

## Simultaneous Extraction of Copper and Iron from Chalcopyrite Concentrates in Hydrochloric Acid Media: Effect of Additives and Temperature

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**Abstract:** Studies on the chlorination of a chalcopyrite concentrate in aqueous slurry by gaseous chlorine have been demonstrated in this investigation. The effect of time, acid concentration, pulp density (PD) of the sulphide concentrate, effect of sodium chloride on dissolution of copper and the temperature of chlorination, on the fraction of copper dissolved, has been investigated. At the optimum flow rate of Cl<sub>2</sub> gas (400 mL min<sup>-1</sup>), the percent of copper dissolved is found to be increasing with increase in acid concentration, temperature in the range of 318K to 333K and also increasing with decrease with pulp density, addition of sodium chloride, studied. The activation energy of the chlorination process has been calculated to be 7.26 kJ mol<sup>-1</sup>. The best fit of kinetic data to a diffusion-controlled model indicated that diffusion through the product layer was the rate-controlling step during the dissolution. At 333K, with 10wt% concentrate in the slurry and using pure Cl<sub>2</sub> gas with a flow rate of 400 ml/min, nearly 93% of copper extraction has been achieved in about 1 hr. The mechanism of the leaching was further established by characterising the original concentrate and the leach residue by XRD phase identification studies.

**Keywords:** Chalcopyrite concentrate, Chlorine leaching, Dissolution, Hydrochloric acid, and Copper, Iron.

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### 1. Introduction

Extractive metallurgy consists of the science and art of obtaining commercial grades of metal from ore material mined from the earth's crust. CuFeS<sub>2</sub> (chalcopyrite) is the most abundant primary copper ore, and as a result, the extractive metallurgy of copper is based largely on this mineral. Amongst the non-ferrous metals copper is one of the most commonly used metal over thousand years. The traditional industries are continuing to survive and flourish due to the art of making and shaping of copper and copper alloys. Developmental of non-conventional energy sources and the superiority of copper in solar heating are expected to dictate the use of the metal in large quantities in the near future [1]. Chalcopyrite is the principal source from which copper is commercially extracted. The current practice of extracting copper from sulphidic ores such as chalcopyrite involves beneficiation through froth flotation, which produces a concentrate, followed by smelting and electro-refining to produce copper metal. In the traditional pyrometallurgical processes, chalcopyrite concentrates are smelted in reverberatory/flash smelters. These processes provide an energetically efficient route for the extraction of metals from sulphide concentrates because the sulphide sulphur is used as a fuel [2]. Besides the pyrometallurgical methods where environmental pollution resulting emission of SO<sub>2</sub> gas is a real problem, also hydrometallurgical methods are increasingly used [3]. However, it has been established that chalcopyrite requires the presence of an oxidizing agent for its dissolution [4]. Numerous leaching processes have been advocated for recovering copper values from chalcopyrite concentrate. Conventional pyro-/hydro metallurgical process for recovery of copper from copper concentrate usually follows roasting-leaching and electrowinning steps [5]. Elimination of copper in the roasting step for such a system is considered most attractive from the economic and environmental points of view. The roasting of chalcopyrite has been an important step for the extraction of copper, in the traditional smelting route and more so in newer processes. As a result, numerous attempts have been employed to study the roasting parameters; its mechanism and the reactions involved. Elimination of copper in the roasting step for such a system is considered most attractive from the economic and environmental points of view.



However, it has been established that chalcopyrite requires the presence of an oxidizing agent for its dissolution [6]. Pressure leaching at high temperature and oxygen pressure has not found favour because of problems associated with the operation and maintenance of autoclaves and materials of construction [7-8]. Therefore an alternative process such as direct oxidative leaching is considered an impart option to address some of these problems [9-10]. The selection of an oxidizing agent suitable for hydrometallurgical recovery of

copper from copper concentrate has been given considerable attention results on the direct leaching of copper have been reported in several processes. These processes involve ferric sulphate and ferric chloride, cupric chloride and ozone as the oxidants [11-19]. But due to the corrosive nature and difficulty in storage of chlorine gas, its use has been restricted so far [20]. Today, with the availability of improved corrosion-resistant metals and alloys, 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, dissolution kinetics of oxidized and sulphide copper ores in water saturated with chlorine gas been studied by many authors [21-26]. Dutrizac showed that the activation energy in chlorine solution is about 42 KJ /mole as compared to 75 KJ/mole in sulphate system [27]. Palmer et al reported dissolution of chalcopyrite in chloride solution containing hydrochloric acid, sodium chloride and ferric chloride [28]. Lu et al studied mixed chloride sulphate leaching of chalcopyrite in acidic solution and reported very poor leaching efficiency in absence of chloride [2]. Groove et al achieved 90% extraction with chlorine leaching of copper sulphide minerals in an enclosed percolation column [29-30]. In this paper, studies on chlorine gas has been chosen as the leaching agent because leaching in chloride media is much more effective than sulphate system and yields high current efficiency with better quality with respect to purity during electrolysis. Therefore the main objective of the present work is to study the leaching behaviour of chalcopyrite mineral in chlorine media using chlorine gas and the effects of acid concentration, temperature, sodium chloride on the dissolution kinetics have been systematically investigated.

## 2. Experimental

The chalcopyrite concentrate sample, used for this investigation was a high grade and collected from Ghatsila, (Jharkhand, India). The material was sieved to 45 $\mu$ m size to obtain the particle distribution and chemical analysis of the sample is incorporated in Table 1.

Fe	Cu	Mn	As	Zn	Ni	Pb
35.18	21.80	0.01	0.002	0.045	0.003	0.001

Table 1. Chemical composition (%) of chalcopyrite concentrate.

The material was sieved to obtain the particle size distribution. The XRD of concentrate is given in Figure 1. Hydrochloric acid and sodium chloride of laboratory reagent grade were used in this study. Analytical grade chemicals were used for analysis. Leaching experiments were carried out in a closed three-necked glass vessel, which was placed on a thermostatically controlled magnetic stirrer. Chemically pure Cl<sub>2</sub> gas stored in cylinder was used in the leaching experiments. For each experiment the desired amount of copper concentrate was added to the 0.25L leaching solution containing a known amount of hydrochloric acid maintained at the required temperature. The temperature was monitored and controlled by passing water through the bath. At selected time intervals, a known amount of slurry sample was withdrawn and filtered by Whatmann 41 filter paper; copper and iron in the filtrate were analysed titrimetrically using standard methods (Vogel, 1989). The samples were chemically analysed for the copper and iron content percentage by atomic absorption spectrophotometer (AAS). The solid residue was also analysed sometimes to check the material balance. Analytical grade reagents were used for chemical analysis. Purity of the oxygen and chlorine gas used in the leaching experiments was of good quality. Phases in the concentrate, chalcopyrite ore and leach residue were analysed by XRD. In this manner, the dissolution of copper and iron at different periods of chlorination under the desired experimental conditions was determined.

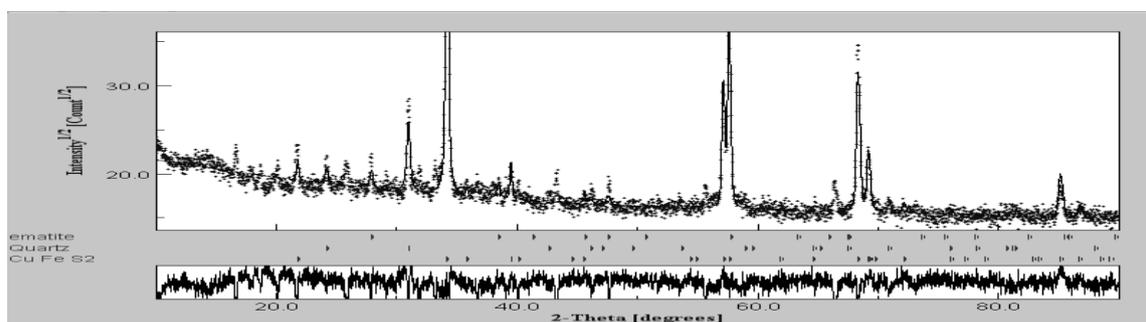


Figure 1. The XRD pattern of chalcopyrite concentrate used in this study.

### 3. Results & Discussion

X-ray diffraction studies as well as petrological studies indicated the presence of chalcopyrite as the major copper and iron containing phase along with hematite and quartz in minor quantities. In the present investigation, various leaching parameters such as acid concentration, effect of sodium chloride and temperature with time were studied to optimise the leaching condition for dissolution of chalcopyrite.

#### 3.1 Leaching of Chalcopyrite in Presence of Oxygen Gas

Leaching of chalcopyrite in presence of oxygen gas, the effect of acid concentration, sodium chloride and temperature with time, on the extent of copper and iron present in the concentrate, has been investigated. The results are summarised and discussed in the following pages.

##### 3.1.1. Effect of Oxygen

Leaching experiment in absence of oxygen was carried out under the condition: PD – 10%, HCl – 1.5 N at temperature of 90°C. The experimental results are presented in Fig. 2 which shows very poor dissolution of both copper and iron. Dissolution of copper is nil even after 4 h of leaching where as only 18% iron gets dissolved. However, when the same experiment was repeated by passing oxygen gas, very fast dissolution of copper as well as iron occurs. The percentage dissolution increases with time. A maximum of 68.2% Cu and 90.5% Fe dissolution occurs at 7 h time interval.

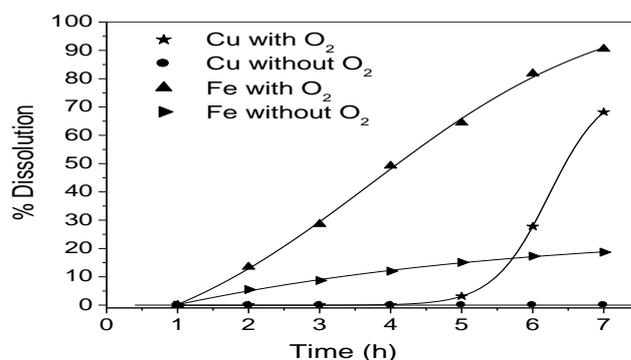


Figure 2. Leaching of chalcopyrite in presence and absence of oxygen, HCl – 1.5 N, O<sub>2</sub> flow rate 400 mL/min, Temp. – 363K, PD - 10%.

##### 3.1.2 Effect of Sodium Chloride

Effect of sodium chloride on chalcopyrite dissolution in hydrochloric acid was studied at 363K; 400 ml/min oxygen flow rate and 10% PD and the results are represented in Fig. 3 (a) & 3 (b) for copper and iron respectively. The percentage recovery increases with increase in time. Surprisingly, sodium chloride has a negative effect on chalcopyrite dissolution. The results showed copper recovery decreased from 68.2% to 46.4% by addition of 5% (w/v) of sodium chloride. The percentage dissolution further decreased to only 3.8% with increase in sodium chloride from 5% to 10% (w/v). Similar trend is also observed for iron dissolution. With addition of 5% sodium chloride iron recovery decrease from 90.5% to 79.4% at 4h duration which is further decreased to 77.4% with addition of 10% sodium chloride. The decrease in dissolution rate of both copper and iron may be due decrease in the solubility of oxygen during leaching.

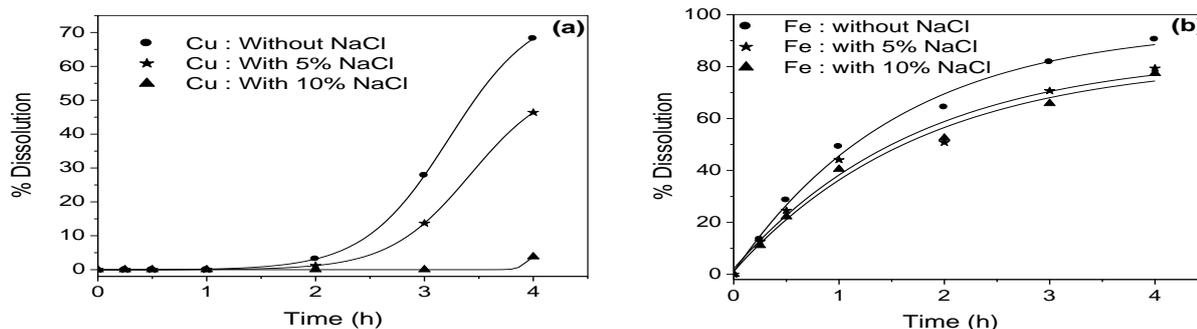


Figure 3. (a) Effect of sodium chloride on copper dissolution during leaching of chalcopyrite in presence of oxygen, HCl – 3.0 N, Temp. - 363K, PD - 10%, Oxygen - 400 mL/min. and (b) Effect of sodium chloride on iron dissolution during leaching of chalcopyrite in presence of oxygen, HCl – 3.0 N, Temp. - 363K, PD - 10%, Oxygen - 400 mL/min.

### 3.1.3. Effect of Temperature

In the dissolution behaviour of chalcopyrite, the leaching experiments were carried out at different temperature between 353K and 363K. The recoveries of different metals at different time intervals are plotted in Fig. 4 in the presence of 3 N hydrochloric acid, 10% sodium chloride and 400 mL/min oxygen flow rate. Copper recovery decreases with increasing the temperature from 353K to 363K. At 353K recovery of copper increased from 7.6% at 2h to 48% at 4 h duration. However with increase in leaching temperature to 363K copper recovery decreased from 48% to 3.8% at 4h time interval. The temperature has reverse trend for iron dissolution i.e. with the increase in temperature recovery of iron is also increased. Percentage dissolution increased from 66.7% to 77.4% at 4 h duration.

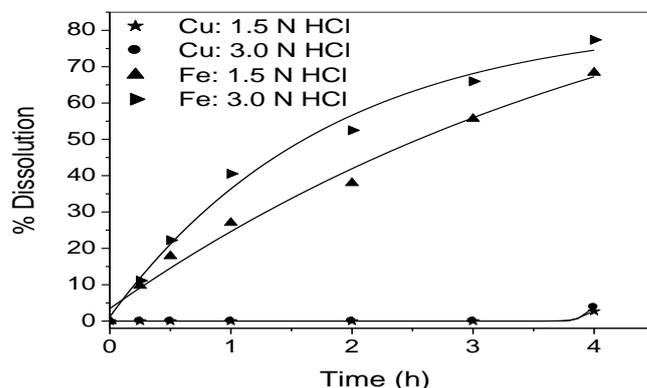


Figure 4. Effect of temperature on copper and iron recovery from chalcopyrite. PD - 10%, [HCl] – 3 N, Oxygen - 400 mL/min.

### 3.1.4. Effect of Acid Concentration

The effect hydrochloric acid concentration on the leaching of different metal from the bulk sulphide was studied using 1.5 to 3.0 N HCl and the results are presented in Fig. 5. In these experiments, the leaching temperature 363K with oxygen flow rate of 400 ml and pulp density of 10% were maintained constant. The results showed that dissolution of metals increased with increase in acid concentration. However a very marginal effect acid concentration on percentage copper recovery was observed when hydrochloric acid concentration increased. Copper recovery increased from 2.7% to 3.8% with increase in acid concentration from 1.5 N to 3 N at 4h duration. In both the cases copper dissolution is almost nil till 3 h. Increase in percentage of iron recovery is observed with increase in time interval as well as acid concentration. Iron recovery is increase from 68.4% to 77.4% with increase in acid concentration from 1.5N to 3.0N at 4 h duration.

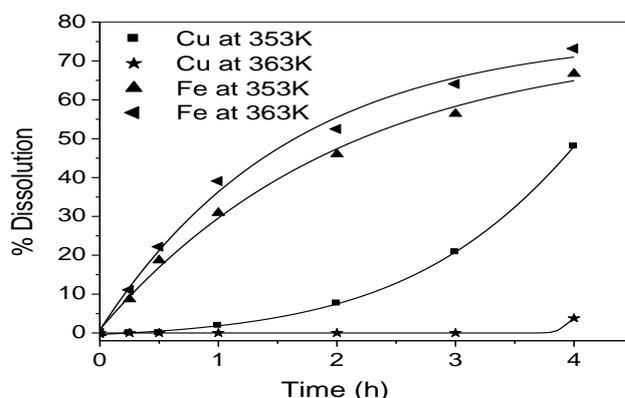


Figure 5. Effect of acid concentration on copper and iron recovery from chalcopyrite. PD - 10%, Temp. - 363 K, Oxygen - 400 mL/min.

## 3.2. Leaching in presence of chlorine gas

### 3.2.1 Effect of Acid Concentration

Leaching of chalcopyrite of composition mentioned in Table 1 was carried out at 333 K by passing chlorine gas in presence absence of HCl. Chlorine gas from the cylinder was passed in to the reaction mixture through a series of valves and rotameter. Dissolution occurs very fast with chlorine gas and a maximum

recovery of about 92% copper and 82.5% iron is achieved. Faster dissolution occurs in presence of acid as compared to dissolution in absence of acid (Fig. 6). Percentage recovery of both copper and iron increase from 80.9 and 71.4 in absence of acid to 92.7 and 82.5 respectively with 2 N HCl in 1h.

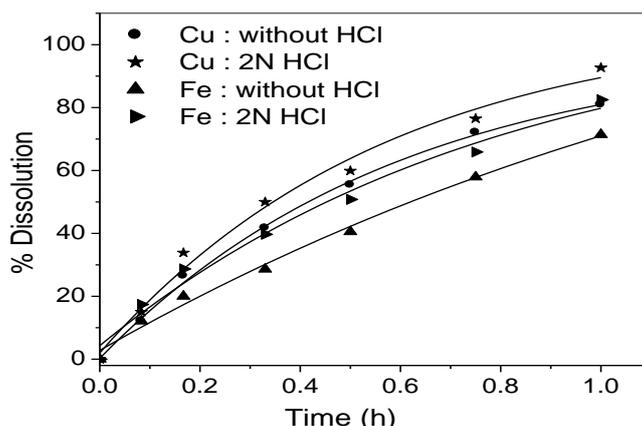


Figure 6. Effect of acid concentration on dissolution of chalcopyrite in presence of chlorine gas. Temp. – 333 K. PD – 10%, Cl<sub>2</sub> flow rate – 400 mL/min.

### 3.2.2 Effect of Temperature

Experiments on the dissolution behaviour of chalcopyrite were carried out at varying temperature between 318K and 348K in the presence of 1.0 N hydrochloric acid, and 400 mL/min chlorine gas flow rate. The data are represented in Fig. 7 (a) for copper and in Fig. 7 (b) for iron. Copper recovery was found to be maximum at 333K and similar leaching behaviour was obtained at temperature 318K and 348K. Recovery of copper at 333K decreases from 82.4% to 76.5% at 318K and 70% at 348K in 1 h duration. Temperature has very marginal effect on iron dissolution in chalcopyrite with chlorine gas. Final recovery at 1 h duration increased from 71.4% to 77.8% with increase in temperature from 318K to 333K. Again iron recovery decreased to 70.6% with further increase in temperature to 348K. Decrease in chalcopyrite dissolution at higher temperature may be due to decrease in the solubility of chlorine gas in the lixiviant.

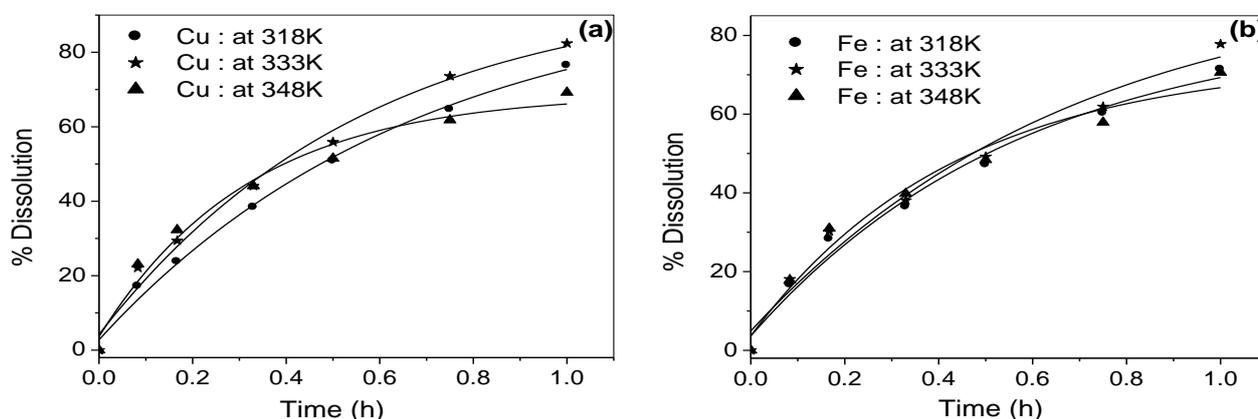


Figure 7. (a) Effect of temperature on dissolution of copper from chalcopyrite in presence of chlorine gas. [HCl].- 1.0 N. PD – 10%, Cl<sub>2</sub> flow rate – 400 mL/min. and (b) Effect of temperature on dissolution of iron from chalcopyrite in presence of chlorine gas. [HCl] - 1.0 N. PD – 10%, Cl<sub>2</sub> flow rate – 400 mL/min.

### 3.2.3 Effect of Sodium chloride

Effect of sodium chloride on dissolution of chalcopyrite in hydrochloric acid media was studied at 333K, 400mL/min chlorine gas flow rate, 10% PD and the results are presented in Fig. 8(a) & Fig. 8(b) for copper and iron respectively. Due to the addition of sodium chloride, it lowers the dissolution of chalcopyrite. The results showed that dissolution of metals decrease with the addition of sodium chloride. Copper recovery decreased from 82.4% to 67.7% with addition of 5% (w/v) of sodium chloride. The percentage dissolution of copper further decreased to only 4.4% with further increase of sodium chloride from 5% (w/v) to 10% (w/v). Similarly with the addition of 5% (w/v) sodium chloride, iron recovery decreases from 77.7% to 74.3% at 1h which further decreases to 70.4% with the addition of 10% (w/v) with addition of 10% sodium chloride. The decrease in dissolution rate of both copper and iron may be due decrease in the solubility of chlorine gas in presence of sodium chloride during leaching.

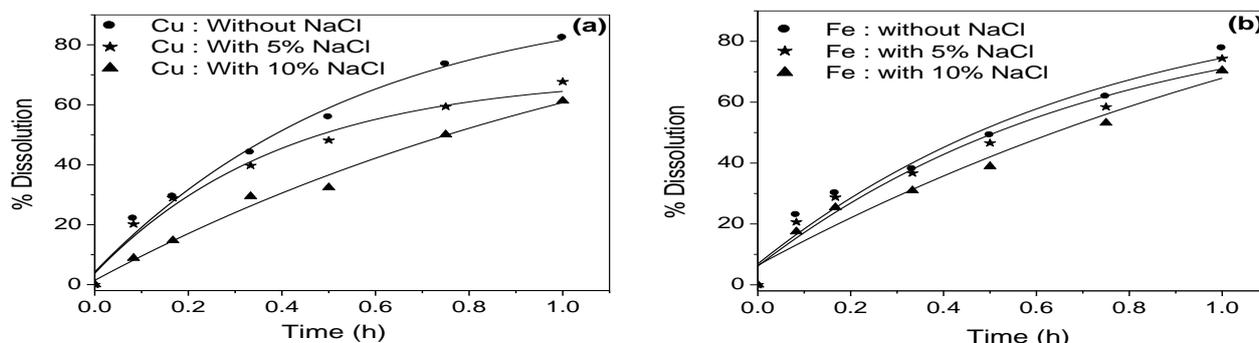


Figure 8. (a) Effect of sodium chloride on copper dissolution during leaching of chalcopyrite in presence of chlorine gas, [HCl]- 1.0 N, PD – 10%, temperature – 333K and Cl<sub>2</sub> flow rate – 400 mL/min. & (b) Effect of sodium chloride on iron dissolution during leaching of chalcopyrite in presence of chlorine gas, [HCl]- 1.0 N, PD – 10%, temperature – 333K and Cl<sub>2</sub> flow rate – 400 mL/min.

#### 4. Conclusion

Systematic investigation on dissolution of copper and iron from chalcopyrite ore in oxygen and chlorine gas atmosphere in different reaction media, the following conclusions may be drawn from this study: Dissolution of copper and iron from chalcopyrite ore in presence of oxygen and chlorine gas is affected in different environments like acid concentration, temperature and presence of sodium chloride. A amount of copper and iron dissolution from chalcopyrite ore is maximum in acidic media in both the cases in oxygen and chlorine gas environment, keeping the other parameters constant. Oxidative dissolution of chalcopyrite in presence of chlorine gas is faster than that in presence of oxygen gas. At 333 K temperature, 10% PD, 400 mL/min. Cl<sub>2</sub> flow rate and 2N HCl in presence of chlorine gas is an optimum condition for leaching. Presence of sodium chloride as a leachant decreases the rate of metal extraction from the chalcopyrite ore both in oxygen and chlorine media. The presence of chloride ions in acidic solution enhances the formation of porous sulfur reaction product that allows the diffusion of reactants through the product sulfur film.

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