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Mechanochemical leaching of chalcopyrite concentrate by sulfuric acid

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Abstract: This study aimed to introduce a new cost-effective methodology for increasing the leaching efficiency of chalcopyrite concentrates at ambient temperature and pressure. Mechanical activation was employed during the leaching (mechanochemical leaching) of chalcopyrite concentrates in a sulfuric acid medium at room temperature and atmospheric pressure. High energy ball milling process was used during the leaching to provide the mechanochemical leaching condition, and atomic absorption spectroscopy and cyclic voltammetry were used to determine the leaching behavior of chalcopyrite. Moreover, X-ray diffraction and scanning electron microscopy were used to characterize the chalcopyrite powder before and after leaching. The results demonstrated that mechanochemical leaching was effective; the extraction of copper increased significantly and continuously. Although the leaching efficiency of chalcopyrite was very low at ambient temperature, the percentages of copper dissolved in the presence of hydrogen peroxide (H_2O_2) and ferric sulfate ($Fe_2(SO_4)_3$) after 20 h of mechanochemical leaching reached 28% and 33%, respectively. Given the efficiency of the developed method and the facts that it does not require the use of an autoclave and can be conducted at room temperature and atmospheric pressure, it represents an economical and easy-to-use method for the leaching industry.

Keywords: chalcopyrite; mechanical activation; mechanochemical leaching; sulfuric acid; cyclic voltammetry

1. Introduction

Copper is found in various combinations of Cu, S, Fe, and other elements in nature; among these naturally occurring compounds, chalcopyrite ($CuFeS_2$) is an abundant source that accounts for almost 70% of all copper resources in the world [1]. The pyrometallurgical process is widely used to extract copper from chalcopyrite; however, with increasing worldwide copper production, high-grade copper ores are becoming increasingly scarce, and more sulfur dioxide (SO_2) is being released into the atmosphere. Both circumstances warrant the development of enhanced copper extraction methods [2].

Hydrometallurgical processes are reliable extraction methods that circumvent the aforementioned problems. Sulfate leaching, as a cost-competitive hydrometallurgical method, is categorized into atmospheric-pressure or high-pressure methods and chemical or biological methods [3]. Chalcopyrite, as the most abundant source of copper, is resistant to leaching in sulfate media for two reasons: (1) a passive layer of elemental sulfur, polysulfides, and disulfides forms and (2) chalcopyrite particles are surrounded by liquid elemental sulfur during high-temperature processing. However, researchers disagree about the nature of the passive layer, and no hypothesis has been proposed concerning the formation mechanism of this layer [4]. Nevertheless, numerous successful experiments have been conducted to increase the dissolution of chalcopyrite in sulfate media by exploiting autoclave advancements, the utilization of efficient oxidants, and intensive milling (i.e., the breaking down of a chalcopyrite concentrate to finer particles to increase its surface area and induce defects in its structure) [5].

Hydrogen peroxide is one of the most efficient leaching agents used for both reduction and oxidation in the extraction of uranium, manganese, and silver [6−7]. The chalcopyrite dissolution percentage is directly proportional to the hydrogen peroxide concentration; hydrogen peroxide, as an oxidant, reacts with chalcopyrite in the sulfuric acid solution according to Eq. (1) [8]:

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$$2CuFeS_2 + 2H_2SO_4 + 14H_2O_2 \rightarrow$$
$$2CuSO_4 + Fe_2(SO_4)_3 + 16H_2O + S^o \quad (1)$$

Moreover, many researchers have investigated the effects of $Fe_2(SO_4)_3$ as a low-cost, abundant oxidant in the leaching of a chalcopyrite concentrate [9–12]. The oxidation of chalcopyrite by ferric sulfate in sulfuric acid and the regeneration of Fe^{3+} in the presence of oxygen are governed by equations as follows [3,13]:

$$CuFeS_2 + 2Fe_2(SO_4)_3 \rightarrow CuSO_4 + 5FeSO_4 + 2S^o \quad (2)$$

$$4FeSO_4 + O_2 + 2H_2SO_4 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O \quad (3)$$

Difficulties in extracting copper from chalcopyrite, which stem from its chemical stability, have led to various efforts in developing an effective pre-leaching treatment; a prevalent example of such a treatment is mechanical activation [14]. Senna [15] was the first to investigate the effects of surface area and structural disordering on the leaching efficiency of a mineral activated by milling. These effects in both chloride and sulfate media have been investigated by numerous researchers, and all reported results demonstrate a beneficial effect of mechanical activation on the dissolution of chalcopyrite [16–17]. Table 1 summarizes several reported works on copper extraction from a mechanically activated chalcopyrite concentrate.

Table 1. Summary of some similar results reported by different authors for copper extraction by hydrometallurgical processing under various conditions

Authors and Ref. No.	Leachant used	Solution concentration / M	Temperature / °C	Ball milling time / h	Leaching time / h	Copper extraction / %
Bafghi *et al.* [18]	H_2SO_4	0.5	70	10	8	70
Vafaeian *et al.* [19]	H_2SO_4	0.5	80	6	7	43
Achimovicová *et al.* [20]	H_2SO_4	2	90	0.5	2	34
Palaniandy [21]	H_2SO_4	2	Ambient	ND, 80 kWh/t	120	10
Kamali and Khaki [17]	HCl	0.4	80	24	1	100
Maurice and Hawk [22]	HCl	0.25	90	2.5	5	90

Note: ND—not determined.

As clearly evident Table 1, mechanical activation has been used as an effective pre-treatment for enhancing copper dissolution. In this regard, increasing surface area by decreasing particle size, structural disordering, and defect formation result in an enhanced dissolution of chalcopyrite. However, defects are often short-lived, and thus, they are not present during the leaching step [23]. The novelty of the present research is the study of mechanochemical effects on a chalcopyrite concentrate during sulfate leaching involving high-intensity grinding (using a planetary ball mill), which has not yet been extensively investigated [22]. Thus, the main aim of the present study was to investigate the effects of applying mechanical activation during leaching to eliminate the passive layer, thereby making all excitation states available. It is worth mentioning that this process is believed to increase copper dissolution from a chalcopyrite concentrate at ambient temperature and pressure. Moreover, the effect of using two oxidants on the leaching efficiency is also investigated.

2. Experimental

2.1. Material

The research was conducted on a chalcopyrite concentrate from the Sarcheshmeh Mine in Iran. The elemental composition of the concentrate was determined by X-ray fluorescence (XRF) analysis; the results are shown in Table 2. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis of the as-received concentrate powder indicated the existence of chalcopyrite ($CuFeS_2$), pyrite (FeS_2), and quartz (SiO_2) (Figs. 1 and 2).

Table 2. Chemical composition of chalcopyrite concentrate used in the experiments wt%

Cu	Fe	S	Si	Al	Zn	Mg	K	Others
21.11	31.37	32.95	5.6	1.4	1.6	0.83	0.94	4.2

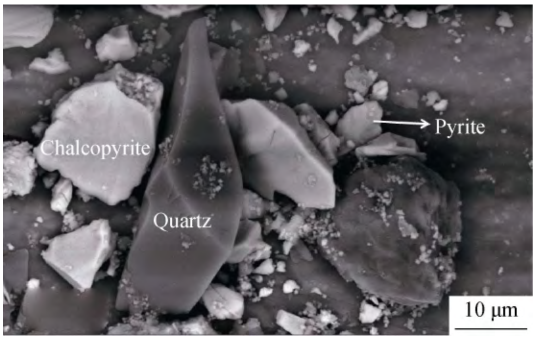

Fig. 1. SEM micrograph of the as-received chalcopyrite concentrate.

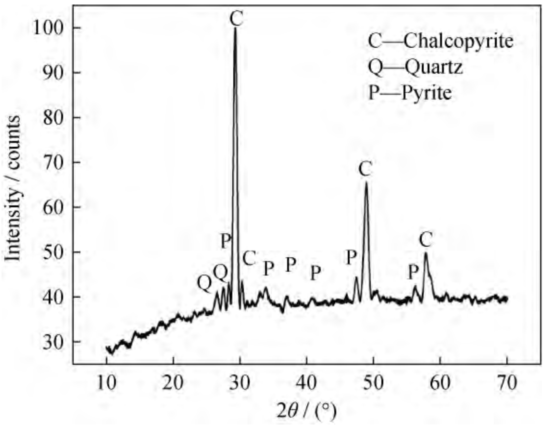

Fig. 2. XRD pattern of the as-received chalcopyrite concentrate.

2.2. Leaching tests

The concentrate powder was mechanically activated using a two-jar planetary ball mill. The jars and milling balls were made of stainless steel, and the diameter of the balls was 10 mm. The rotation speed was 250 r/min, and the ball-to-powder mass ratio was 1:40 for all tests. The milling time was varied from 1 to 20 h, and each sample was leached immediately after activation.

The pre-activated and inactivated concentrate was leached (chemical leaching) by magnetic stirring of the sample in a glass beaker (250 mL). Chemical leaching was performed under conditions as follows: pulp density, 1:40 g/mL; H_2SO_4 concentration, 9 M; temperature, 25°C (for all tests).

Mechanochemical leaching experiments were performed on the chalcopyrite powder concentrate in steel jars (two jars, each with 295 mL volume) coated with a polymeric material to inhibit the corrosion of the jar in acidic media. Leaching was performed under conditions as follows: eight zirconia balls of 18 mm diameter were used, and the mass of each ball was 18.5 g; pulp density was 1:40 g/mL; H_2SO_4 concentration was 9 M; temperature was 25°C; and rotational speed was 250 r/min. Moreover, leaching was performed under air atmosphere. In the same investigation, $Fe_2(SO_4)_3$ and H_2O_2 were used as oxidants to compare their effects on leaching behavior in each method. The concentration ranges of $Fe_2(SO_4)_3$ and H_2O_2 were 0–0.3125 M and 0–1.5 M, respectively.

2.3. Characterization

XRD analysis was performed using a Philips PW1800 diffractometer equipped with a Cu K_α radiation source. Micrographs of the morphology of the activated and inactivated samples were obtained using a Leo 1450VPSEM set. XRF (Philips PW1404) analysis was performed to determine the chemical composition of the as-received chalcopyrite.

The concentration of the copper dissolved in solutions was measured using an atomic absorption spectrometer (SHIMADZU AA 6800). The extraction percentage of copper was obtained by the following equation:

$$\text{Copper extraction} = \frac{C_1 v}{C_2 w} \times 100\% \qquad (4)$$

where C_1 is the copper concentration in diluted solution, g/L; v is the volume of diluted solution, L; C_2 is the copper concentration in the chalcopyrite concentrate, wt%; and w is the mass of concentrate used in each leaching test, g.

2.4. Electrochemical tests

A total of 0.6 g of graphite was mixed with 2.4 g of activated chalcopyrite in an agate mortar. Silicone oil (0.8 mL) was then added to the resulting powder, and the resulting mixture was mixed until a homogeneous paste was obtained. The paste was then placed inside a plastic tube with a diameter of 0.4 cm and a length of 7 cm; the tube was equipped with a plunger to remove the already-reacted paste (Fig. 3) and with a glass spatula to level the paste. With this setup, the surface could be renewed in each experiment. Electrical contact was achieved with a platinum wire. The method of carbon paste electrode (CPE) preparation has been recommended and previously confirmed [24−25].

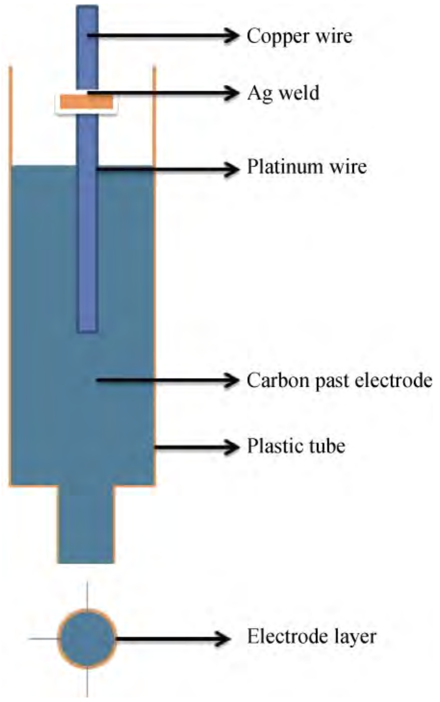

Fig. 3. Schematic of the carbon paste electrode.

All electrochemical experiments were performed at 25°C using a Biologic SP-300 potentiostat/galvanostat controlled by EC-Lab software (version 10.39, Biologic SAS). A conventional three-electrode electrolytic cell was used for electrochemical analysis. A graphite counter electrode and a glass Ag/AgCl reference electrode filled with saturated KCl solution were used. The initial solution was 200 mL of 9 M H_2SO_4, which was prepared by diluting reagent-grade sulfuric acid in desalinated water.

3. Results and discussion

3.1. Effects of activation on structure and particle size

Ball milling (BM) was performed at five time intervals: 1, 3, 5, 10, and 20 h under the conditions described in section 2.2. Samples activated for 10 and 20 h were analyzed by XRD, and the resulting patterns were compared with that of the primary concentrate (Fig. 4). This comparison revealed that, with increasing activation time, some peaks broadened and the intensity of the diffraction peaks decreased, particularly until 10 h activation; these effects are a consequence of disordering of the mineral structure [26]. Moreover, the increased intensity of the background from 30 in the pattern of the first sample to 50 in the pattern of the second sample is attributed to a reduction in the proportion of crystalline phase and to the formation of an amorphous structure with increasing activation time [18−19]. SEM images of the unmilled and 5 h activated concentrates are shown in Fig. 5. As evident in the figure, an increase in milling time from 0 to 5 h resulted in a decrease of the particle size in the concentrate from an average size of 50 μm to an average size of 10 μm. Moreover, slight agglomeration was observed after 5 h. This result is consistent with those reported by Baláž [27] and Emami *et al.* [28].

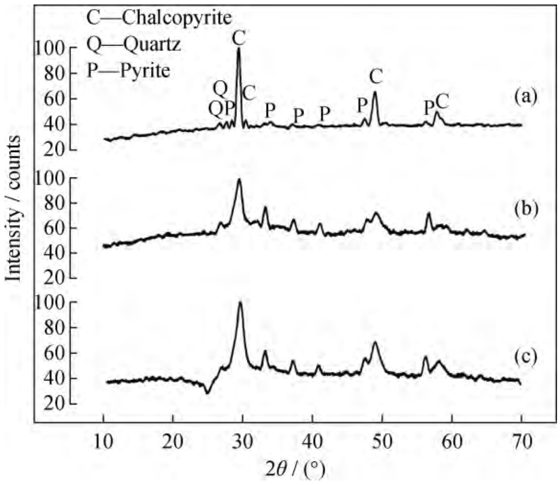

Fig. 4. Comparison of the XRD patterns of chalcopyrite concentrate as-received (a) and subjected to mechanical activation for 10 h (b) and 20 h (c).

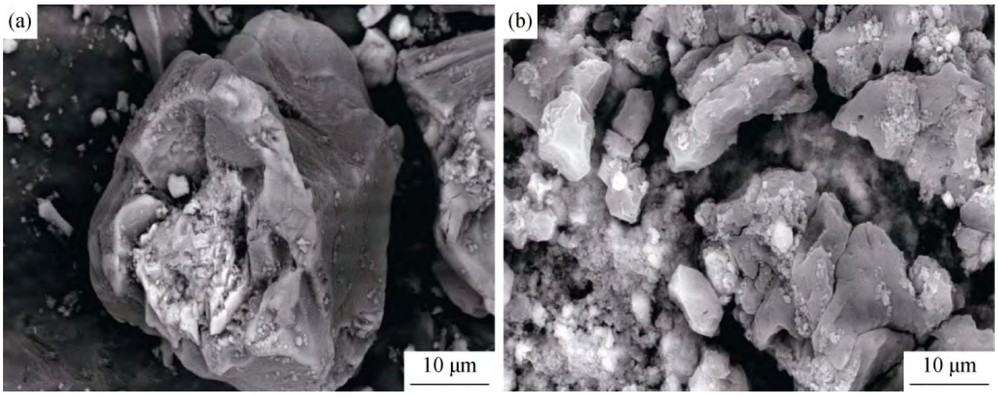

Fig. 5. SEM micrographs of unmilled concentrate (a) and concentrate milled for 5 h (b).

3.2. Effects of activation on leaching efficiency

As outlined in section 2, two methods of leaching were used in this study. To investigate the effects of activation on the leaching efficiency, all of the activated concentrate samples were leached in stirrer mode under the conditions described in section 2.2; the results are presented in Fig. 6. Achimovicová *et al.* [20] predicted that the dissolution of a chalcopyrite concentrate without activation and in the absence of an oxidizing agent at ambient temperature would be negligible. As evident from the results, increasing the activation time from 0 to 10 h positively affected the extraction of copper from chalcopyrite. This increase in copper extraction is related to (1) an intensive enhancement in reactivity of the particles due to the lattice defects formed on their surface [29], (2) lattice distortions of the mechanically activated concentrates, and (3) a reduction in particle size and subsequent formation of amorphous chalcopyrite phases. Figs. 4–5 confirm the validity of these claims. After 20 h of mechanical activation, the maximum amount of copper extracted dramatically decreased. This intense decrease is attributed to the production of elemental sulfur due to the formation of reactive sites on the surface of activated chalcopyrite particles after 20 h of activation; this elemental sulfur creates unsuitable conditions for the leaching step [30]. The intense decrease in the amount of copper extracted is also attributed to the agglomeration of chalcopyrite particles in the sample activated for 20 h before (Fig. 7) and after leaching. Vafaeian *et al.* [19] have reported similar results.

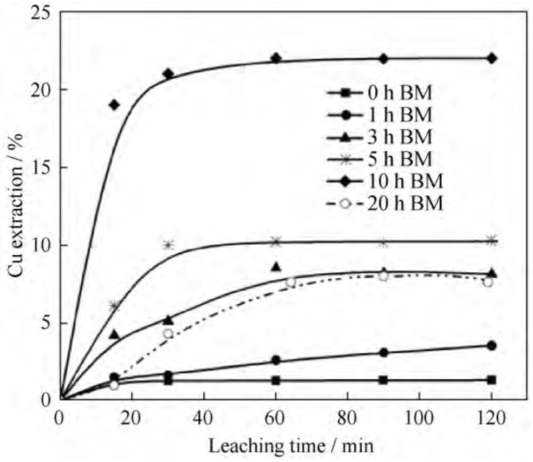

Fig. 6. Effect of mechanical activation on the leaching efficiency.

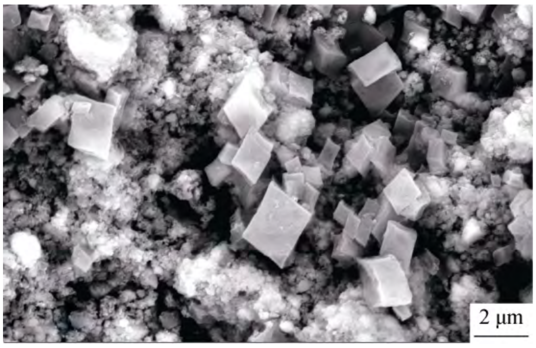

Fig. 7. Chalcopyrite fine particles and formation of agglomerates in chalcopyrite concentrate ball-milled for 20 h.

In the case of the samples ball-milled for 1, 3, and 5 h, the time required to complete the leaching tests was reduced from more than 120 min to only 30 min. In general, the greatest copper extraction, 22%, corresponds to activation time and leaching time of 10 h and 1 h, respectively. The decrease in the rate of copper dissolution with increasing leaching time, which was observed in all of the leaching experiments, is associated with the formation of sulfur and polysulfide layers. These insulating layers hinder the transfer of electrons that would reduce ferric ions [1].

3.3. Electrochemical measurements

Fig. 8 shows the current density of immersed chalcopyrite vs. time. This plot reveals that the formation of a passive layer on chalcopyrite causes a significant reduction in current density before the steady-state condition is reached. This behavior is observed in both the mechanically activated concentrate and the non-activated concentrate. The difference is that the mechanically activated samples reached the steady-state in a shorter time. As previously mentioned, the activated samples contain a larger amount of defects; therefore, the rate of the reactions that lead to the formation of passive layers is greater and the passive layers form faster. Notably, after the formation of the passive layer, the rate of leaching is controlled by the diffusion of reactant components through the passive layer, which then results in the steady-state condition.

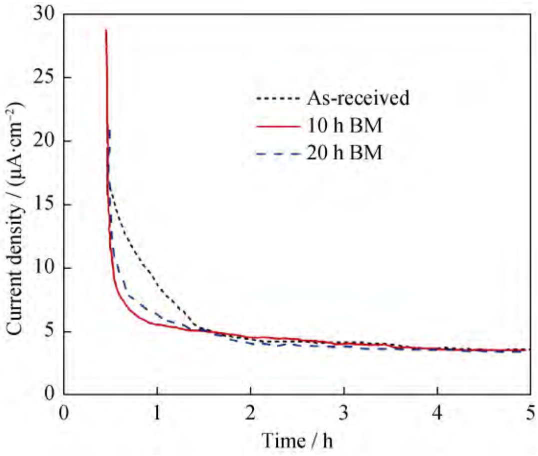

Fig. 8. Current density vs. time for a carbon paste electrode (CPE) immersed in 9 M H_2SO_4.

The cyclic voltammograms of the activated electrodes and the given powders in the range from 0.6 to 1.5 V are both shown in Fig. 9. Fig. 9(a) shows an anodic peak in this voltage range. However, in Fig. 9(b), this peak is no longer observed. The anodic peak at 1.15 V has been attributed to the following reaction [31−32]:

$$CuFeS_2 \rightarrow CuS_2^* + Fe^{2+} + 2e^- \tag{5}$$

The initial chalcopyrite dissolution has been suggested to result in the formation of a metastable copper sulfide phase (by preferential dissolution of iron over copper) with a stoichiometry of Cu:2S, appearing as CuS_2^* [31]. The formation of the passive layer and the accelerated formation of this layer in mechanically activated cases are consistent with the observations that the peak is not formed under the steady-state condition (Fig. 9(b)) and that the activated samples exhibit greater currents at the beginning of the immersion (Fig. 9(a)). Moreover, the cyclic voltammetry samples exhibit higher currents before the formation of passive layers. These two points demonstrate the positive effect of

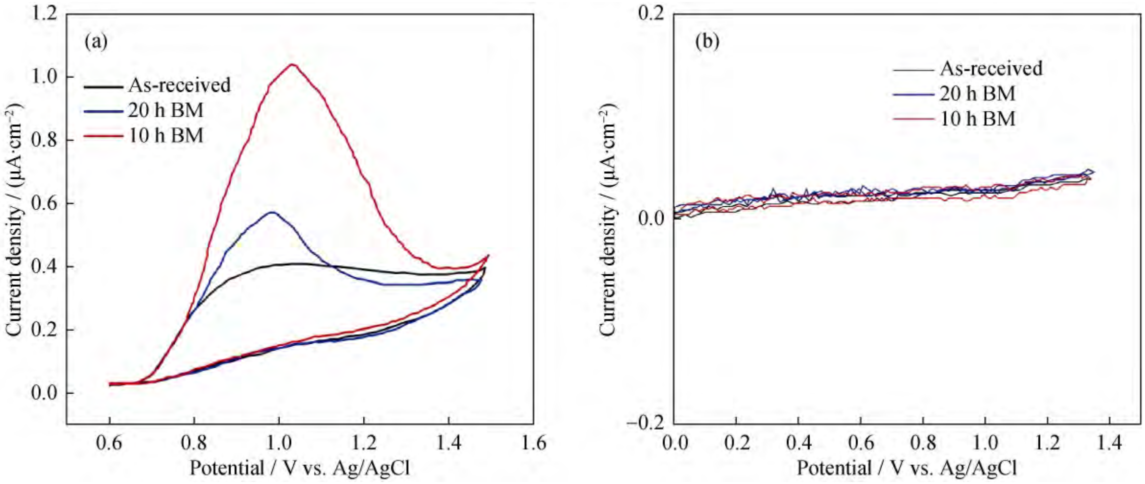

Fig. 9. Cyclic voltammograms of carbon paste electrodes (CPEs) in 9 M H_2SO_4: (a) 10 min after immersion and (b) 10 h after immersion.

mechanical activation on the dissolution of chalcopyrite and can confirm the Cu-ion extraction percentages in activated concentrates.

As is evident in Fig. 8, the initial current density of the sample activated for 20 h is less than that of the sample activated for 10 h, which may be due to the formation of elemental sulfur during ball milling when the activation time is increased. Fig. 9(a) also confirms that the elemental sulfur produced by ball milling in a sample subjected to 20 h of activation causes a lower current density by increasing the voltage in comparison to that of the sample subjected to 10 h of activation. All of these results are consistent with the results in Fig. 6.

3.4. Mechanochemical leaching

To investigate the effect of mechanochemical leaching on extracted copper ions in a solution, we performed ball milling and chemical leaching simultaneously in a single step. Fig. 10 compares the test results of mechanochemical and chemical leaching. As evident in the figure, the extraction percentage of copper reached 18% after 30 h in the case of the mechanochemical method; by contrast, in the case of chemical leaching of the inactivated concentrate, only 4% of copper was leached during the same time. The main point is that, in the first method, the amount of copper recovered tended to consistently increase, in contrast to the case of stirrer leaching, where the amount reached a maximum and then remained steady for the both activated and inactivated samples. The results of this comparative experiment reflect the beneficial effects of combining ball milling and leaching. As previously mentioned, subjecting the concentrates to ball milling for more than 10 h negatively affected subsequent leaching (Fig. 6). However, in the case of mechanochemical leaching, the amount of copper recovered continuously increased because of the elimination of the passive layer through the collision of the balls with concentrate particles and because the short-lived and metastable defects were exploited; by contrast, these defects remain unused in chemical leaching because of a time gap between the activation and leaching steps [23].

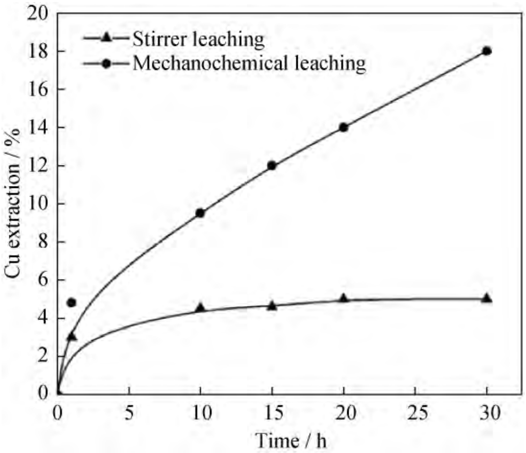

Fig. 10. Effect of mechanochemical and stirrer leaching on copper extraction at 25°C and in 9 M H_2SO_4.

Chalcopyrite concentrate leaching was performed in the presence of H_2O_2 and $Fe_2(SO_4)_3$ for both mechanochemical and stirrer leaching for a constant time of 20 h. As evident from Fig. 11, the extraction percentage of copper increased as the H_2O_2 concentration was increased in both leaching methods. Compared to the stirrer leaching method, where the maximum amount of extracted copper was 8% or less, mechanochemical leaching proved to be far more effective, with the maximum amount of extracted copper reaching 28% (Fig. 11). Almost every strong oxidizer will oxidize sulfide to sulfur at low temperatures. The mechanism of the reaction between sulfide and hydrogen peroxide is given in Eqs. (6)–(8). In the first step, H_2O_2 dissociates into highly reactive radicals (in diluted solutions) [33]:

$$H_2O_2(aq) \Leftrightarrow H^+(aq) + HO_2^-(aq) \tag{6}$$

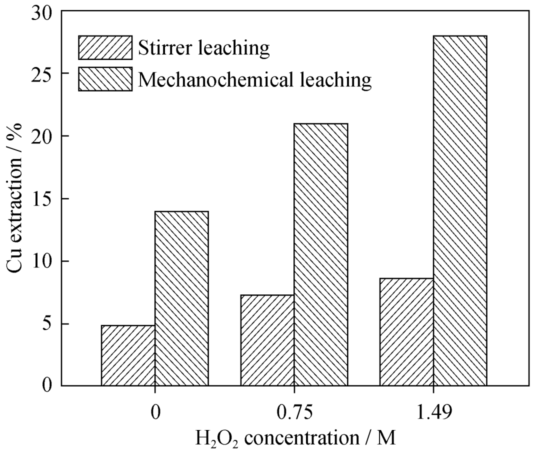

Fig. 11. Effect of hydrogen peroxide concentration on copper extraction in mechanochemical leaching for 20 h, at 25°C, and in 9 M H_2SO_4.

In the next step, reactive radicals oxidize sulfide ions according to Eq. (7):

$$HO_2^-(aq) + S^{2-}(s) + 3H^+ \rightarrow S(s) + 2H_2O \tag{7}$$

Meanwhile, copper reacts with sulfate:

$$Cu^{2+}(aq) + SO_2^{2-}(aq) \rightarrow CuSO_4(aq) \tag{8}$$

The results in Fig. 11 show that hydrogen peroxide influenced both leaching procedures; however, because of the regeneration of new surfaces through elimination of the sulfur layer and crushing of the particles into finer particles in mechanochemical leaching mode, the peroxide radicals react much better with sulfide ions on the surface of concentrate particles in comparison to radicals that diffuse thorough passive layers, as in the case of stirrer leaching.

Fig. 12 presents the data obtained during chalcopyrite concentrate leaching in the presence of Fe^{3+} ions. The addition of $Fe_2(SO_4)_3$ as an oxidant resulted in substantial increases in copper extraction in mechanochemical leaching. When the Fe^{3+} concentration was increased, the copper extraction reached almost 32%. Conversely, when the same conditions were applied to stirrer leaching, the obtained extraction percentage was 6% or less. The addition of ferric sulfate as an oxidant at concentration up to 0.1 M noticeably increased the chalcopyrite leaching in sulfate media. Higher concentrations, however, had no or even a negative effect on the chemical leaching efficiency. In our research adding $Fe_2(SO_4)_3$ almost has no effect on copper extraction in stirrer leaching.

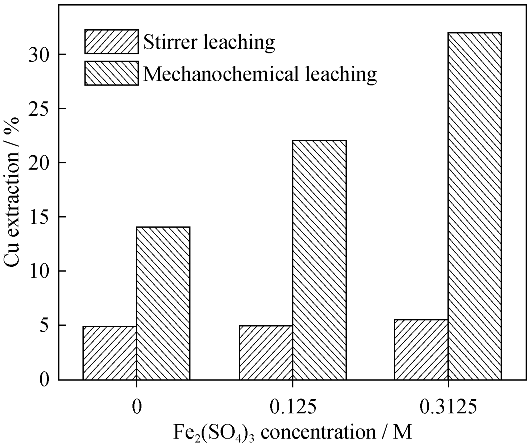

Fig. 12. Effect of ferric sulfate concentration on copper extraction in mechanochemical leaching for 20 h, at 25°C, and in 9 M H_2SO_4.

Hirato *et al.* [13] have attributed this diminishing effect on the leaching efficiency to the distribution of the Fe^{3+} species in the H_2SO_4–$Fe_2(SO_4)_3$ solution systems. The components present in these systems are Fe^{3+}, $FeHSO_4^{2+}$, and $FeSO_4^+$; the first two species may be more easily reduced (i.e., they are strong and effective oxidants) than the last species [34]. Consequently, the amount of Fe^{3+} added to the solution should be adjusted to ensure the control of the amount of $FeSO_4^+$ generated.

Copper dissolution increased when more $Fe_2(SO_4)_3$ was added (even when the $Fe_2(SO_4)_3$ concentration exceeded 0.1 M) in mechanochemical leaching experiments. As previously outlined, the main reason for this behavior is that, through elimination of the passive layer, the oxidant can interact with new surfaces instantaneously.

4. Conclusion

Pre-activation of chalcopyrite concentrates for 0 to 10 h, where the pre-activation was conducted before chemical leaching, caused an increase in copper dissolution, which remained steady after 2 h of chemical leaching at ambient temperature and pressure. Nevertheless, ball milling for more than 10 h was demonstrated to adversely affect the dissolution rate in the subsequent leaching step. This negative effect was linked to the formation of elemental sulfur by ball milling for 20 h and to the agglomeration of particles, which was observed in electrochemical tests and SEM micrographs. Although the results obtained in this study indicate a negligible rate of chemical leaching (stirrer leaching) for a chalcopyrite concentrate at room temperature and atmospheric pressure, in mechanochemical leaching, copper extraction increases continuously during all of the leaching steps and reaches 18% after 30 h of leaching at 25°C and atmospheric pressure. This behavior is concluded to result from the elimination of the passive layer during sulfate leaching. Furthermore, the presence of ferric sulfate and hydrogen peroxide as oxidants significantly increased the rate of copper extraction up to 33% and 28%, respectively, after 20 h of leaching. The results of this study provide a framework for future studies to investigate the kinetics of mechanochemical leaching; moreover, studies of the effects of other significant parameters such as the acid concentration, ball-to-powder mass ratio, etc., could lead to further increases in the dissolution rate of copper in solution.

Acknowledgements

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