



Agglomeration–aggregation and leaching properties of mechanically activated chalcopyrite

Su-xing ZHAO, Gai-rong WANG, Hong-ying YANG, Guo-bao CHEN, Xue-min QIU

School of Metallurgy, Northeastern University, Shenyang 110819, China

Received 28 May 2020; accepted 24 December 2020

Abstract: The effect of mechanical activation on the granulometric parameters, microstructure, and leaching efficiency of chalcopyrite was evaluated, and the occurrence/transition of agglomeration and aggregation was discussed. The results showed that in 8 h of milling treatment, the agglomeration and the microstructure did not affect each other. However, with prolonging milling time, the crystallite size tended to reach a saturation value, and the stagnating microstructural changes led to the replacement of agglomeration by aggregation. The leaching results indicated that the mechanical activation can strongly enhance the reactivity of chalcopyrite and the hindering effect of aggregation on leaching was considerably greater than that of agglomeration. Consequently, after 8 h of milling, the maximum Cu leaching rate of 80.13% was achieved after 4 h of acid leaching.

Key words: chalcopyrite; mechanical activation; agglomeration; aggregation; leaching

1 Introduction

Chalcopyrite is the most abundant copper resources, which is mainly treated by pyrometallurgical methods. With the reduction of high-grade copper resources and increased environmental regulation, the hydrometallurgical approaches become more important due to their economic and environmental advantages, such as the low-cost of processing, and the absence of harmful gas emissions [1]. However, the chalcopyrite leaching performance is negatively affected by the formation of surface passive layers [2] containing compounds such as polysulfides, elemental sulfur allotropes and jarosite [3], limiting the application of hydrometallurgical treatments. Many attempts have been made to solve this problem including the use of non-sulfate oxidants [4], bioleaching [5] and catalysts [6]. However, these methods still have the drawbacks of long leaching time, high-cost and/or

low-leaching rates.

The fine milling is an effective method to promote leaching processes [7]. Finely milled chalcopyrite particles ($<20\ \mu\text{m}$), however, are known to become passivated shortly after the initiation of the leaching process [8]. It should also be mentioned that the mechanical activation (MA) caused by the high-energy ball milling process often changes the microstructure and surface properties of the ball-milled materials [9]. MA can promote the chalcopyrite leaching performance [7,10], thus providing an efficient and low-cost alternative for traditional pressure leaching methods [11].

It is worth mentioning that the effect of MA on chalcopyrite leaching can be explained based on the increase of the specific surface area [12], distortion of the crystal structure [13], the surface oxidation [14], and the increase of amorphization degree [15]. On the other hand, the leaching performance is known to decrease for prolonged-milled samples, which is attributed to the

occurrence of agglomeration in the milled samples [16].

JUHÁSZ and OPOCZKY [17] suggested distinguished three stages of interaction between the particles in fine milling, namely, adherence, aggregation, and agglomeration. They also reported that the MA and microstructural changes only occur at the last agglomeration stage. It should be considered that with the development of milling technologies, MA could take place within a few minutes of milling. In this case, the aggregation and agglomeration are frequently interchanged, and therefore, the three-stage mechanism mentioned above is not clearly distinguishable.

Agglomeration can be defined as the clustering of ground particles, which are held together by physical interactions in order to reduce their surface free energy. The bonding of agglomerates is weak and can usually be readily broken [18,19], which makes it difficult for agglomeration to dramatically affect the reactivity of materials [20]. In contrast, the aggregation is defined as the clustering of particles interconnected by chemical bonds. This interparticle bonding is strong, and provides a barrier for the accessibility of the internal surfaces for the leaching agents [18], which may seriously counteract the positive influence of MA on leaching.

In this study, the MA of chalcopyrite concentrate using a planetary ball mill, and its effects on the subsequent leaching process were reported. Particular emphasis was put on the distinguishment of agglomeration and aggregation by the analysis of granulometric parameters and microstructure. Meanwhile, the effects of agglomeration and aggregation on the reactivity of chalcopyrite were also investigated, and a considerable leaching rate was obtained.

2 Experimental

2.1 Materials

The chalcopyrite concentrate used in this study was obtained from Shenyang, China. The chemical composition of the sample was measured by XRF (ZSX100e, Japan) to be 28.4 wt.% Cu, 30.0 wt.% Fe, 35.7 wt.% S, and 4.3 wt.% Si.

2.2 Experimental methods

A laboratory high energy ball milling equipment (QM-3SP2 planetary mill, China) was

used in this study for MA. Four 100 mL jars of ZrO_2 , charged with 4 and 12 ZrO_2 balls with diameters of 20 and 5 mm, respectively, were used as the milling medium [21,22]. The ball-to-powder mass ratio was constant at 20:1 and the milling speed was kept at 400 r/min. The rotation direction was reversed every 15 min for different milling periods from 10 min to 10 h. The milling was operated at ambient temperature. After milling, the received samples were washed, filtered, dried, sealed in plastic bags, and stored at -37°C .

2.3 Analytical methods

The particle size distribution (PSD) of non-activated and activated samples was measured by a laser particle size analyzer (Malvern Instruments Mastersizer 3000). The uniformity (U), span (S), and specific granulometric surface area (S_G) were calculated according to the following formulas [23]:

$$U = \frac{\sum x_i |D_{50} - D_i|}{D_{50} \sum x_i} \quad (1)$$

$$S = \frac{D_{90} - D_{10}}{D_{50}} \quad (2)$$

$$S_G = \frac{6}{\rho D_{3,2}} \quad (3)$$

where x_i and D_i are the volume fraction and mean diameter in class i , respectively, D_{10} , D_{50} , and D_{90} are related to the particle sizes below which 10%, 50%, and 90% of particles exist, ρ is the density of particles, and $D_{3,2}$ is the surface area moment mean diameter.

The specific surface areas of the initial and milled minerals were measured by the BET method (N_2 adsorption) using a surface area and porosity analyzer (ASAP 2460, Micromeritics, USA). The micromorphology was evaluated by SEM (SIGMA 300, ZEISS, Germany). The mineral phases were analyzed by X-ray diffractometer (XRD) (XRD-7000, Shimadzu, Japan) with $\text{Cu K}\alpha$ radiation ($\lambda=0.154$ nm). The XRD patterns of the samples were recorded using a step size of 0.0200° and a counting time of 30 s/step at 40 mV and 30 mA. The X Powder 12 software was used for qualitative and quantitative characterization such as peak search and phase identification. The amorphization degree of the samples during MA was calculated according to the following equation [24]:

$$A=100-X=100-\left(\frac{U_0 I_X}{I_0 U_X}\right) \quad (4)$$

where A is the amorphization degree and X is the degree of crystallinity, U_0 and U_X are the background intensities of non-activated and activated samples, while I_0 and I_X are the integral intensities of non-activated and activated samples, respectively.

2.4 Acid leaching

The leaching experiments were conducted at 80 °C in a 250 mL baker containing 200 mL of leaching solution (0.5 mol/L H_2SO_4 + 0.5 mol/L NaCl) and 1 g of the chalcopyrite sample. The stirring speed was set at 200 r/min [25]. The Cu^{2+} concentration in solutions was measured by the atomic absorption spectroscopy (AAS, Varian 220Z, Australia). The leaching rate of copper $\varepsilon_{Cu^{2+}}$ was obtained using the following equation:

$$\varepsilon_{Cu^{2+}} = \frac{\rho_1 V}{xm} \times 100\% \quad (5)$$

where ρ_1 is the Cu^{2+} concentration in leaching solution (g/L), V is the volume of leaching solution (L), x is the copper content in the chalcopyrite concentrate (wt.%), and m is the mass of concentrate used in each leaching experiment (g).

3 Results and discussion

3.1 Particle size and surface area

Figure 1 shows the PSD of non-activated and activated samples as a function of the milling time, and the corresponding changes of granulometric parameters such as D_{10} , D_{50} , D_{90} , $D_{3,2}$, $D_{4,3}$ (volume moment mean diameter), U , and S are shown in Table 1.

It can be found from Fig. 1 and Table 1 that, the particle sizes of the activated samples decrease rapidly after 10 min of MA. Also, the reductions in the uniformity (U) and span (S) observed in Table 1 suggest that an overall comminution has occurred in the first 10 min. In this period, the particle size distribution is characterized as strong unimodal

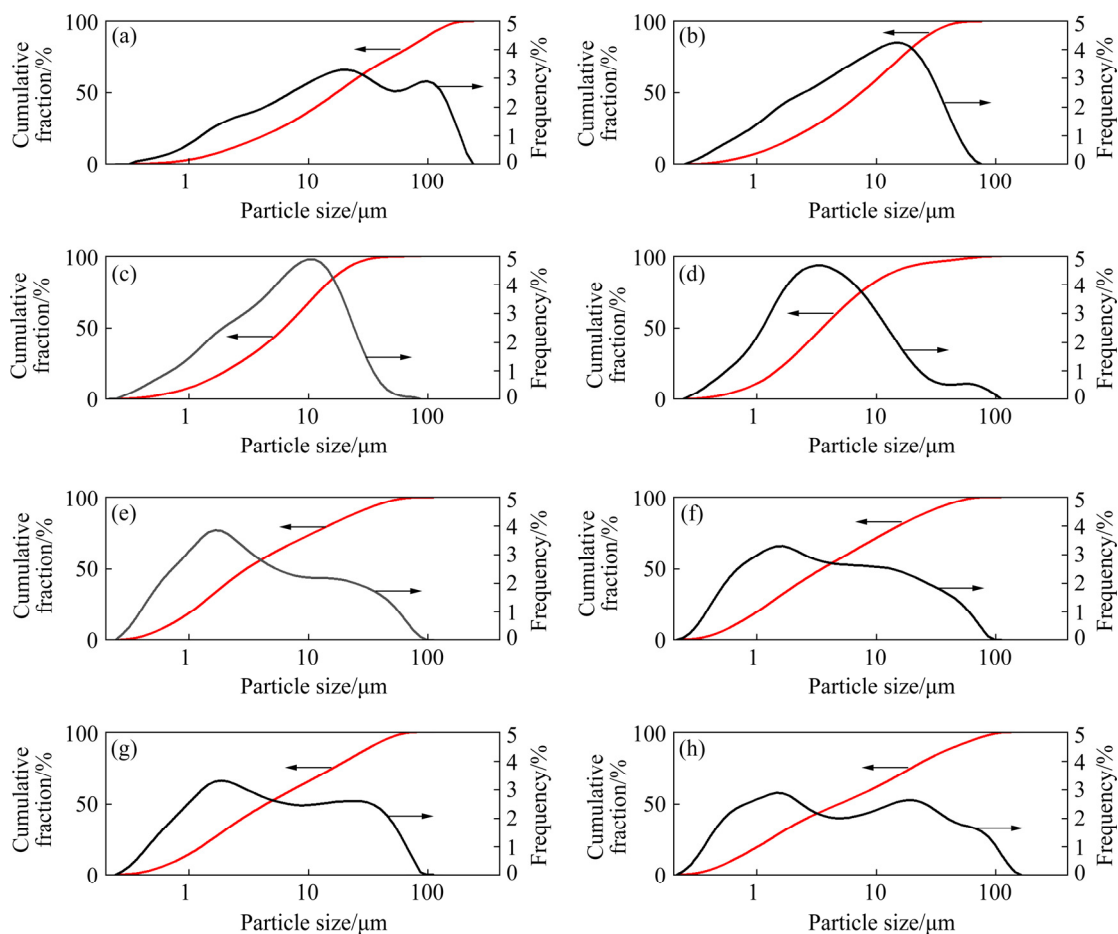


Fig. 1 Particle size distributions of chalcopyrite samples milled for different periods: (a) Non-activated (0 min); (b) 10 min; (c) 15 min; (d) 60 min; (e) 240 min; (f) 360 min; (g) 480 min; (h) 600 min

Table 1 Particle size distribution and surface area of non-activated and activated chalcopyrite samples

Milling time/min	$D_{10}/\mu\text{m}$	$D_{50}/\mu\text{m}$	$D_{90}/\mu\text{m}$	$D_{3,2}/\mu\text{m}$	$D_{4,3}/\mu\text{m}$	U	S
0	2.34	19.50	115.00	6.40	40.00	1.66	5.77
10	1.34	8.41	30.40	3.48	12.60	1.08	3.45
15	1.33	7.11	22.20	3.31	9.90	0.94	2.94
60	1.08	4.00	17.10	2.48	8.13	1.52	4.01
120	0.80	2.91	25.90	1.94	8.73	2.48	8.60
240	0.81	3.30	30.70	2.04	10.40	2.66	9.08
360	0.76	3.41	30.60	1.97	10.20	2.53	8.74
480	0.73	3.69	31.60	1.99	10.80	2.49	8.53
600	0.71	5.60	52.40	2.07	17.30	2.76	9.24

with gentle left slope and sharp right slope, showing that the fracture mechanism is shattering [26].

After 15 min of MA, the left half of the PSD curve and D_{10} change slightly, while the right half of the PSD curve moves toward left and the other parameters decrease, indicating the continuous comminution of the sample. However, a little tail appears in the rightmost curve, and the maximum particle size increases from 58.90 to 76.00 μm , indicating the occurrence of agglomeration and the first apparent grinding limit [27]. With increasing the MA time to 60 min (1 h), the little tail is replaced by a new peak, leading to the transformation of unimodal distribution into a bimodal one. However, the D values in Table 1 keep decreasing, especially for the D_{90} . It should be noticed that the effect of dry milling on PSD includes two elementary counteracting processes, namely breakage and agglomeration [28], and the relative proportions change with milling time. With 240 min (4 h) of milling, the bimodal distribution becomes more obvious. The main peak representing fine particles shifts towards left and the tail peak representing agglomerated particles keeps increasing, indicating that the proportions of fine and agglomerated particles increase simultaneously with prolonging time [29]. During 240–480 min (4–8 h) of milling, the main peak stops shifting and its height declines, while the peak of agglomerated particles heightens slowly. Meanwhile, the stable D values indicate that the milling enters a state of dynamic equilibrium [18].

After 10 h of milling, the existence of breakage is still manifested by the decreased D_{10} . Meanwhile, the PSD curve extends towards the right and the bimodal distribution transforms into a trimodal one. By this time, D_{50} , D_{90} , $D_{4,3}$ (Table 1),

and the maximum particle size (Figs. 1(g, h)) increase from 3.60, 31.60, 10.80, and 86.40 μm (8 h) to 5.60, 52.40, 17.30, and 144.10 μm , respectively. The dramatic increase in PSD is drastically different from that of the dynamic equilibrium in the agglomeration state, which may be due to the occurrence of aggregation.

For a better distinction of the agglomeration and aggregation, the specific surface areas at different milling time were measured, and results are shown in Fig. 2. As can be observed, both S_G and BET surface area (S_{BET}) dramatically increase after milling, because the comminution intrinsically increases the surface area. When comparing the results obtained up to 8 h, it is obvious that the S_{BET} slowly increases while S_G reaches the maximum at milling time of 2 h and then levels off. Additionally, the S_{BET} becomes much larger than S_G and their changing trends are different, which is the typical phenomenon of particle agglomeration [30]. We need to emphasize that the agglomerates act as individual particles in the dynamic light scattering,

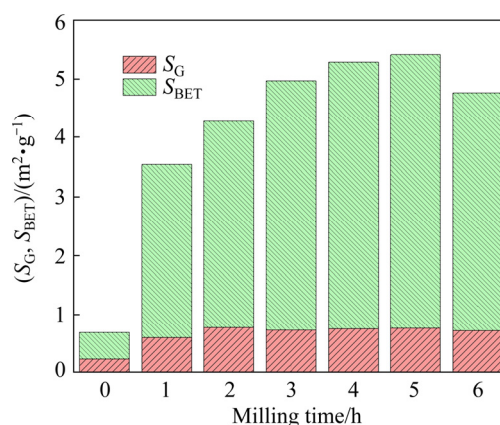


Fig. 2 Variation of specific surface area of non-activated and activated chalcopyrite samples at various milling time

while in the BET method, the nitrogen could access most of the inner surfaces of agglomerates, thus providing a higher value of surface area [31].

The S_{BET} increases slowly to the maximum value in the first 8 h. This changing trend is in close agreement with previous studies on chalcopyrite [20]. However, both S_{G} and S_{BET} decrease at prolonged milling time of 10 h, which is consistent with the change of PSD. When the aggregation happens, an increase in $D_{3,2}$ (see Table 1) can cause a decrease in S_{G} , according to Eq. (3). Meanwhile, the particles are tightly compressed after aggregation, leading to a decrease of porosity. Thus, the nitrogen could not penetrate to the inner surfaces, resulting in a decrease of S_{BET} [18].

3.2 SEM images

Figure 3 presents the SEM images of non-activated and activated chalcopyrite concentrates. As seen in Fig. 3(a), the non-activated sample has

the characters of unequal size, irregular shape, and smooth surface. Figure 3(b) indicates that after milling for 4 h, large flaky particles become rough with small particles sticking on the surface, which display the agglomeration. Meanwhile, in large particles, slightly layered structures could be found, transforming from the bulk structure. This can be explained by the brittle–ductile transition in MA process. The chalcopyrite particles approaching the grinding limit (proved by PSD analysis) undergo plastic deformation instead of fracture, and the brittle–ductile transition occurs. In this way, the input energy can be stored [32], and then the ductile chalcopyrite particles repeat flattening, cold welding, fracturing, and rewelding [33], leading to the formation of the layered structure. When the milling time increases to 8 h, the surfaces of particles remain rough, while the layered structure becomes much more obvious (Fig. 3(c)). Figure 3(d) illustrates that the surface is slightly smooth after

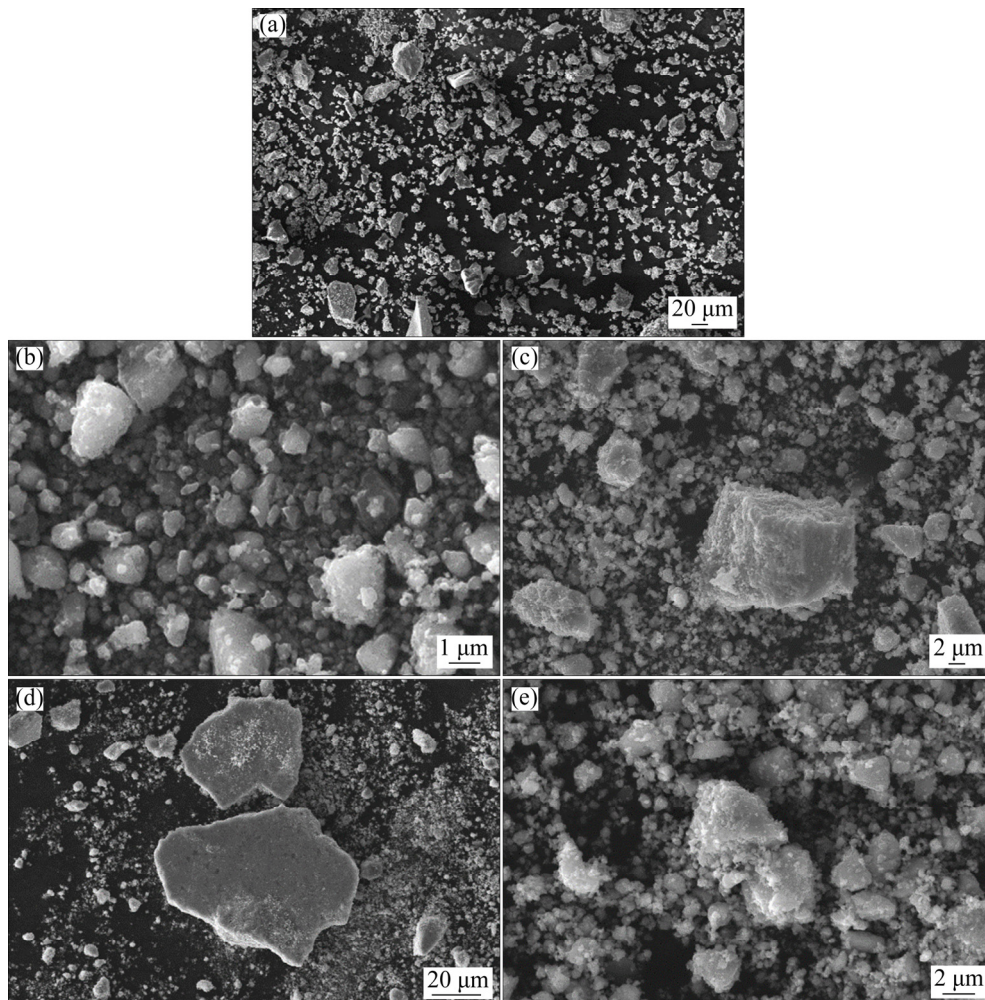


Fig. 3 SEM images of chalcopyrite samples milled for different periods: (a) Non-activated (0 h); (b) 4 h; (c) 8 h; (d, e) 10 h

10 h of milling and the joints between layers are inconspicuous, which forms a sharp contrast with different stacking directions displayed in Fig. 3(c). Consequently, the layer-packed particles are tightly compressed, indicating the occurrence of aggregation instead of agglomeration after long time milling, which agrees with previous observations [15]. At a higher magnification, fine particles are necked together (Fig. 3(e)), showing obvious sintering effect and local heating in the planetary ball mill.

3.3 XRD patterns

XRD analysis was carried out to study the microstructural changes of chalcopyrite during agglomeration and aggregation. Figure 4 shows the XRD patterns of samples milled up to 10 h. As can be seen, the main phases of the non-activated sample are chalcopyrite, pyrite, and quartz. The comparison of non-activated and activated samples shows that as the milling goes on, the chalcopyrite peaks broaden and the intensities of peaks gradually decline. Furthermore, some adjacent peaks broaden to overlap, such as peaks (220) with (204) and (312) with (116). This may be due to the microstructural changes such as the lattice strain, and the decrease in crystallite size [34]. Also, some weak peaks with low intensities become invisible, such as (400) and (008), indicating the selective rupture of the lattice through these planes, and the amorphization of the well-crystallized chalcopyrite [35]. However, there is neither a new peak nor a shifted peak, implying no phase transformation or new phase formation. Moreover, the changes of quartz and pyrite peaks are much

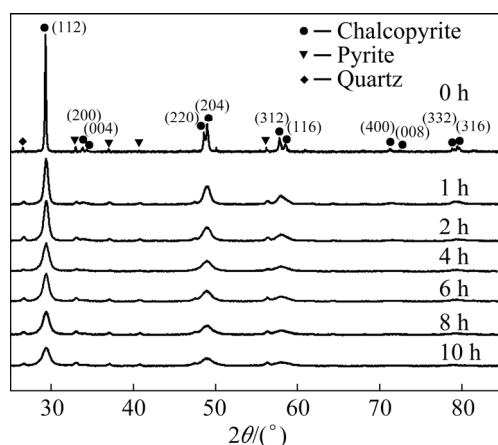


Fig. 4 XRD patterns of non-activated and activated chalcopyrite samples at various milling time

less than that of chalcopyrite, which is due to the lower hardness of chalcopyrite (3.5–4 on Mohs scale), whilst the hardness of pyrite (6) and quartz (7) is much higher, and the microstructural change in softer phase is preferred during milling [18].

The rising of the background intensity with prolonging milling time manifests the reduction of the degree of crystallinity. Usually, the amorphization degree (A) and the full width at half maximum (FWHM) were used to measure the effect of MA. In this work, the A (Eq. (4)) and FWHM were investigated using the main peak (112), and their variations versus milling time are shown in Fig. 5. The results illustrate that the increase of A is substantial in the first 3 h, while the increasing rate diminishes gradually to 8 h and then levels off till 10 h. Besides, the FWHM increases with prolonging milling time, corresponding to the induced lattice strain and the decrease of crystallite size. The FWHM changes little after 8 h, indicating the stability of crystallite size and lattice strain.

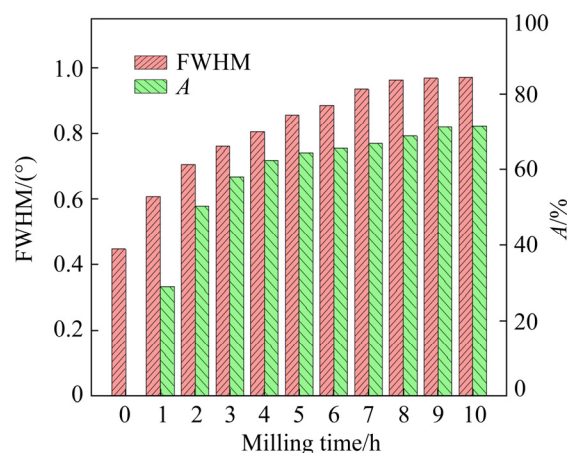


Fig. 5 Amorphization degree (A) and FWHM of non-activated and activated chalcopyrite samples at various milling time

Combined with the PSD and SEM analysis, it can be seen that in 8 h of milling treatment, the agglomeration and the microstructure do not affect each other. Because the agglomeration does not involve the micro-level, it is only the result of particles gathering together to reduce their surface free energy. While after milling for 8 h the crystallite size reaches a saturation value and the change of microstructure is stagnating [36]. To store the input energy, the chalcopyrite particles are sintered and tightly compressed [37], and then the aggregation occurs.

4 Leaching results

The effect of MA on the leaching rate was evaluated, and the results are shown in Fig. 6. In this figure, the leaching rate is plotted against the milling time for the non-activated and activated samples. It is observed that in the first 0.5 h, the similar leaching speed of activated samples is much faster than that of the non-activated sample, which can mainly be explained due to the dissolution of surface oxidation products [35]. Both the leaching speed and the Cu leaching rate increase with the increase of milling time, indicating that the reactivity of chalcopyrite is enhanced by MA. After milling for 8 h, the highest Cu leaching rate of 80.13% is achieved, which decreases to 58.42% with 10 h of milling, due to the occurrence of aggregation.

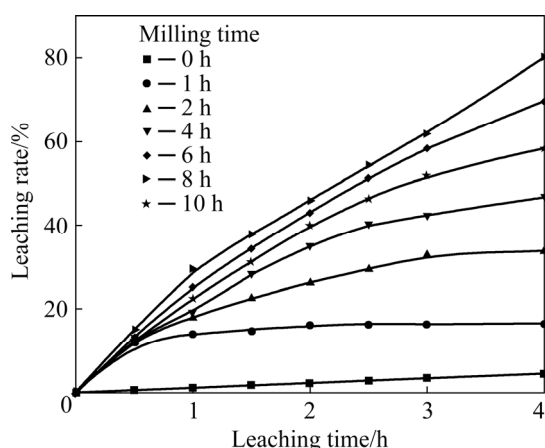


Fig. 6 Leaching rate of Cu as function of milling time

To examine the kinetics of the Cu leaching, a special case of the Erofejev–Kolmogorov equation was selected to fit the leaching data [38]. The equation is expressed as

$$\varepsilon_{\text{Cu}^{2+}} = 1 - \exp(-kt) \quad (6)$$

where t is the leaching time, and k is an empirical rate constant. This equation is a purely empirical equation without assumptions about the mechanism of the leaching reaction, which is often used for the description of solid–liquid reactions.

The comprehensive evaluation of MA properties on the leaching reaction rate constant is shown in Fig. 7. The relationship between leaching rate constant and the milling time and the violation degree of the structure (S_{BET}/X) [39] is shown in

Figs. 7(a) and (b), respectively. Besides, the rate constant is divided by the surface area, and plotted against the milling time (Fig. 7(c)) [40]. As can be seen from Fig. 7(a), although the agglomeration occurs in the first 8 h of milling, the leaching rate constant still increases with the extension of milling

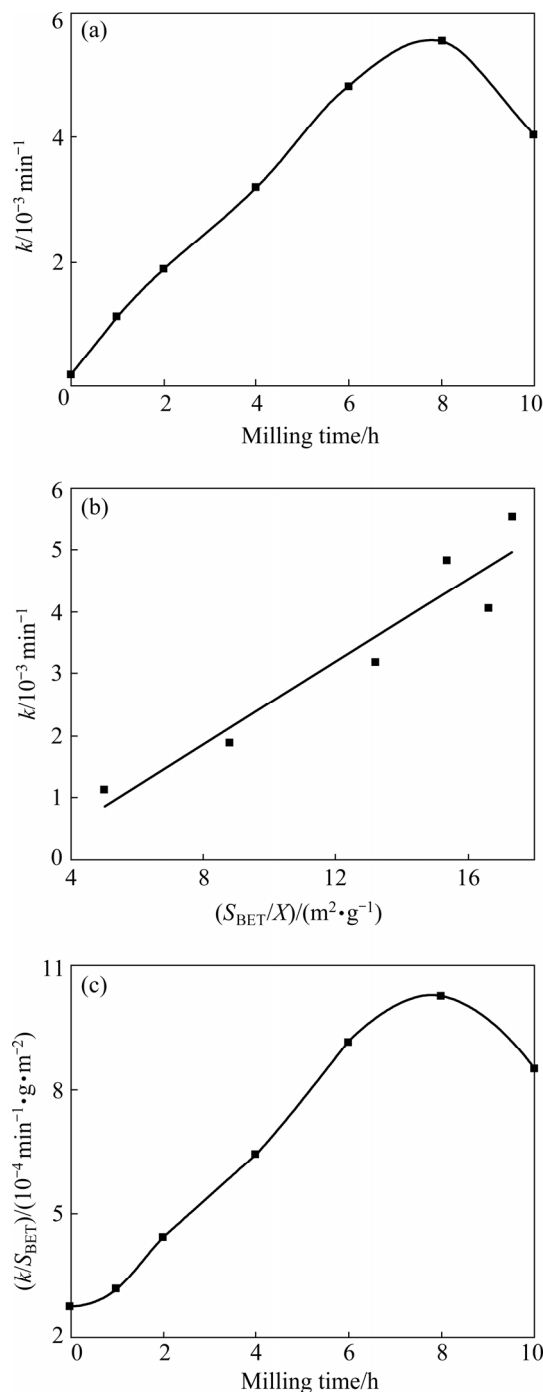


Fig. 7 Effect of MA on leaching of chalcopyrite samples: (a) Change of leaching rate constant versus milling time; (b) Influence of ratio of BET surface area to volume distortion of chalcopyrite S_{BET}/X on leaching rate constant; (c) Changes in ratio of leaching rate constant to BET surface area versus milling time

time, indicating that the hindering effect of agglomeration on leaching is not important. While after milling for 8 h, the leaching rate constant decreases significantly due to the occurrence of aggregation. From Fig. 7(b), it can be concluded that the promoting effect brought about by the increased amorphization degree on k is equal to that of the BET surface area, indicating the structural sensitivity of the reaction [41].

However, the specific surface area decreases dramatically after the occurrence of aggregation after 10 h milling, and then the Cu leaching rate decreases with the slight increase of the amorphization degree. The value of k/S_{BET} increases in the first 8 h of milling, as shown in Fig. 7(c), indicating the overlapping effect of the structural imperfection as a result of MA [40]. Also, the value of k/S_{BET} decreases with prolonging milling time to 10 h, indicating that the effective surface area in leaching is less than the BET surface area, and the leaching is limited seriously. The reasons for this observation include three aspects: (1) the structure of aggregated particles is compact, therefore, the inaccessibility of the internal surface of the aggregates decreases the solid–liquid contact surface in the leaching process; (2) the microtopography-enhanced dissolution decreases due to the flat surface of large aggregate particles [42]; (3) the aggregated particles are much more stable than the agglomerated ones, and these particles could not be dispersed during the leaching, sharply decreasing the reactivity. It can be concluded that the hindering effect of aggregation on the leaching process is considerably greater than that of agglomeration.

5 Conclusions

(1) The PSD transformation of chalcopyrite in MA can be distinguished as three stages: quick comminution (0 to 15 min), dynamic process of comminution and agglomeration (15 min to 8 h), and the transition from agglomeration to aggregation (after 8 h).

(2) The S_{BET} was much larger than S_{G} and their changing trends were different, while the aggregation occurred in the later stage of MA, then both S_{G} and S_{BET} decreased.

(3) Plastic deformation, reduction in crystallite size, and the increase in lattice strain and

amorphization degree occurred after MA. In 8 h of milling treatment, the agglomeration and the microstructure did not affect each other, after that the crystallite size reached a saturation value, the chalcopyrite particles were sintered and tightly compressed, and aggregation took place.

(4) The promoting effect of amorphization and surface area on leaching was important, while, the hindering effect of aggregation on leaching was severer than that of agglomeration. After milling for 8 h (before aggregation), the Cu leaching rate reached its maximum value of 80.13%.

Acknowledgments

This work was supported by the Special Fund for the National Natural Science Foundation of China (U1608254), and the National Key R&D Program of China (2018YFC1902002).

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机械活化黄铜矿的团聚—集聚及浸出性能

赵素兴, 王改荣, 杨洪英, 陈国宝, 丘学民

东北大学 冶金学院, 沈阳 110819

摘 要: 研究机械活化对黄铜矿粒度参数、显微组织和浸出性能的影响, 并探讨活化过程中团聚和集聚的发生和转变。结果表明, 研磨 8 h 前黄铜矿的团聚与显微组织变化互不影响; 然而, 研磨 8 h 后晶粒尺寸的降低达到极限, 显微组织变化停滞, 使得团聚被集聚取代。浸出实验结果表明, 机械活化能显著提高黄铜矿的浸出性能, 而集聚对浸出的阻碍作用远强于团聚。经 4 h 酸浸实验后, 活化 8 h 的矿样获得最高铜浸出率, 其值为 80.13%。

关键词: 黄铜矿; 机械活化; 团聚; 集聚; 浸出

(Edited by Wei-ping CHEN)