Effect of Specific Surface Area of a Mechanically Activated Chalcopyrite on Its Rate of Leaching in Sulfuric Acid-Ferric Sulfate Media

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The aim of the current study has been to investigate the influence of mechanical activation through intensive milling of a chalcopyrite mineral sample on its BET surface area and the subsequent effect on its leaching reaction rate and mechanism. Leaching kinetics mechanisms of the raw and mechanically activated chalcopyrite in the sulfuric acid-ferric sulfate media have been investigated. Rate-controlling step seems to be the diffusion through the protective product layer, and mechanical activation apparently has no significant effect on the leaching mechanism. An attempt has been made to describe the apparent rate constant as a function of BET specific surface area (S), specific surface energy (σ), and leaching temperature (T). An equation in the form of $k = AS^2 \exp(\sigma \Delta S/RT)$ has been developed (A is a constant) and fitted to the experimental data with a fairly good agreement.

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I. INTRODUCTION

CHALCOPYRITE ($CuFeS_2$) is the most abundant copper-bearing mineral. The current method of treating chalcopyrite concentrates involves smelting and refining. Large volumes of sulfur dioxide emitted into the atmosphere from this type of treatment cause serious pollution problems. Hydrometallurgical processing is believed to be a capable method of solving such environmental problems.[1]

Direct hydrometallurgical treatment of chalcopyrite is performed most frequently by oxidative leaching with low-cost ferric sulfate oxidant which allows for possible regeneration of the oxidizing agent. The reaction of chalcopyrite with ferric sulfate in acid medium is governed by the following equation:

$$CuFeS_2 + 2Fe_2(SO_4)_3 \rightarrow CuSO_4 + 5FeSO_4 + 2S. \quad [1]$$

There has been disagreement over the factors influencing the leaching rate of chalcopyrite.[2] Nevertheless, it is well known that the reaction [1] has a slow kinetics, and its rate decreases with time. This phenomenon has been ascribed to the formation of a passivating layer during the leaching course under oxidizing conditions. The protective layer so formed inhibits further reaction. Many previous studies suggested that this layer is composed of nonporous sulfur. On the basis of the results of electrochemical experiments, it has been proposed that passivation is caused by an amorphous nonstoichiometric sulfide.[3] On the other hand, the more chemically stable the sulfide layer, the more difficult the leaching process is. Hence, to overcome this obstacle, chemical stability of the protective film has to be modified by a suitable preleaching treatment. Mechanical activation of the ore by intensive milling is a relatively simple method for this purpose.[4] The effect of mechanical activation of some minerals as a preleaching treatment has been investigated by Hu *et al.*[5] and Yang *et al.*[6] Although milling exerts an additional cost because of its high energy consumption, it should be noted that milling is a compulsory step for the preparation of ores.[7] Almost all mineral processing plants use a milling step for size reduction of the particles prior to physical and chemical processing. Continuation of milling beyond that limit required for size reduction, leads to the mechanical activation.[8]

To be able to have a convincible judgment about the overall process cost, it is essential to find out whether the energy cost of milling exceeds the energy saving resulted from reducing the temperature and pressure levels of the subsequent leaching steps.[7] Research results reported in the literature show that ultra fine milling of chalcopyrite increases its activity so that less severe leaching conditions are required for copper recovery.[9]

Pretreatment of various minerals through mechanochemical processing has been successfully applied in both fundamental research studies and plant operations.[10] Some of its benefits may include lower reaction temperatures, increased reaction rate, increased dissolution efficiency and the formation of water soluble compounds.[11] Due to these attractive benefits, mechanical activation by intensive milling is becoming increasingly important in extractive metallurgy processes.[12]

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Comprehensive increase of specific surface area and creation of defective structures are supposed to be the main factors which accelerate the leaching step in hydrometallurgical processes.[13] Distortion of the mineral lattice can be evaluated by reference to the magnitude of the reduction of intensity of X-ray diffraction lines.[1]

It has been known that the wet grinding and/or the use of small milling balls is more favorable for new surface formation, whereas dry grinding and/or use of larger milling balls favor the amorphization phenomenon.[2]

The current study has been designed and performed to evaluate the influence of the increase of specific surface area of a chalcopyrite mineral sample resulted from intensive milling on its leaching behavior, *i.e.*, dissolution rate and mechanism. In addition, an attempt has been made to derive a mathematical expression for the relationship between the leaching rate constant and the specific surface area.

II. EXPERIMENTAL

A. *Materials*

The experiments were made on a natural chalcopyrite mineral. The mineral was originated from *Mazra-e* mines, south-east Iran. Some ore lumps containing high amounts of chalcopyrite were selected by hand picking. Wet chemical analysis of the ore showed its copper content as high as 12 wt pct. Ore samples were first crushed to less than about 2 mm and then milled to less than about 300 μm. A concentrate was subsequently obtained by repeated froth flotation using xanthate collectors. XRD analysis of the concentrate showed a mineralogical analysis of about 96 wt pct chalcopyrite ($CuFeS_2$) together with around 4 wt pct gangue minerals.[14] BET analysis showed the specific surface area of the raw concentrate as 0.3678 m^2/g.

B. *Intensive Milling*

Sampling was performed by coning and quartering method. Intensive milling experiments were carried out in a FP2 four milling jar planetary ball mill (Farapajouhesh, Iran). Milling jars were made of tempered chrome steel (11.5 pct Cr, 2.1 pct C, 0.7 pct W) with a volume of 125 ml. Milling balls were made of stainless steel (0.45 pct C, 13 pct Cr). Each jar was loaded with 3 balls of 20 mm diameter and 2 balls of 10 mm diameter. The effect of ball-to-powder mass ratio (m_B/m_P) was studied at a constant milling time (t_M) of 1 hour and the effect of milling time was investigated at a(m_B/m_P) ratio of 10. The rotation speed of the supporting disk was set at 600 rpm with a direction reversal after every 15 minutes. Milling experiments were carried out at both ambient temperature and under air atmosphere.

C. *Characterization*

X-ray diffraction analysis was performed by means of a D8-ADVANCE diffractometer (Bruker, Germany) using Cu-k_α radiation with a 0.5 deg s^{-1} goniometer rate. The specific surface area was determined by the low-temperature nitrogen adsorption technique (BET method) by means of a Gemini 2375 sorption apparatus (Micromeritics).

D. *Leaching*

Leaching tests were carried out in a glass beaker heated in a WNB14 water bath (Memmert, Germany) with a temperature tolerance of 1 K (1 °C). Agitation was carried out by means of a RZR2021 mechanical stirrer (Heidioph, Germany). With reference to a previous study[15] together with performing some preliminary tests, leaching conditions were fixed as follows: leaching agent, 0.5 M sulfuric acid together with 0.4 M ferric sulfate solution; pulp density, 5 g/L; and rotation speed, 230 rpm. Leaching temperature and time were varied from 313 K to 343 K (40 °C to 70 °C) and 15 to 450 minutes, respectively. Cu concentration of the solution was analyzed using AvantaΣ atomic absorption spectrometer (GBC, Australia). The reacted fraction (α) was calculated according to $\alpha = m/m_0$ where m is the mass of Cu in the solution resulting from the leaching of 1-g sample, and m_0 is the mass of Cu in the initial sample.

III. RESULTS AND DISCUSSION

A. *Mechanical Activation*

It has been shown that the chalcopyrite sample does not undergo any sensible changes in crystal structure during high-energy milling as no shift happens in its XRD peaks. Nevertheless, some line broadening and reduction in height of the diffraction peaks due to disordering of crystal structure and plastic deformation as well as some rising of the background owing to the formation of amorphous materials could be manifested.[16]

The change in specific surface area as a function of milling time and ball-to-powder mass ratio are shown in Table I. Although milling exerts a noticeable influence of the specific surface area of the chalcopyrite sample, changes in specific surface area are small as the milling became more intense.

Table I. Specific Surface Area Values of Chalcopyrite Samples Varied by Milling Times (t_M) and Ball-to-Powder Mass Ratios (m_B/m_P)

$m_B/m_P = 10$		$t_M = 60$ min	
t_M (min)	S (m^2/g)	m_B/m_P	S (m^2/g)
0 (Unmilled)	0.3678	2.5	2.6208
15	1.7074	10	3.1622
30	2.7446	30	3.2852
60	3.1622	40	3.8310
180	3.1808		
300	3.6316		
600	3.7516		

B. *Leaching*

Typical examples of the leaching curves (reacted fraction α against leaching time t_L) are shown in Figure 1. Full experimental data have been documented elsewhere.[17] Reduced time plot method has been used to determine the rate-controlling step. By means of this approach, for any given reaction mechanism, a unique dimensionless equation could be found to represent all the kinetic data irrespective of the nature of the system and the factors which influence the rate. This method offers a useful approach for rapid determination of the rate-controlling step and the appropriate rate equation.[18] A literature survey shows that dissolution kinetics of chalcopyrite obeys either a chemical reaction mechanism mainly in chloride systems[19,20] or most probably diffusion through the product layer in sulfate systems.[3,15,19–21] Hence, a reduced time plot based on rate equations in the shrinking core model,[22] *i.e.*, $1-(1-\alpha)^{1/3}=k\,t_L$ for chemical reaction control and $3-2\alpha-3(1-\alpha)^{2/3}=k\,t_L$ for diffusion control, have been constructed as shown in Figures 2 and 3 for unmilled and milled samples, respectively. Comparatively, leaching rate of unmilled sample is extremely so low that its 1.55 pct conversion (reaction) consumes around 7 hours at 343 K (70 °C). Such low leaching rates of chalcopyrite in ferric sulfate media have also been reported by some researchers.[23] Tremendous effect of mechanical activation on the leaching rate can be recognized by comparing Figures 2 and 3. The figures also show that a diffusion control mechanism governs the reaction kinetics for both raw (unmilled) and mechanically activated (milled) mineral. Moreover, it is clear from the figures that the reaction mechanism does not change because of variations of either milling conditions or leaching temperatures in the range of 313 K to 343 K (40 °C to 70 °C).

To determine the apparent rate constant k, the $3-2\alpha-3(1-\alpha)^{2/3}$ function was plotted against leaching time (t_L) for the raw sample and all of the activated samples for different leaching temperatures (T). A typical example of those plots is shown in Figure 4 for a sample milled for 5 hours with a m_B/m_P ratio of 10 which has been subsequently leached at temperatures 313, 323, 333, and 343 K (40 °C, 50 °C, 60 °C, and 70 °C). Values of the rate constant can be derived from the slop of the lines. A summary of the leaching data obtained in this way for all the samples, is given in Table II. As evidently seen in the table, mechanical activation has had a drastic effect on the leaching rate, so that the apparent rate constant has increased by five orders of magnitude from around 10^{-6} for unactivated chalcopyrite to about 10^{-1} h^{-1} for an intensively activated chalcopyrite.

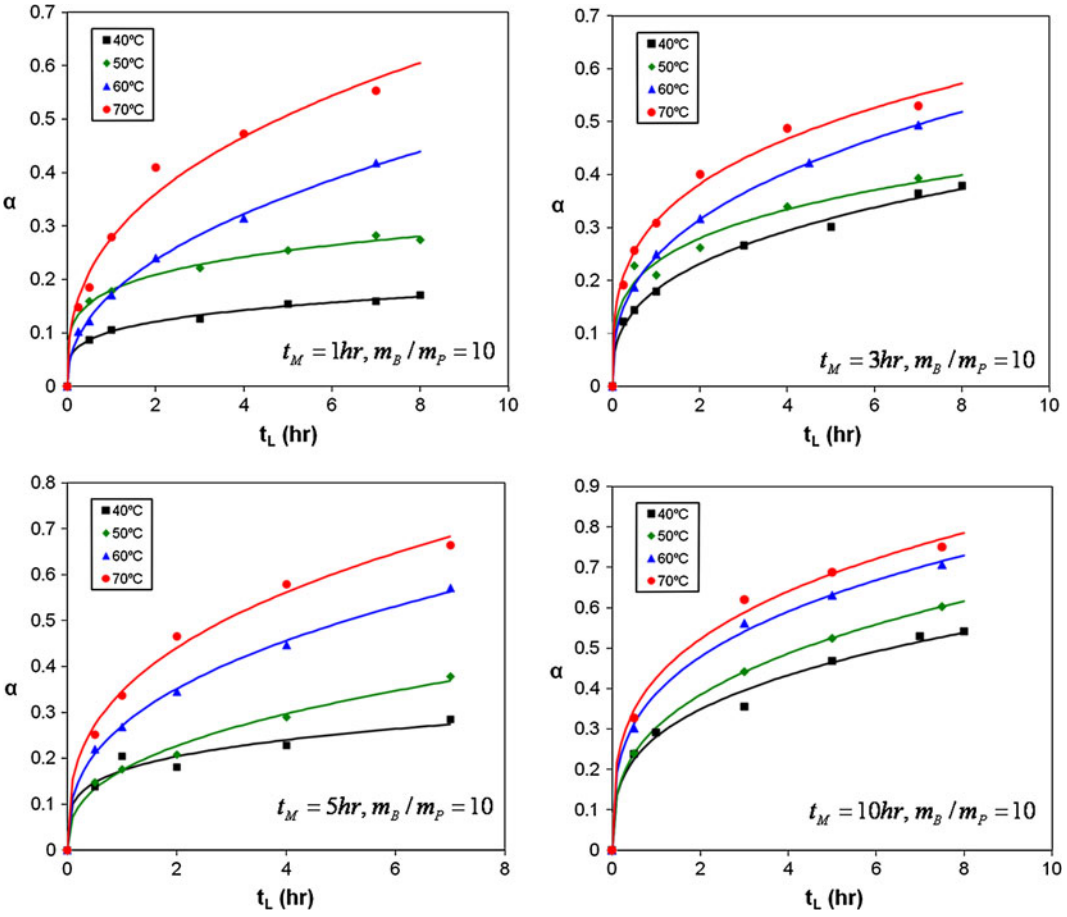

Fig. 1—Typical leaching curves of the activated chalcopyrite.

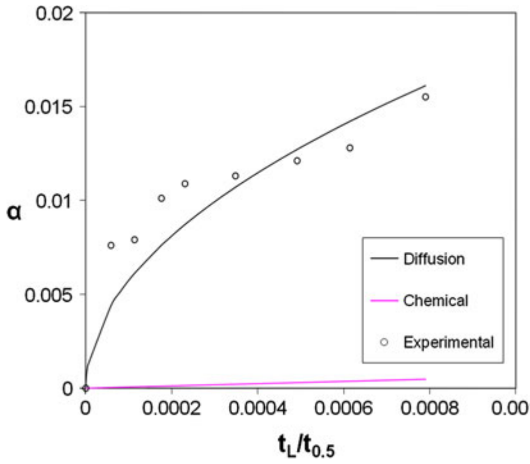

Fig. 2—Examination of reacted fraction (α)-reduced time ($t_L/t_{0.5}$) data points against different rate equations for unmilled chalcopyrite; t_L is the leaching time; and $t_{0.5}$ is the time required for $\alpha = 0.5$.

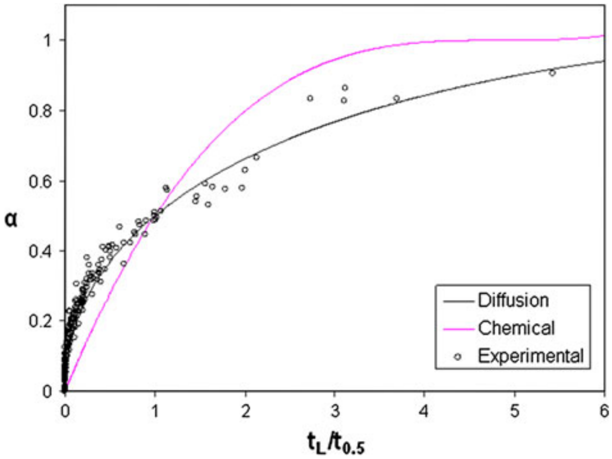

Fig. 3—Examination of reacted fraction (α)-reduced time ($t_L/t_{0.5}$) data points against different rate equations for all the milled samples; t_L is the leaching time; and $t_{0.5}$ is the time required for $\alpha = 0.5$.

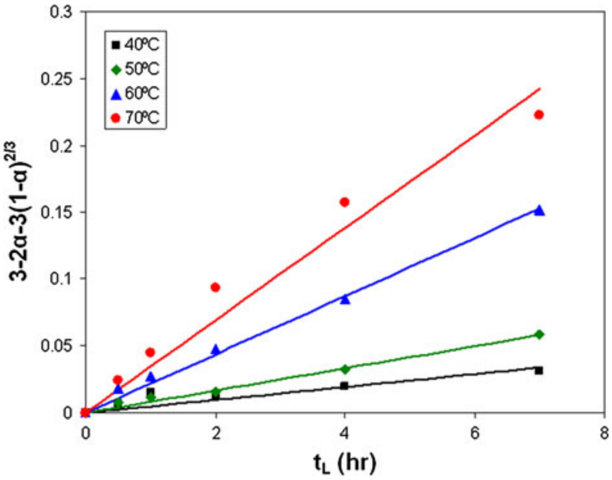

Fig. 4—Plots of $3 - 2\alpha - 3(1 - \alpha)^{2/3}$ expression against leaching time for a typical activated chalcopyrite; $m_B/m_P = 10$ and $t_M = 5$ h.

C. *Mathematical Correlation*

To describe the apparent rate constant, k, as a function of specific surface area, it is worth noting that in the case of diffusion control through the protective product layer on a spherical particle, k obeys the following equation:

$$k = \frac{6b\, D_e\, C}{\rho\, r_0^2} \qquad [2]$$

where, b is the stoichiometric factor, D_e is effective diffusivity of the reacting species through the product layer, C is the bulk fluid concentration (almost constant), ρ is the particle molar density, and r_0 is the initial particle radius. Eq. [2] can be written as

$$k = \frac{k_0}{r_0^2} \qquad [3]$$

Intrinsic leaching rate constant, k_0, includes all the remaining parameters. Therefore, the plot of k against the inverse square of particle diameter yields a straight line.[24] On the other hand, the mean diameter of particles, $\bar{d}_0$, is related to the specific surface area, S, according to the following equation[25]:

$$\bar{d}_0 = \frac{6}{\Phi\, \rho_P\, S}, \qquad [4]$$

where ρ_P is the mass density of the particles, and Φ is the particle shape factor. Combining Eqs. [3] and [4] gives

$$\frac{k}{S^2} = \frac{\Phi^2 \rho_P^2\, k_0}{9} \qquad [5]$$

According to Eq. [5], the plot of k against S^2 at a constant leaching temperature should yield a straight line. However, experimental data of the current investigation do not confirm such a linear dependency as seen in Figure 5. As mechanical activation through milling simultaneously increases the surface area and lattice defects, the concept of "activated state of solid substance by residual Gibbs energy" proposed by Balaž[2] may be useful to describe this behavior,:

$$\Delta G^* = \Delta G_1^* + \Delta G_2^*, \qquad [6]$$

where ΔG^* is the residual Gibbs energy (the difference between the Gibbs energy of activated and nonactivated solid substance), ΔG_1^* is the residual surface energy, and ΔG_2^* is the energy of lattice defect formation. The effect of lattice defect formation on the leaching kinetics has been studied by Bogatyreva *et al.*[26]

It holds the following form for the residual surface energy[2]:

$$\Delta G_1^* = \sigma\, \Delta S, \qquad [7]$$

where σ is the specific surface energy, and ΔS is the change in overall surface of the solid. Combining Eqs. [6] and [7] gives

Table II. Values of the Apparent Rate Constant for Various Milling Times (t_M), Ball-to-Powder Mass Ratios (m_B/m_P), and Leaching Temperatures (T)

t_M (h)	m_B/m_P	T [K (°C)]	k (h^{-1})	t_M (h)	m_B/m_P	T [K (°C)]	k (h^{-1})
Unmilled sample		313 (40)	2.39×10^{-6}	0.25	10.0	313 (40)	4.45×10^{-4}
		323 (50)	3.00×10^{-6}			323 (50)	8.65×10^{-4}
		333 (60)	9.68×10^{-6}			333 (60)	1.60×10^{-3}
		343 (70)	1.24×10^{-5}			343 (70)	2.34×10^{-3}
1.0	2.5	313 (40)	5.38×10^{-4}	0.5	10.0	313 (40)	4.83×10^{-3}
		323 (50)	1.29×10^{-3}			323 (50)	8.31×10^{-3}
		333 (60)	3.36×10^{-3}			333 (60)	2.18×10^{-2}
		343 (70)	2.83×10^{-3}			343 (70)	3.46×10^{-2}
1.0	10.0	313 (40)	1.43×10^{-3}	3.0	10.0	313 (40)	7.55×10^{-3}
		323 (50)	4.30×10^{-2}			323 (50)	1.00×10^{-2}
		333 (60)	1.03×10^{-2}			333 (60)	1.60×10^{-2}
		343 (70)	2.20×10^{-2}			343 (70)	2.10×10^{-2}
1.0	30.0	313 (40)	2.12×10^{-2}	5.0	10.0	313 (40)	1.31×10^{-2}
		323 (50)	5.06×10^{-2}			323 (50)	1.70×10^{-2}
		333 (60)	5.28×10^{-2}			333 (60)	2.18×10^{-2}
		343 (70)	6.52×10^{-2}			343 (70)	3.46×10^{-2}
1.0	40.0	313 (40)	3.55×10^{-2}	10.0	10.0	313 (40)	1.76×10^{-2}
		323 (50)	5.95×10^{-2}			323 (50)	2.40×10^{-2}
		333 (60)	8.63×10^{-2}			333 (60)	3.74×10^{-2}
		343 (70)	1.02×10^{-1}			343 (70)	4.56×10^{-2}

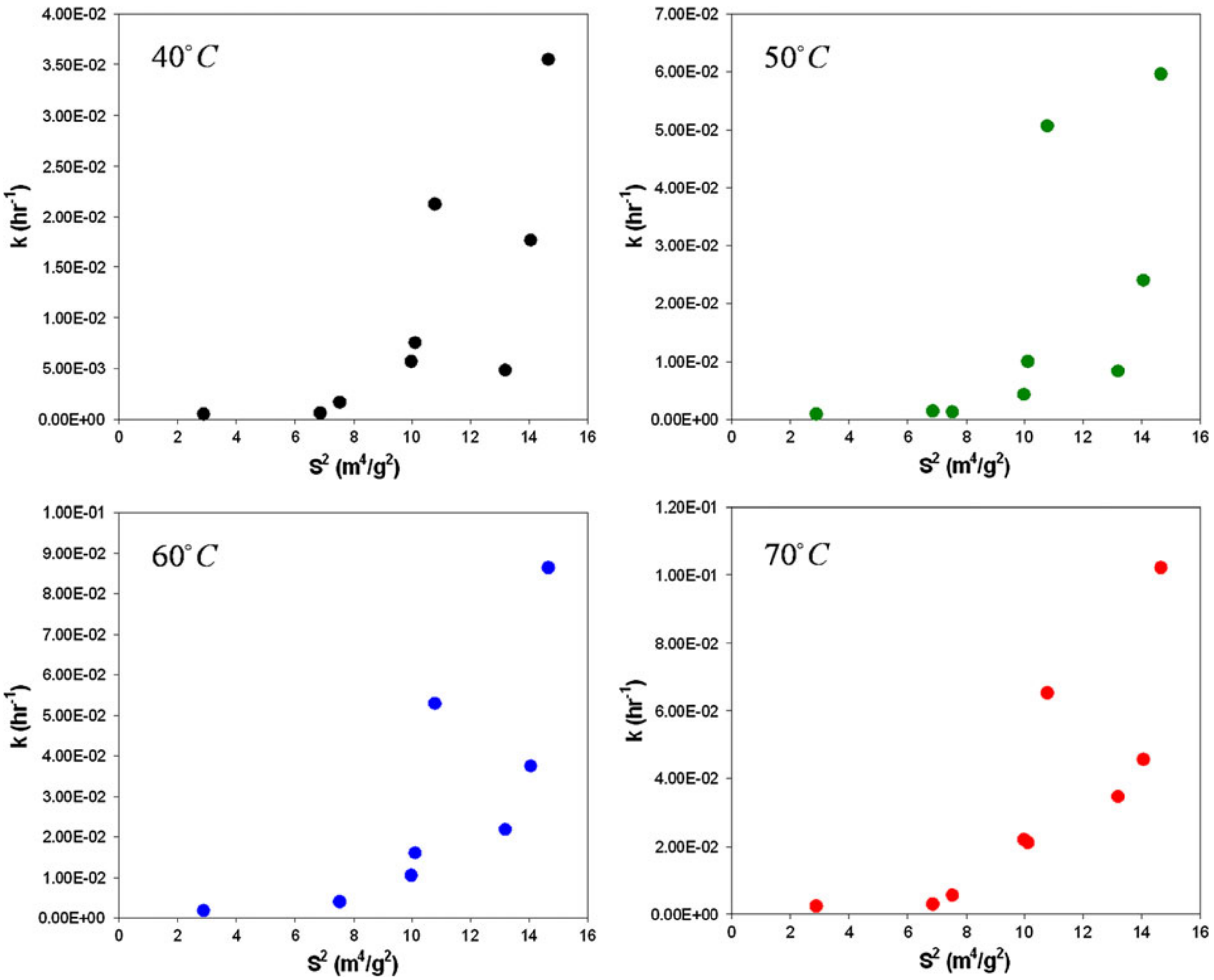

Fig. 5—Plot of k against S^2 for different leaching temperatures.

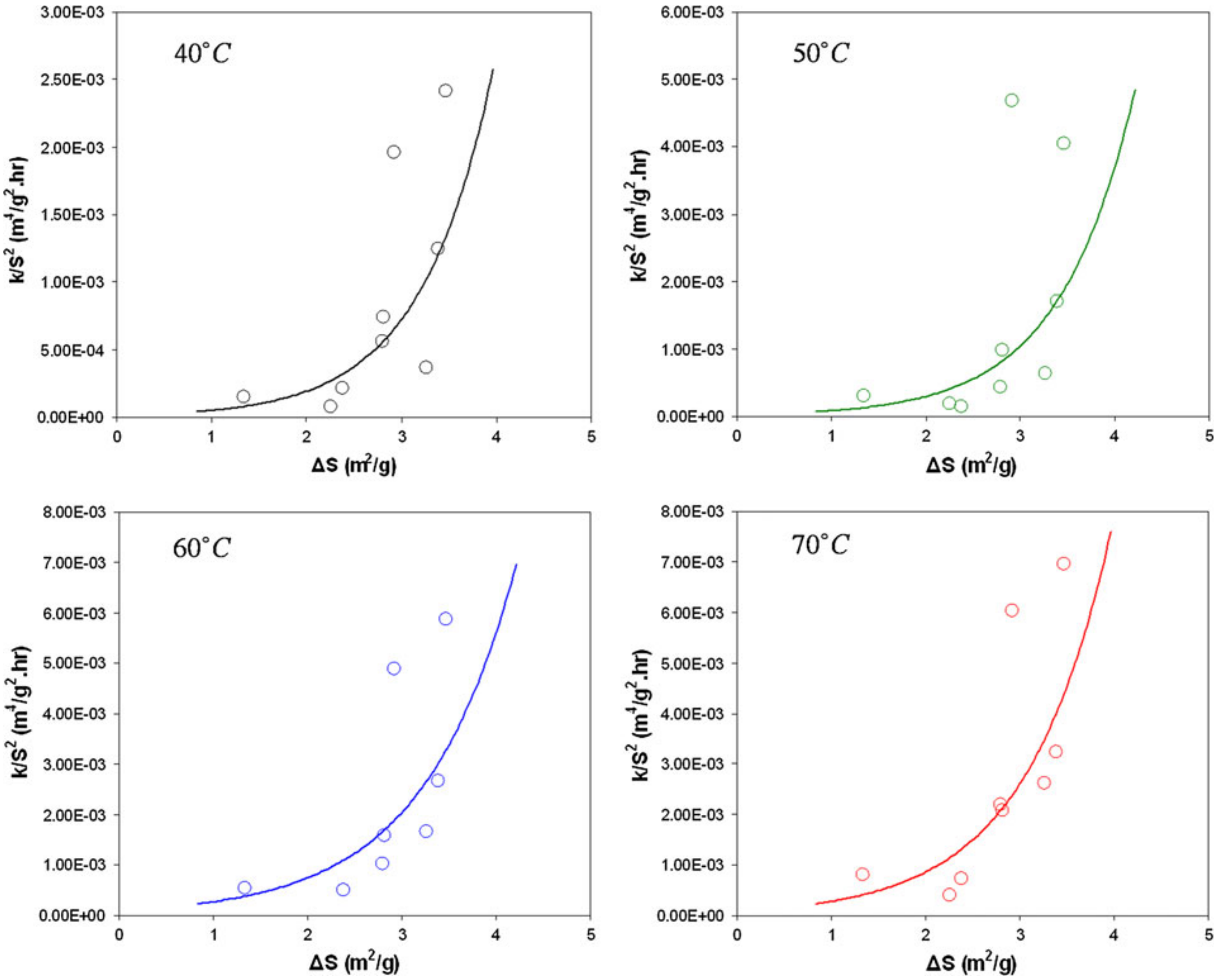

Fig. 6—Plot of k/S^2 against ΔS for different leaching temperatures.

$$\Delta G^* = \sigma\,\Delta S + \Delta G_2^* \qquad [8]$$

On the other hand, increase in the reactant free energy is assumed to be equal to the decrease in activation energy of dissolution.[27] Mathematically, it can be written as

$$E_1 - E_2 = \Delta G^*, \qquad [9]$$

where E_1 and E_2 are the activation energies for the dissolution of nonactivated and activated samples, respectively. Combining Eqs. [8] and [9] gives

$$E_1 - E_2 = \sigma\,\Delta S + \Delta G_2^* \qquad [10]$$

For the dissolution of the activated substance, temperature dependency of k is a consequence of the dependency of k_0 (intrinsic rate constant), as Eq. [2] shows. Among all parameters included in k_0, only D_e is a temperature dependent factor, temperature dependency of which is usually described by an Arrhenius type equation. Consequently, the dependency of the intrinsic rate constant (k_0) to the leaching temperature (T) may be given by Eq. [11]:

$$k_0 = A_0 \exp\left(-\frac{E_2}{RT}\right) \qquad [11]$$

Combination of Eqs. [10] and [11] yields

$$\begin{aligned} k_0 &= A_0 \exp\left(-\frac{E_1 - \sigma\,\Delta S - \Delta G_2^*}{RT}\right) \\ &= A_0 \exp\left(-\frac{E_1 - \Delta G_2^*}{RT}\right) \exp\left(\frac{\sigma\,\Delta S}{RT}\right) \end{aligned} \qquad [12]$$

Substituting Eq. [12] to [5] gives

$$\frac{k}{S^2} = A \exp\left(\frac{\sigma\,\Delta S}{RT}\right), \qquad [13]$$

where A is determined by

$$A = \frac{\Phi^2 \rho_P^2 A_0}{9} \exp\left(-\frac{E_1 - \Delta G_2^*}{RT}\right) \qquad [14]$$

To simplify the calculations, it could be assumed that the energy of lattice defects, ΔG_2^* is not a direct function of the substance surface area, and A is supposed to be independent of S. Fitting of the model expressed by Eq. [13] to the experimental data has been depicted in Figure 6. In each plot in this figure, leaching temperature is fixed, and therefore, A in Eq. [13] is regarded as a constant. Although a perfect fitness is not observed, the model could satisfactorily predict the observed trend of enhancing the leaching rate with increasing the specific surface area due to mechanical activation. Reasons for scattering may be attributed to the influence of substance surface area on ΔG_2^* and/or the change of specific surface energy (σ) during intensive milling due to the changes of both chemical composition[12,28,29] and morphology[30] of the milled substance.

IV. CONCLUSIONS

Leaching behavior of a natural chalcopyrite sample activated by high energy ball milling was investigated, with an attempt to establish a relationship between the specific surface area of the activated mineral powder and its apparent leaching rate constant. The principal findings of the study are as follows:

1. Leaching rate of chalcopyrite is greatly enhanced by intensive milling by around five orders of magnitude.
2. The rate-controlling step of the leaching of chalcopyrite in sulfuric acid-ferric sulfate media is found to be diffusion through protective product layer. More notably, it does not undergo any sensible changes under a wide range of mechanical activation conditions.
3. The change in BET surface area has a significant effect on the apparent rate constant of chalcopyrite dissolution. To describe the dependency of apparent rate constant to the specific surface area, an equation in the form of $k = AS^2 \exp(\sigma \Delta S/RT)$ has been developed and examined against experimental data.
4. The idea of correlating the leaching rate of mechanically activated minerals with specific surface area is of practical importance. The mathematical correlation developed in this research study has been obtained on the basis of fundamental facts and concepts using a novel approach. Further efforts and/or modifications are needed to adequately improve the proposed model.

REFERENCES

1. F. Habashi: *Chalcopyrite: Its Chemistry and Metallurgy*, McGraw-Hill, Ghatham, 1978.
2. P. Balaž: *Extractive Metallurgy of Activated Minerals*, Elsevier, Amsterdam, 2000.
3. M.F.C. Carneiro and V.A. Leão: *Hydrometallurgy*, 2007, vol. 87, pp. 73–82.
4. H. Hu, Q. Chen, Z. Yin, P. Zhang, and A. Tang: *Thermochim. Acta*, 2003, vol. 395, pp. 139–44.
5. H. Hu, Q. Chen, Z. Yin, G. Gotlstein, P. Zhang, and G. Guo: *Metall. Mater. Trans. B*, 2004, vol. 35B, pp. 1203–07.
6. Z. Yang, Z. Shi-li, D. Hao, X. Hong-bin, and Z. Yi: *Trans. Nonferrous Met. Soc. China*, 2010, vol. 20, pp. 888–91.
7. D. Maurice and J.A. Hawk: *Hydrometallurgy*, 1999, vol. 51, pp. 371–77.
8. N.J. Welham: *Hydrometallurgy*, 2001, vol. 62, pp. 165–73.
9. H. Hu, Q. Chen, Z. Yin, and P. Zhang: *Thermochim Acta*, 2003, vol. 398, pp. 233–40.
10. J. Ficeriova, P. Balaž, and C.L. Villachica: *Hydrometallurgy*, 2005, vol. 77, pp. 35–39.
11. P. Balaž, A. Alacova, M. Achimovicova, J. Ficeriova, and E. Godocıkova: *Hydrometallurgy*, 2005, vol. 77, pp. 9–17.
12. E. Godocıkova, P. Balaž, and E. Boldizarova: *Hydrometallurgy*, 2002, vol. 65, pp. 83–93.
13. P. Balaž, E. Boldizarova, M. Achimovicova, and R. Kammel: *Hydrometallurgy*, 2000, vol. 57, pp. 85–96.
14. M.Sh. Bafghi, A.H. Emami, J. Vahdati Khaki, and A. Zakeri: *Int. J. Miner. Process.*, 2009, vol. 93, pp. 149–54.
15. S. Moradi, M.S. Bafghi, and J.V. Khaki: *Proc. 11th Int. Miner. Process. Symp.*, Turkey. 2008. pp. 499–505.
16. A.H. Emami, M.Sh. Bafghi, J. Vahdati Khaki, and A. Zakeri: *Iran. J. Mater. Sci. Eng.*, 2009, vol. 6, pp. 30–36.
17. A.H. Emami. Ph.D. Thesis, Iran University of Science and Technology, 2009.
18. J.H. Sharp, G.W. Brindley, and B.N. Narahari Achar: *J. Am. Ceram. Soc.*, 1966, vol. 49, pp. 379–82.
19. J.E. Dutrizac: *Metall. Trans. B*, 1981, vol. 12B, pp. 371–78.
20. T. Havlik, A. Miskufova, and P. Tatarka: *Acta Metall. Slovaca*, 2001, vol. 4, pp. 62–68.
21. P.B. Munoz, J.D. Miller, and M.E. Wadsworth: *Metall. Trans. B*, 1979, vol. 10B, pp. 149–58.
22. H.S. Ray: *Kinetics of Metallurgical Reactions*, Oxford & IBH Publishing Co., New Delhi, 1993.
23. E.M. Córdoba, J.A. Muñoz, M.L. Blázquez, F. González, and A. Ballester: *Hydrometallurgy*, 2008, vol. 93, pp. 88–96.
24. O. Levenspiel: *Chemical Reaction Engineering*, 2nd ed., Wiley, New York, 1972.
25. W.L. McCabe, J.C. Smith, and P. Harriot: *Unit Operations of Chemical Engineering*, 5th ed., McGraw-Hill, New York, 1993.
26. E. Bogatyreva, A. Ermilov, T. Sviridova, O. Savina, and K. Podshibyakina: *Inorg. Mater.*, 2011, vol. 47, pp. 791–97.
27. D. Tromans and J.A. Meech: *Miner. Eng.*, 2001, vol. 14, pp. 1359–77.
28. M. Achimovicova, P. Balaz, and J. Briancin: *Metalurgija*, 2006, vol. 45, pp. 9–12.
29. P. Donato, M. Kongolo, O. Barres, J. Yvon, F. Enderlé, E. Bouquet, M. Alnot, and J.M. Cases: *Powder Technol.*, 1999, vol. 105, pp. 141–48.
30. D. Tromans and J.A. Meech: *Miner. Eng.*, 1999, vol. 12, pp. 609–25.