

THE OPTIMUM LEACHING CONDITIONS OF ARTVİN MURGUL CHALCOPYRITE ORE IN HYPOCHLORITE SOLUTION

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ABSTRACT

The optimum leaching conditions of primary chalcopyrite ore from Artvin-Murgul region in Turkey have been examined in hypochlorite solution. The effects of various parameters as initial pH, hypochlorite concentration, stirring speed, solid/liquid ratio and temperature to the copper dissolution from chalcopyrite were investigated. It was found that chalcopyrite reacted with chlorine generated from hypochlorite in acidic pH values. pH effectively decreased during the dissolution. It was determined that the optimum leaching conditions were initial pH of 5-6, hypochlorite concentration of 0.2 N for 4 g/L solid/liquid ratio, 600 rpm stirring speed and it was seen that sulphate formation was over 50 %.

Keyword - Chalcopyrite, hypochlorite leaching, the optimum leaching conditions

ARTVİN-MURGUL KALKOPİRİT CEVHERİNİN HİPOKLORİT ÇÖZELTİSİNDEKİ OPTİMUM LİÇ ŞARTLARI

ÖZET

Artvin-Murgul'dan temin edilmiş olan kalkopirit cevherinin hipoklorit çözeltisindeki optimum liç şartları incelenmiştir. Başlangıç pH'sı, hipoklorit konsantrasyonu, karıştırma hızı, katı/sıvı oranı ve sıcaklığın kalkopirit cevherinden bakırın çözünürlüğüne etkisi araştırılmıştır. Kalkopirit mineralinin asidik pH değerlerinde hipoklorit çözeltisi ile dengede olan klor ile reaksiyon verdiği bulunmuştur. Çözünme esnasında pH önemli derecede düşmektedir. Optimum liç şartları olarak başlangıç pH'sının 5-6, 4 g/L katı/sıvı oranı için hipoklorit konsantrasyonunun 0,2 N, karıştırma hızının 600 rpm olduğu ve % 50 üzerinde bir sülfat oluşumu olduğu belirlenmiştir.

Anahtar Kelimeler – Kalkopirit, hipoklorit liçi, optimum liç şartları

1. INTRODUCTION

Chalcopyrite (CuFeS_2 or $\text{Cu}_2\text{S}\cdot\text{Fe}_2\text{S}_3$) is the most abundant mineral in the sulphide copper-bearing deposits and the principle source from which copper is produced commercially. Conventional pyrometallurgical copper production results in SO_2 and toxic metals emissions to environment. This situation has led to the development

of hydrometallurgical methods of copper extraction as opposed to the classic pyrometallurgical routes [1]. Hydrometallurgical processes, not only reduce environmental pollution, but also offer many other potential advantages as cost of production and recovery of other metals in low concentrations [2,3].

There are a lot of papers on the leaching chemistry and kinetics of chalcopyrite. Dissolution of copper sulphides as chalcopyrite is performed by usage of suitable reactants in the presence of oxidants or electrochemical systems such as iron (III) [4-6], oxygen or ozone [7], nitric acid [1], electrochemical oxidation [8], hydrogen peroxide [9,10], chlorine [11], chlorine generated from manganese dioxide [12], etc. On the other hand, Puvvada and Murthy (2000) have studied selective precious metals leaching from chalcopyrite in chloride/hypochlorite media [13].

Chalcopyrite is one of the refractory and difficult to leach among the copper ores [3]. Ferric salts in the leaching of chalcopyrite below 373 K temperature give a high yield of elemental sulphur and copper rich polysulphides which cause a slow leaching rate because of passivation [4]. Similarly the leaching of sulphide minerals by oxygen also gives elemental sulphur at low temperature [2,6,14].

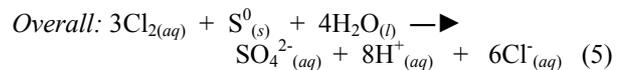
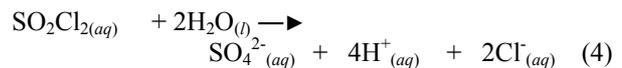
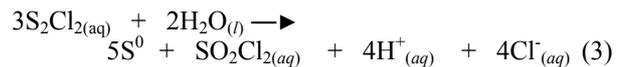
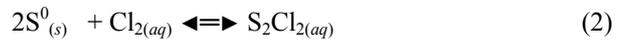
The leaching of chalcopyrite in hydrogen peroxide in acid medium was studied by some researchers and they found an interfacial chemical reaction controlled in the dissolution and the activation energy of 39-60 $\text{kJ}\cdot\text{mol}^{-1}$. The activation energy has a high value in H_2O_2 leaching [9,10]. Çolak *et al.* studied dissolution kinetics of chalcopyrite in water saturated with chlorine. They found that the dissolution was controlled by diffusion through the product layer and the activation energy was 9.06 $\text{kJ}\cdot\text{mol}^{-1}$ [11]. Devi *et al.* investigated the oxidation of chalcopyrite in hydrochloric acid medium in the presence manganese dioxide. Chlorine generated from manganese dioxide was effective in the dissolution of chalcopyrite [12].

Some researchers used chlorine, hypochlorite and chlorine generated from manganese dioxide as oxidant for sulphide ores such as chalcopyrite, enargite, sphalerite and pyrite etc. They aimed to dissolve copper or precious metals, remove arsenic, or desulfurize from sulphide ores or coal [11-13,15-22].

Both chlorine and hypochlorite, strong oxidants, have got high redox potentials 1.358 and 1.630 volts, respectively. Therefore they are good at leaching of sulphide minerals. They are in equilibrium as reversible each other in hydrochloric acid solution related to pH [2].



Because of the corrosive nature and difficulty in storage of chlorine gas, its use has been restricted so far. Today with availability of improved corrosion-resistant metals, alloys or polymeric materials, the use of chlorine gas as a leaching agent seems to have potential for development and growth in many specific areas of base-metal extraction and processing. Hypochlorite solution means storage chlorine and it gives aqueous chlorine. Free chlorine reacts with elemental sulphur to give sulphate. If elemental sulphur forms during leaching, it causes to the passivation in leaching. Chlorine/hypochlorite leaching has an advantage of sulphate formation [2].



Concentrated ores don't need to use in leaching processes, unlike in pyrometallurgical routes. Primary ore can be used. In this study, a primary chalcopyrite ore, not concentrated, was used and hypochlorite solution was chosen as the leaching agent. The effects of initial pH, hypochlorite concentration, particle size, stirring speed have been studied.

2. EXPERIMENTAL

The chalcopyrite ore used in this study was supplied from Artvin-Murgul, Turkey. The ore was mainly composed of quartz, chalcopyrite, pyrite and others. Chemical analysis of the chalcopyrite ore was given in Table-1.

Table 1. Chemical analysis of the chalcopyrite (%)

SiO ₂	Cu	Fe	S	CaO
69.85	3.00	11.15	11.67	2.10

The chalcopyrite sample used in the experiments was ground and distribution of particle size of the ore was given in Table-2.

Table 2. Particle size distribution

Particle Size (μm)	% (w/w)	%Cu (w/w)
-53	5.61	5.55
-100+53,	15.67	3.93
-150+100	35.89	3.36
212+150	34.22	1.98
-315+212	8.61	0.89

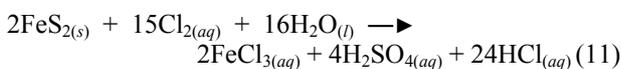
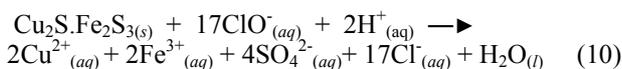
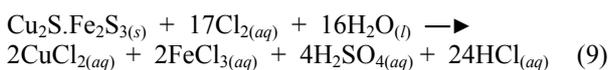
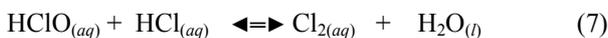
Hypochlorite solution was used as the reagent in leaching experiments. It was technical grade and is used as cleaning agent and disinfectant in most home, office etc. in Turkey. In this solution active chlorine was analyzed by iodometric titration method. Then it was diluted for different concentrations. pH was adjusted with hydrochloric acid solution in reagent grade.

Leaching experiments were carried out at atmospheric pressure in a beaker or a balloon with reflux systems in constant temperature bath on a magnetic stirrer. Periodically Cu^{2+} and Fe^{3+} ions in solution were analyzed by atomic absorption spectrophotometer, Shimadzu AAS-6700.

3. RESULTS AND DISCUSSION

3.1. Dissolution Reactions

Possible reactions in the dissolution process are given in Eqs. (6-10). One of hypochlorite and aqueous chlorine may react with chalcopyrite and pyrite to form sulphate compounds (Eqs.-5, 9-11). In the leaching solutions, sulphate analysis was done by gravimetric method with BaCl_2 and it was found that sulphate formation was over 50%. This showed that sulphide in chalcopyrite can oxidize in chlorine/hypochlorite media about copper dissolution ratio. On the other hand, it was seen that pH decreased during the dissolution. So it was concluded that aqueous chlorine in hypochlorite solution reacted with chalcopyrite [11,19,23].



3.2. Effect of Initial pH

To determine the optimum initial pH value, the tests were conducted at pH values of 1-8 and in 0.04, 0.10 and 0.20 N hypochlorite concentrations, holding constant the other parameters. The results were given in Fig.-1. It was seen more copper and less iron dissolutions from chalcopyrite. High copper dissolution ratio continues up to initial pH of 6. On the other hand, high iron dissolution was obtained below initial pH of 4. It was decided the optimum pH in which is 5-6, that is more copper and less iron dissolutions from the chalcopyrite.

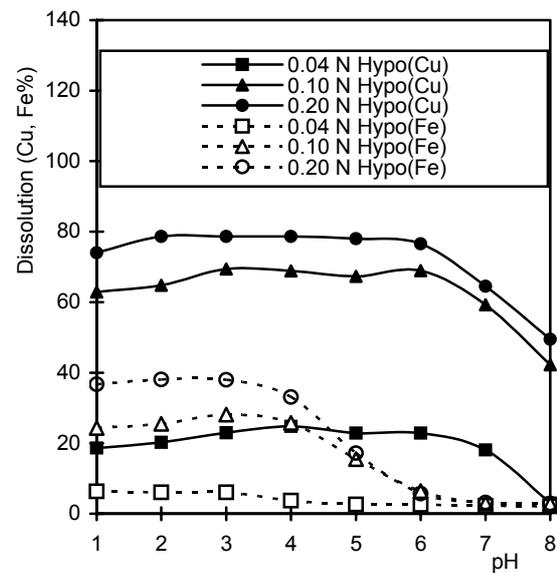


Figure 1. Effect of initial pH (Solid/liquid ratio: 4 g/L, leach solution: 0.25 L; time: 5 min; stirring speed: 800 rpm; temperature: 293 K)

3.3. Change of pH During the Dissolution

It was thought that pH values in the pulp may increase or decrease during the dissolution depending on the reaction with chlorine or hypochlorite in the equilibrium. If chalcopyrite reacted with hypochlorite, pH would increase according to Eq. (10) because of H^+ consumption. However it was found that pH during the dissolution decreased and this decrease was dependent on temperature.

On the other hand, pH decreased less at high hypochlorite concentrations due to hypochlorite/hypochlorite acid buffer solution (Fig.-2a,b).

An advantage of using hypochlorite solution the leaching is the fact that homogeneous and aqueous chlorine formation. Hypochlorite solution provides homogeneous chlorine in solution unlike chlorine gas.

3.4. Effect of Hypochlorite Concentration

Figure-3 presents the dissolution of copper from chalcopyrite related to time in 0.02-0.25 N hypochlorite concentrations. The other parameters were held at constant values. The optimum hypochlorite concentration was 0.20 N for 1 g chalcopyrite in 0.25 L leaching solution. If chalcopyrite quantity changes or concentrated chalcopyrite is used in leaching, hypochlorite concentration should increase or decrease because of hypochlorite consumption related to chalcopyrite or pyrite quantities.

3.5. Effect of Stirring Speed

Figure-4 shows the leach results at stirring speeds of 0, 100, 200, 400, 600, 800 and 1000 rpm (rotating per minute). It was seen that the settling in the pulp occurred at low stirring speeds (0-400 rpm). At high speeds (600-1000 rpm), more dissolution was found due to homogeneous distribution of particles in the solution. The dissolutions at 800 and 1000 rpm are lower than ones at 600 rpm because of chlorine loss from solution. The best results for stirring speed were obtained at 600 rpm.

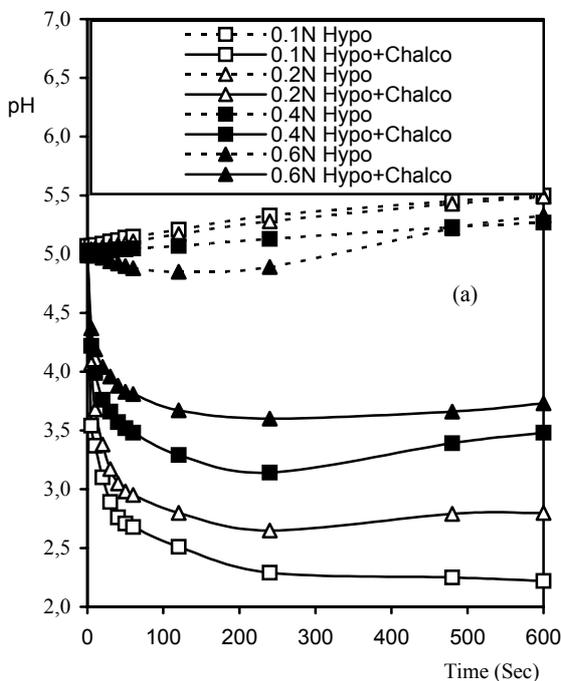


Figure 2.a. pH changes during the dissolution in different hypochlorite concentrations.

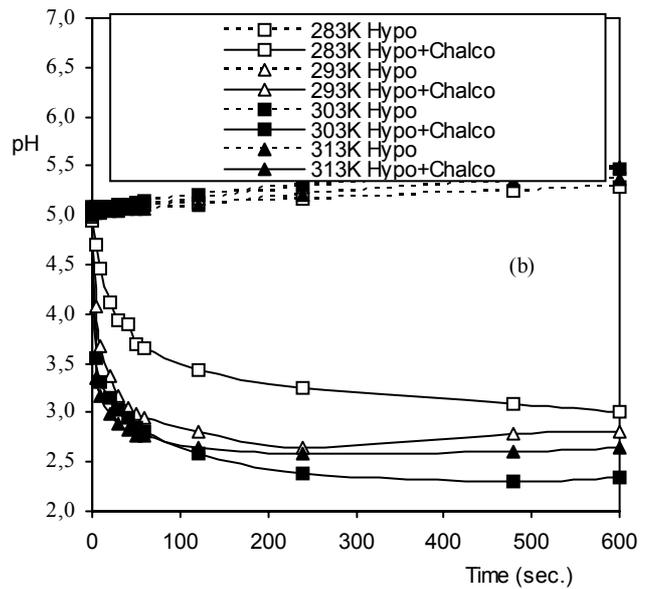


Figure 2.b. pH changes during the dissolution at different temperatures

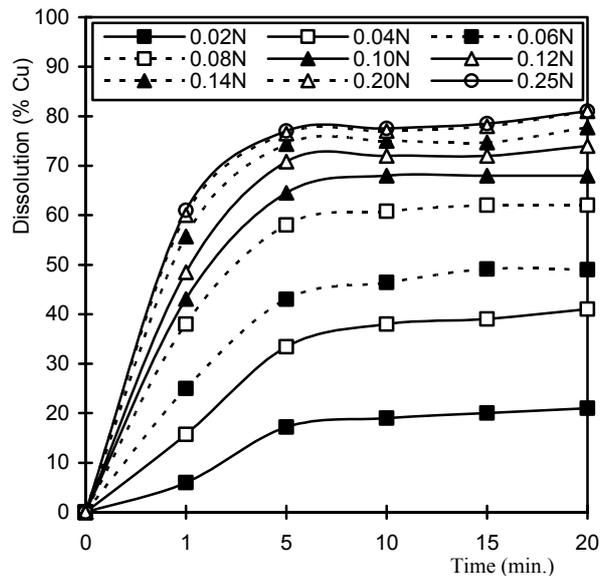


Figure 3. Effect of hypochlorite concentration (Solid/liquid ratio: 4 g/L, leach solution: 0.25 L; initial pH: 5; stirring speed : 800 rpm; temperature: 293 K)

3.6. Effect of Particle Size

In examining the effect of particle size, it was found that the finer chalcopyrite was to be more suitable for high extraction, naturally (Fig.-5). Particle size is effective in the dissolution of copper from the chalcopyrite.

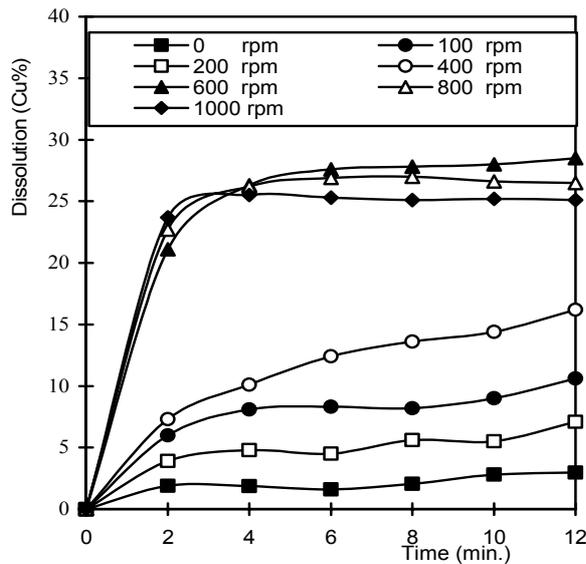


Figure 4. Effect of stirring speed (Solid/liquid ratio: 10 g/L, leach solution: 0.25 L, initial pH: 5, hypochlorite concentration: 0.2 N, temperature: 293 K)

3.7. Effect of Solid/Liquid Ratio

Different initial quantities of chalcopyrite in the solution of 0.25 L were leached to determine the effect of solid/liquid ratio on the leaching rate. The obtained results were given in Fig.-6.

It was found that high dissolution occurred at low solid/liquid ratios. This showed that to dissolve copper from the chalcopyrite required the solid/liquid ratio of 4 g/L for enough hypochlorite concentration. The best solid/liquid ratio to dissolve copper from chalcopyrite was at 4 g/L.

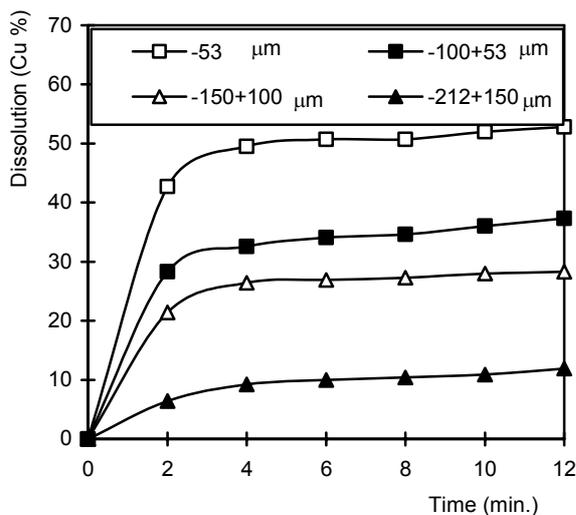


Figure 5. Effect of particle size (Solid/liquid ratio: 10 g/L, leach solution: 0.25 L, initial pH: 5, stirring speed: 600 rpm, hypochlorite concentration: 0.2 N, temperature: 293 K)

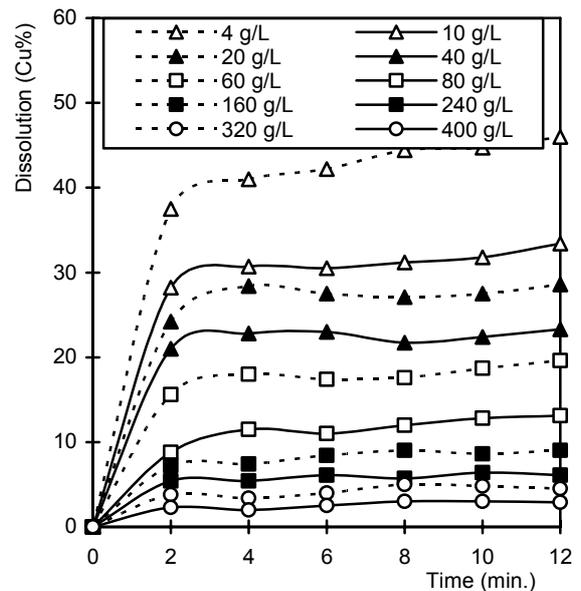


Figure 6. Effect of solid/liquid ratio (Leach solution: 0.25 L, initial pH: 5, stirring speed: 600 rpm, hypochlorite concentration: 0.2 N, temperature: 293 K)

3.8. Effect of Temperature

The effect of temperature to the dissolution was examined and the obtained results were given in Fig.-7. Because chlorine in equilibrium with hypochlorite was loosed at high temperatures, the tests were carried out at low temperatures. It was seen that the dissolution increased by increasing temperature but temperature was less effective in the dissolution.

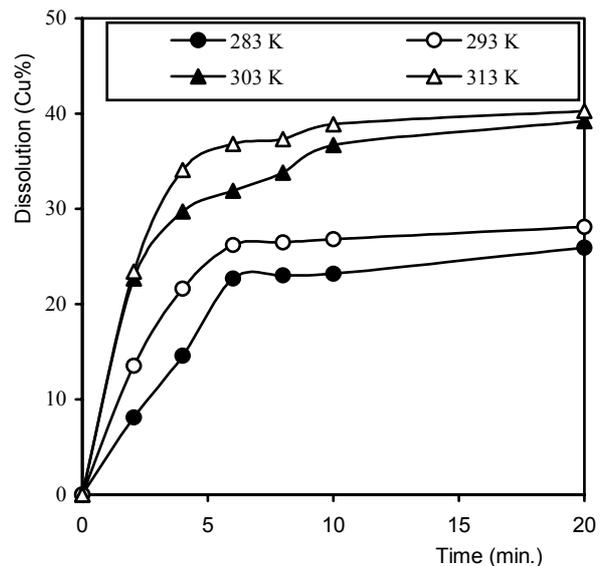


Figure 7. Effect of temperature (Conditions; Initial pH: 5, Solid/liquid ratio: 10 g/L, leach solution: 0.25 L, stirring speed: 600 rpm, hypochlorite concentration: 0.2 N)

4. CONCLUSIONS

Based on the foregoing experimental results, the following conclusions may be drawn.

- a. The dissolution reaction occurs between chalcopyrite mineral and chlorine generated from hypochlorite solution.
- b. Sulfide in the chalcopyrite can oxidize over 50 % in agreement with copper dissolutions to give the sulphate compounds in chlorine/hypochlorite media.
- c. In general, high dissolution ratios (40-80% at different conditions) were obtained in periods of 5-10 minutes. This is important for fast processes.
- d. The optimum leaching conditions were determined, which initial was pH 5-6, hypochlorite concentration was 0.2 N for 4 g/L solid/liquid ratio, stirring speed was 600 rpm and temperature was about room temperature. Required hypochlorite concentration depends on chalcopyrite mineral quantity in the pulp. At high temperatures and high stirring speeds, chlorine loss occurred from solution. Therefore it should be studied at low temperatures.

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