (J/mol);
f_1, f_2	Upper and lower sizes in a particular size fraction, respectively;
k_c	Liquid–solid mass transfer coefficient (m/s);
k_d	Apparent rate constant for product layer diffusion (s^{-1});
k_r	Apparent rate constant for surface chemical reaction (s^{-1});
k_s	Intrinsic reaction rate constant;
R	Mole gas constant ($8.3145 \text{ J}/(\text{mol}\cdot\text{K})$);
r_0	Initial particle radius (m);
t	Time (h or s);
T	Temperature (K);
α	Fraction of extraction;
ρ_s	Density of solid

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氨浸出混合铜矿石的表征及动力学

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摘要: 研究了含 8.8%Cu 和 36.1%Fe 的混合铜矿石的氨浸出动力学。矿物学表征表明, 该矿石的含铁成分以菱铁矿为主, 硫化矿以黄铜矿为主。研究了工艺参数, 如搅拌速度、反应温度、氨浓度、矿石粒径、氧分压对氨浸出过程的影响。在标准的浸出条件下, 即粒径 125–212 μm、反应温度 120 °C、NH₃ 浓度 1.29 mol/L、氧分压 202 kPa, 在 2.5 h 内 Cu 的浸出率达到 83%。在使用较高浓度的氨和较小粒径的矿石时, Cu 的浸出率能够达到 95%。动力学研究结果表明, 浸出过程为表面反应控制, 估算出的活化能为(37.6±1.9) kJ/mol, 氧分压与氨浓度的反应级数分别为 0.2 和 1。

关键词: 氨浸出; 黄铜矿; 菱铁矿; 浸出动力学

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