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Dissolution study of chalcopyrite concentrate in oxidative ammonia/ammonium carbonate solutions at moderate temperature and ambient pressure

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ABSTRACT

In this research, the dissolution behaviour and leaching kinetics of Sarcheshmeh chalcopyrite concentrate was investigated in oxidative ammonia/ammonium carbonate solution. Temperature, concentration of ammonia and ammonium carbonate, agitation speed, solid to liquid ratio, oxygen flow rate, pH and particle size were chosen as parameters in the experiments. About 70% of copper was effectively recovered at temperature 60 °C; ammonia/ammonium carbonate concentrations: 5 M NH_3 + 0.3 M $(NH_4)_2CO_3$; agitation speed: 1000 rpm; solid to liquid ratio: 1:20 g/mL; oxygen flow rate: 1 L/min; leaching times: 240 min and 80% passing size finer than 42 μm. Also kinetic results and morphology and elemental composition of residue at the most suitable conditions show that, the leaching process is controlled by the diffusion of reagents or products from iron oxide passive layer formed on chalcopyrite surface. Activation energy was determined to be 25 kJ/mol.

1. Introduction

Chalcopyrite ($CuFeS_2$) is the most abundant and important source of copper metal available in the earth's crust (Dutrizac, 1978) counting for about 70% of copper reserves in the world (Wang, 2005). Over the years, considerable research has been devoted to developing hydrometallurgical processes for leaching copper sulphide concentrates, especially chalcopyrite, at moderate and high temperatures and pressure. Numerous leaching processes, such as ammoniacal systems, (Kuhn et al., 1974; Beckstead and Miller, 1977) acid sulphate systems, (Dutrizac, 1978; Hirato et al., 1987; Guan and Han, 1997; Sokić et al., 2009) chloride systems, (Kuhn et al., 1974; Dutrizac, 1992; Yoo et al., 2010; Lu and Dreisinger, 2013) and nitrate systems, (Gok and Anderson, 2013) have been investigated. The achievement of a satisfactory copper recovery needs the utilization of high temperatures, high pressures or extended dissolution times, in the order of days, due to its inherently slow kinetics. As a result of these findings for chalcopyrite leaching in acidic media, the ammonia/ammonium carbonate solution was applied to Sarcheshmeh chalcopyrite concentrate to improve extraction at moderate temperature and ambient pressure.

An ammoniacal system was first used at the Kennecott Plant, Alaska, because copper ore contains carbonates in limestone dolomite gangue which are acid soluble, consequently increasing the acid consumption (Habashi, 1970). Being more selective, less corrosive and lowering reagent consumption for calcareous carbonate gangue are the main advantages of alkaline leaching over acid leaching. As it is applied by the Arbiter process, the raffinate is treated with lime to regenerate ammonia and to produce disposable gypsum ($CaSO_4 \cdot 2H_2O$) (Kuhn et al., 1974). Aqueous ammonia is commonly used in cobalt, nickel, and copper industries due to the formation of stable metal ion ammine complexes. Complex ligands include ammonia which binds to metal ions through the reactive nitrogen-containing group, leading to higher solubility in most cases (Forward, 1953). Ammonia is also advantageous in that ammonia and ammonium ion constitute a pH buffer solution (Park et al., 2007).

Literature search reveals that a considerable amount of research has been conducted on the ammoniacal leaching of Cu, Ni and Co bearing oxide and sulphide ores, industrial scraps and wastes, over the past few decades. The thermodynamics and kinetics of reaction systems involving ammonia–copper, ammonia–nickel and ammonia–cobalt have been investigated in detail (Williams and Light, 1978; Vu and Han, 1977; Niinae et al., 1996). Extensive studies on the recovery of Cu, Ni and Co from ocean floor manganese nodules by reductive ammoniacal leaching technology have been reported (Han et al., 1974; Mukherjee et al., 2005). It is well known that, the addition of an oxidant is necessary in order to enhance sulphide dissolution. A number of oxidants have been successfully tested in the ammoniacal leaching of copper sulphides, including bromates, chlorates, oxygen, peroxide, and persulphates (Bell et al., 1995). Oxygen, being the least expensive, is the most widely studied of the oxidants (Park et al., 2007).

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Several ammoniacal pressure leaching processes have been commercialized successfully around the world. As far back as 1947, direct ammonia leaching of Cu, Ni and Co sulphide ores employing high pressure and temperature in an autoclave with oxygen as an oxidant was developed by Sherritt–Gordon at its plant in Fort Saskatchewan, Canada (Forward, 1953). The Arbiter Process developed in 1970s is another example of ammoniacal pressure leaching (Kuhn et al., 1974). The processes were carried out at 60 to 90 °C with 5 to 40 psig oxygen pressure. Intensive mixing is employed to improve the rate of oxygen transfer from the gas phase to the liquid phase and to prevent the formation of a protective hematite surface layer. In oxygenated ammoniacal solutions, chalcopyrite dissolves according to the following reaction (Beckstead and Miller, 1977):

$$CuFeS_2 + 4NH_3 + \frac{17}{4}O_2 + 2OH^- \rightarrow Cu(NH_3)_4{}^{2+} + \frac{1}{2}Fe_2O_3 + 2SO_4{}^{2-} + H_2O. \tag{1}$$

The overall reaction given by Eq. (1) can be written as two half-cell reactions. The anodic half-cell would be the dissolution of chalcopyrite (Beckstead and Miller, 1977):

$$CuFeS_2 + 19OH^- \rightarrow Cu^{2+} + \frac{1}{2}Fe_2O_3 + 2SO_4{}^{2-} + \frac{19}{2}H_2O + 17e^-. \tag{2}$$

While the cathodic half-cell reaction would be the discharge of oxygen, then it is a cathodic reaction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-. \tag{3}$$

The detailed chemistry of the oxidative ammonia leach is quite complex and multistep, but the basic principles are reasonably established (Kuhn et al., 1974). Briefly, the sulphide component is oxidized to a soluble species, predominantly sulphate (SO_4^{2-}) together with some lower oxidation state species such as thiosulphate ($S_2O_3^{2-}$), tri-thionate ($S_3O_6^{2-}$) and sulphamate ($NH_4\ SO_3NH_2$). The iron component is oxidized to the +3 state and precipitated as hydrated ferric oxide ($Fe_2O_3 \cdot H_2O$). The Cu is released in the +2 oxidation state and stabilized in solution by the formation of ammine complexes with NH_3 ligands.

Numerous acid leaching and bioleaching processes for Sarcheshmeh copper concentrate have been investigated (Ahmadi et al., 2011; Behrad Vakylabad, 2011; Koleini et al., 2011). The problem with all of these is slow kinetics hence copper recovery is low. In this study to increase the leaching rate and enhance copper recovery, the leaching and kinetic behaviour of Sarcheshmeh chalcopyrite concentrate at moderate temperature and ambient pressure in ammonia/ammonium carbonate solution were investigated.

2. Material and experiments

2.1. Chalcopyrite concentrate

The chalcopyrite concentrate used in this investigation was obtained from Sarcheshmeh copper complex in Kerman, Iran. The particle size analysis of the sample by sieving and cyclosizer gave a P_{80} of 42 μm.

2.2. Leaching experiments

All leaching experiments were carried out in a 1000 mL double glass reactor equipped with a stainless steel impeller and associated speed controlled agitation motor, condenser, thermometer, glass funnel for adding the solid sample and sampling device. The temperature of the leach solution in the reactor was maintained by a thermostatically controlled water bath. This set-up provides stable hermetic conditions and allows heating at constant temperature. Evaporation of water and ammonia loss to the atmosphere during leaching experiments was prevented by a condenser. Required amount of chalcopyrite concentrate was added into 500 mL agitated $NH_3/(NH_4)_2CO_3$ solution of given concentration at the given temperature. Reaction time was counted after the introduction of oxygen into the reactor. After a specific time, about 8 mL of leaching solution sample was withdrawn from the reactor, and fresh 8 mL of $NH_3/(NH_4)_2CO_3$ solution was immediately added to leaching reactor. After filtration, the sample solution was analyzed for copper by AAS.

2.3. Kinetics models

The shrinking core model considers that the leaching process is controlled either by the diffusion of reactant through the solution boundary layer, or through a solid product layer, or by rate of the surface chemical reaction. The simplified equations for the shrinking core model when either diffusion or the surface chemical reactions are the slowest step can be expressed as follows, respectively (Levenspiel, 1999):

$$\left[1-3(1-\alpha)^{2/3}+2(1-\alpha)\right] = \frac{2M_B DC_A}{\rho_B a r_0{}^2}t = k_d t \tag{4}$$

$$\left[1-(1-\alpha)^{1/3}\right] = \frac{k_c M_B C_A}{\rho_B a r_0}t = k_r t \tag{5}$$

where α is the fraction reacted, k_c the kinetic constant, M_B the molecular weight of the dissolving metal, C_A the concentration of the dissolved lixiviant A in the bulk of the solution, a the stoichiometric coefficient of the reagent in the leaching reaction, r_0 the initial radius of the solid particle, t the reaction time, D the diffusion coefficient in the porous product layer and k_d and k_r are the rate constants, respectively, which are calculated from Eqs. (4) and (5), respectively.

Eq. (4) reveals that if the diffusion through the product layer controls the leaching rate, there must be a linear relation between the left side of equation and time. The slope of the line is the apparent rate constant k_d, which is directly proportional to $1/r_0^2$. If the surface reaction controls the rate, the relation between the left side of Eq. (5) and time must be linear. The slope of this line is called the apparent rate constant and is directly proportional to $1/r_0$. Also the temperature dependence of the reaction rate constant can be calculated by the Arrhenius equation:

$$k_d = A\exp\left(\frac{-E_a}{RT}\right) \tag{6}$$

where A is frequency factor, E_a is activation energy of the reaction, R is universal gas constant and T is absolute temperature.

3. Results

3.1. Chemical assays and characterization

Typical chemical and mineralogical analysis of Sarcheshmeh chalcopyrite concentrate by X-ray fluorescence (XRF) and X-ray diffraction (XRD) are presented in Tables 1 and 2 respectively. Four particle size fractions were obtained by wet sieving. The chemical analysis of each size fraction by X-ray fluorescence is presented in Table 3 and it is obvious that copper content is higher in the finer fractions. Also, the

Table 1
Typical chemical analysis of the Sarcheshmeh copper concentrate and ammoniacal leaching residue in most suitable condition by XRF.

Sample	Component (%)									
	Cu	Fe	Al_2O_3	ZnO	K_2O	S	SiO_2	TiO_2	CaO	PbO
As received	25.0	23.6	2.29	1.01	0.42	30.1	5.42	0.13	0.19	0.38
Leaching residue	11.9	33.2	4.12	1.54	0.92	22.1	8.55	0.33	0.59	0.82