

## EFFECT OF MECHANICAL ACTIVATION ON THE KINETICS OF LEACHING OF CHALCOPYRITE IN THE FERRIC SULFATE MEDIA

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**Abstract:** *The kinetics of chalcopyrite leaching in a ferric sulfate media for raw and mechanically activated samples has been investigated. It has been shown that the mechanism of leaching reaction is diffusion through the product layer and does not undergo any change as a result of mechanical activation in a wide range of experimental conditions. Leaching rate is strongly influenced by milling intensity and the effect of ball to powder mass ratio is stronger than milling time. Curve fitting of experimental data shows that leaching rate constant is approximately a linear function of ball to powder mass ratio, while it obeys a power function with regard to the milling time.*

**Keywords:** *Kinetics, Mechanical activations, Chalcopyrite, Milling, Leaching*

### 1. INTRODUCTION

Sulfide minerals are the main sources of copper, from which copper metal is recovered through pyrometallurgical processing. A large volume of environmentally unpleasant SO<sub>2</sub> gas is emitted as a consequence of these pyrometallurgical processes [1]. A reliable option to avoid this pollution is to produce copper by hydrometallurgical methods [2].

Hydrometallurgical extraction of non-ferrous metals from sulfide ores is a technically difficult and economically important task. The more chemically stable the sulfide, the more difficult the extraction is. Thus, either severe reaction conditions have to be applied or the chemical stability of sulfides has to be modified by suitable pre-leaching treatments. The mechanical activation of the ore by intensive milling is one option [3]. Generally speaking, mechanical activation increases the reactivity of the mineral [4]. Its benefits include lowering reaction temperature and increasing the reaction rate and dissolution efficiency, as well as the formation of water soluble compounds [5]. Although milling exerts additional cost due to high energy consumption, it should be noted that it is a conventional step in the preparation of ores for almost all of the hydrometallurgical and pyrometallurgical operations [6,7].

Chalcopyrite (CuFeS<sub>2</sub> or Cu<sub>2</sub>S.Fe<sub>2</sub>S<sub>3</sub>) is the

most abundant copper-bearing mineral. Leaching conditions of chalcopyrite may become less severe if the mineral is first subjected to an ultra-fine milling treatment involving strong impact, such as milling with vibratory or attritor mills. It has been shown that the rate of copper extraction from milled chalcopyrite in vibratory mills increases proportionally with the milling time. Apart from the size reduction, high distortion of the crystal lattice is caused by this type of milling. Distortion of the lattice could be estimated with reference to the reduction of intensity of x-ray diffraction lines [2,8].

Hydrometallurgical treatment of chalcopyrite most frequently takes place by oxidizing leaching with the use of low cost ferric sulfate oxidant which gives the possibility of regenerating the oxidizing agent through reoxidation. The reaction of chalcopyrite with ferric sulfate in acid medium is governed by the following equation:



Attractiveness of the study of the above reaction has been documented in the literature. Present knowledge of the mechanism of this reaction enables us to elucidate some phenomena, as well as the factors influencing the leaching rate of chalcopyrite [9].

It is believed that reaction (1) has a slow kinetics and its rate reduces with time. This has

been ascribed to the formation of a passive layer during leaching in oxidizing conditions. This protective layer inhibits the progress of the reaction. Many studies have been undertaken to elucidate the nature of this passive film and the conditions under which this layer is formed. It has been suggested that it is composed of either non-porous sulfur or an amorphous non-stoichiometric sulfide [10]. If the rate determining step is diffusion within the solid product layer, the overall rate may be enhanced by structural defects [9].

The aim of the present study is to clarify the effect of mechanical activation pretreatment of the chalcopyrite mineral upon its leaching rate and mechanism in the sulfuric acid-ferric sulfate media.

## 2. EXPERIMENTAL

### 2.1. Material

Milling experiments were done on a natural chalcopyrite concentrate obtained by repeated froth flotation of hand-picked ores (Mazra-e mines, south-east Iran). Wet chemical analysis showed that the concentrate contains around 29 percent copper. X-ray diffraction of the concentrate revealed a mineralogical analysis of  $\text{CuFeS}_2$  as the major phase, no other copper-containing mineral was observed [11]. BET surface area of the concentrate before milling was determined to be  $0.3678 \text{ m}^2/\text{g}$ .

### 2.2. Intensive Milling

Intensive milling experiments were carried out in a laboratory 4-cup planetary ball mill (Fara-pajouhesh, Iran) with rotation speed: 600 rpm, rotation mode: direction reversal every 15 minutes, environment: dry milling in air atmosphere and room temperature. The effect of ball to powder mass ratio ( $m_B/m_P$ ) was studied with a constant milling time ( $t_M$ ) of 1 hr and the effect of milling time was investigated with a ball to powder mass ratio of 10.

### 2.3. Leaching

Leaching conditions were set using the results

of a previous study [12] together with those of some preliminary tests. Leaching media was 0.5 M sulfuric acid solution containing 0.4 M ferric sulfate. Pulp density was 1g solid to 200 ml solution. Leaching temperature was changed from 40 to 70 °C and leaching time was varied from 15 min to 7.5 hr.

Copper concentration was determined by an atomic absorption apparatus (Advanta  $\Sigma$ , GBC, Australia).

## 3. RESULTS AND DISCUSSION

XRD patterns of the mechanically activated chalcopyrite shows that the material samples do not undergo any sensible change in crystal structure during high-energy milling as no shift happens to the XRD peaks [11]. Nevertheless, some line broadening and reduction in height of the diffraction peaks due to disordering of crystal structure and some rising of the background owing to the formation of amorphous material can be manifested.

Some examples of the experimental leaching curves (reacted fraction  $\alpha$  against leaching time  $t_L$ ) are typically shown in Fig. 1. Although the rate controlling step of the overall leaching reaction has not been definitely identified, many authors [10,12,13,14] believe that mass transfer through the product layer is the most probable rate limiting step. Fitness of experimental data of the present study showed that this kinetic model has the best fit. Hence, a reduced time plot based on the rate equation with regard to the chemical reaction control ( $1 - (1 - \alpha)^{1/3} = k t_L$ ) and another one with respect to the shrinking core model ( $3 - 2\alpha - 3(1 - \alpha)^{2/3} = k t_L$ ) for diffusion control, have been constructed. These plots are shown in Fig. 2. An important result of this study is that the reaction mechanism does not change under the influence of mechanical activation (different milling times and ball to powder mass ratios) and/or leaching temperature. Values of the apparent rate constants ( $k$ ), obtained from the slope of  $f(\alpha)$  versus  $t_L$  plots, are displayed in the form of 3-D diagrams in figures 3 and 4. Enhanced effects are very clearly seen in these figures. These figures show that leaching rate of chalcopyrite is strongly influenced by intensive

milling (about  $10^5$  times).

The results of rate constant calculation have been summarized in Fig. 5 for different ball to powder mass ratios and in Fig. 6 for different

milling times. These figures generally show the positive effect of increasing ball to powder mass ratio, milling time and leaching temperature.

To investigate the relationship between

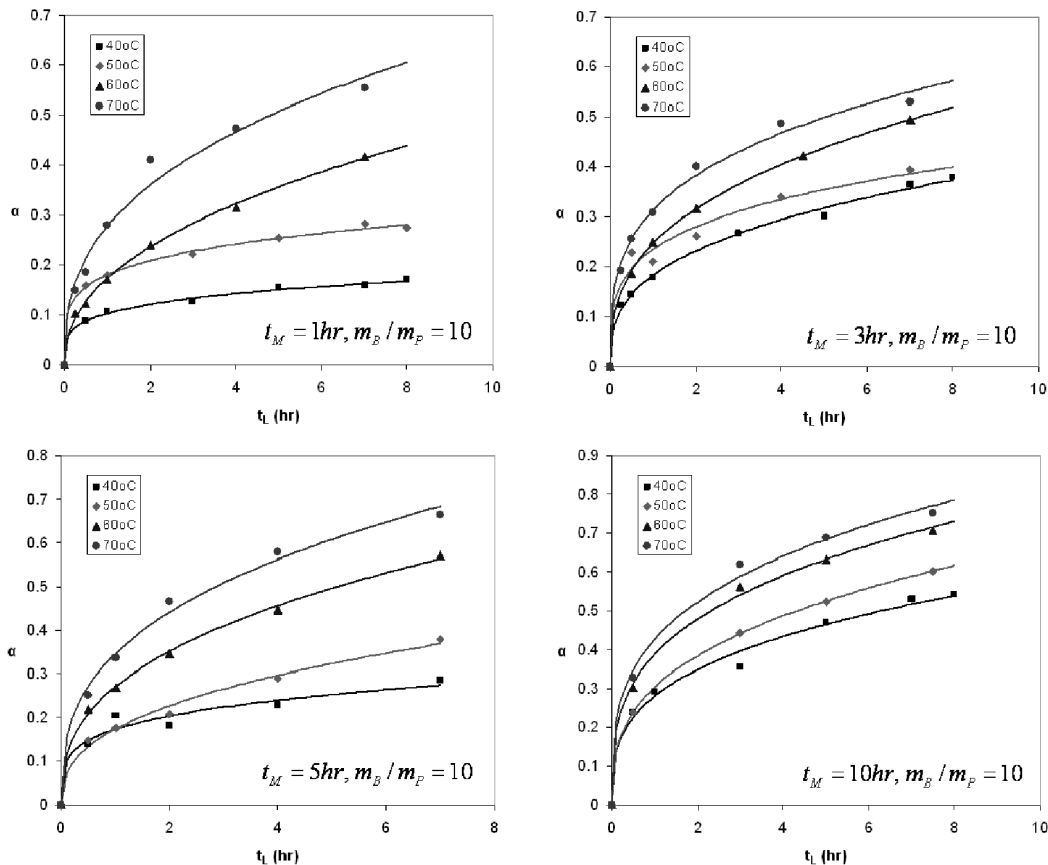


Fig. 1. Typical leaching curves of the activated chalcopyrite.

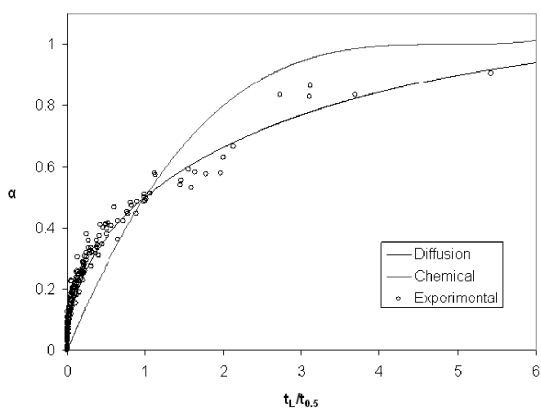


Fig. 2. Examination of reacted fraction ( $\alpha$ )-reduced time ( $t_L/t_{0.5}$ ) data against different rate equations;  $t_L$  is the leaching time and  $t_{0.5}$  is the time required for  $\alpha = 0.5$ .

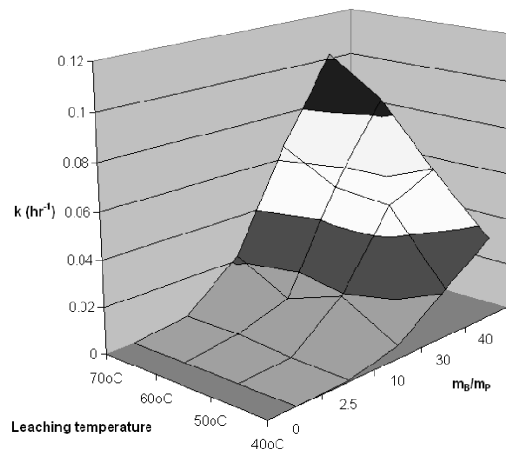


Fig. 3. Effect of ball to powder mass ratio and leaching temperature on the apparent rate constant (milling time: 1 hr).

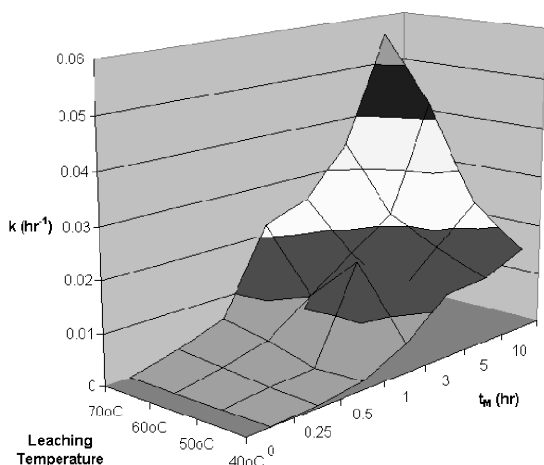


Fig. 4. Effect of milling time and leaching temperature on the apparent rate constant (ball to powder mass ratio of 10).

leaching rate and mechanical activation conditions, rate constants has been plotted against  $m_B/m_P$  with a constant milling time of 1 hr in Fig. 5. With all leaching temperatures, experimental data are best fitted to a linear equation in the form of:

$$k = a \left( \frac{m_B}{m_P} \right) + b \quad (2)$$

where  $a$  and  $b$  are constants. Fig. 5 shows a good fitness of the above equation with experimental data.

Relationship between leaching rate and milling time with a constant ball to powder mass ratio of 10 is illustrated in Fig. 6. For all leaching temperatures, experimental data are best fitted to a power law equation in the form of:

$$k = c t_M^n + d \quad (3)$$

where  $c$ ,  $d$  and  $n$  are constants. As Fig. 6 shows, a relatively good fitness is observed (for all leaching temperature,  $n < 1$ ).

It has been reported that specific milling energy (milling energy divided by mass of the material) is proportionally related to the multiplication of the ball to powder mass ratio and milling time for several milling equipments [15]. Therefore, leaching rate constant has been plotted against  $(m_B/m_P) \times t_M$  in Fig. 7 using the data presented in Table 1. Fig. 7 shows an interesting trend. Values of  $k$  increase up to

$(m_B/m_P) \times t_M = 40$  (related to the test condition of  $m_B/m_P = 40$  and  $t_M = 1$  hr) reaching to a maximum and decrease afterward (e.g.  $m_B/m_P = 10$ ,  $t_M = 5$  hr and  $m_B/m_P = 10$ ,  $t_M = 10$  hr), hence, dividing Fig. 7 into two parts. This behavior shows that  $m_B/m_P$  ratio and  $t_M$  do not have equal effects on the leaching rate and ball to powder mass ratio is more effective than milling time.

#### 4. CONCLUSIONS

1. Leaching rate of chalcopyrite is strongly influenced by intensive milling (about 10.5 times)

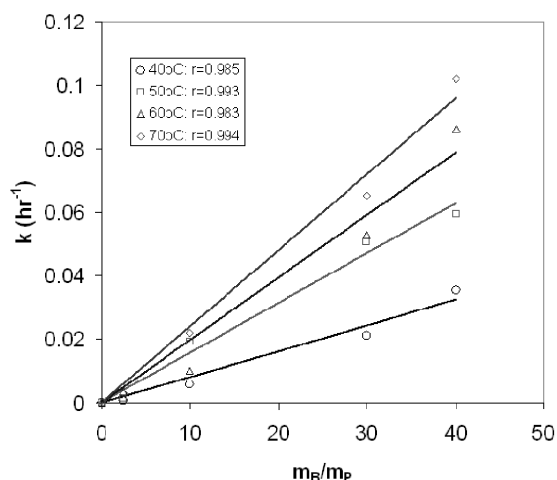


Fig. 5. Leaching rate constant ( $k$ ) as a function of ball to powder mass ratio (milling time: 1 hr).  $r$  is the correlation coefficient.

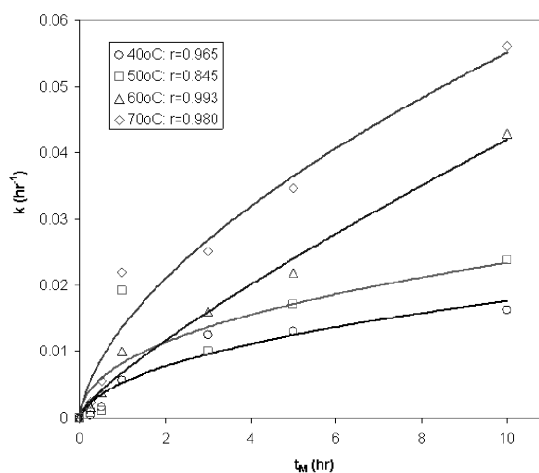


Fig. 6. Leaching rate constant as a function of milling time ( $m_B/m_P = 10$ ).

**Table1.** Values of  $t_M \times (m_B/m_P)$  under different experimental conditions.

Milling time (hr)	Ball to powder mass ratio	$t_M \times m_B/m_P$ (hr)
0	0	0
0.25	10	2.5
0.5	10	5
1	10	10
3	10	30
5	10	50
10	10	100
1	2.5	2.5
1	30	30
1	40	40

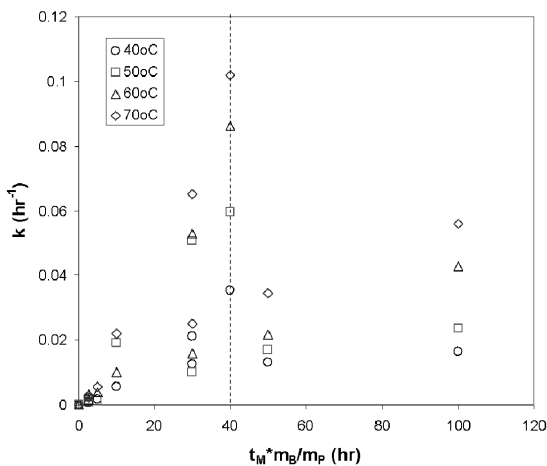
- Rate controlling step of chalcopyrite leaching in sulfuric acid-ferric sulfate media is diffusion through protective product layer and does not undergo any change as a consequence of mechanical activation pretreatment.
- With a constant milling time, leaching rate constant is a linear function of ball to powder mass ratio.
- With a constant ball to powder mass ratio,

leaching rate constant is a power law function of milling time.

- The rate of leaching of mechanically activated chalcopyrite in ferric sulfate media is more strongly influenced by ball to powder mass ratio than the milling time.

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**Fig. 7.** leaching rate constant versus  $t_M \times (m_B/m_P)$ .

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