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, NH_3 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 NH_3 and 202 kPa of p_{O_2}, about 83% Cu could be selectively extracted in 2.5 h. However, when using higher NH_3 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 [NH_3] were about 0.2 and 1, respectively.
Key words: ammonia leaching; chalcopyrite; siderite; leaching kinetics

1 Introduction

Chalcopyrite ($CuFeS_2$) 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 SO_4^{2-} instead of S^0 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 NH_3 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, NH_3/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 Mo $K_{\alpha1}$ 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.
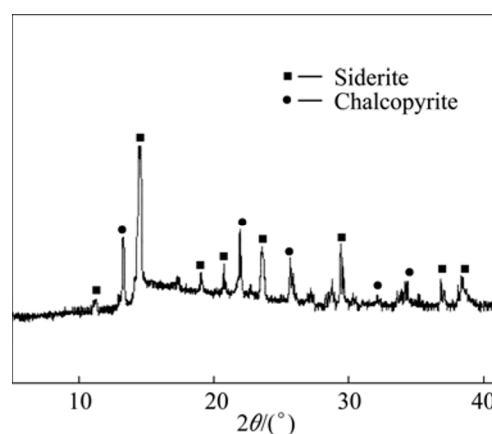
Fig. 1 X-ray diffraction pattern of Cu-ore sample

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 $NH_3−$ $(NH_4)_2SO_4$ solution and oven dried at about 80 °C prior to characterization.

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

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

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