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Development and verification of a mathematical model for variations of the specific surface area of mineral powders during intensive milling

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ABSTRACT

In order to describe temporal evolution of BET surface area of a mineral substance during an intensive milling process, a mathematical model in the form of $S = a + b\,e^{-mt} + c\,e^{-nt}$ has been developed based on well-established phenomena in mechanical activation processes. Validity of the proposed model was verified by the results of experiments performed on a natural chalcopyrite mineral as well as those reported in the literature on a variety of sulfide minerals. It was shown that the model could fit different types of surface area variation with a very good accuracy.

1. Introduction

Mechanical activation pretreatment of minerals by intensive milling can improve the efficiency of subsequent processes such as leaching, reduction, chemical synthesis, etc. Consequential benefits of mechanical activation, besides higher efficiencies, may include lower reaction temperatures and enhanced kinetics. As a result, the subsequent processing can be performed in simpler and less expensive reactors with shorter reaction times [1–3]. Several factors, most importantly the formation of new and additional surface area as well as creation of lattice defects, are responsible for the mentioned improvements [1,4–9]. Different types of milling apparatus such as ball mills, planetary mills, vibratory mills, pin mills and rolling mills may be used for milling operations [10]. It is believed that wet milling and/or employing small milling balls (e.g. attritors) is more favorable for the generation of new and additional surfaces, while dry milling and/or the use of larger milling balls (e.g. vibratory and planetary mills) brings about intensive bulk disorders in the milled material [11]. High-energy milling is accompanied by an increase in the number of material particles as well as generation of fresh surfaces which were unexposed prior to milling operation [10]. Nevertheless, formation of new surfaces is restricted to a limit beyond which aggregation of particles takes place with the consequence of the formation of agglomerates [12].

Balaz [13] has classified the general trend of specific surface area (SSA) of sulfidic minerals with the time of intensive milling into two categories: category I, in which SSA increases first with the milling time and reaches to a constant value after a certain milling period; and category II, wherein the increase in SSA due to mechanical activation reaches to a maximum after the elapse of a certain time, and then decreases to a constant value. For the first category, the following equation has been proposed to describe the process of new surface formation:

$$S = S_{\max}(1 - e^{-k_1 t}) \tag{1}$$

where, S is the SSA at a given time t and $S_{\max}$ is the maximum attainable specific surface area. The constant k_1 implies the significance of rate constant of the new surface formation. Alternatively, the relationship between the milling time and SSA for the second category has been formulated according to the following equation:

$$S = A + (B + k_2 t)\,e^{-\alpha t}. \tag{2}$$

In this equation, A denotes the value of SSA corresponding to mechanochemical equilibrium, i.e. the point at which the rate of comminuting is equal to the rate of agglomeration, and B is a constant whose value is determined by $B = S_0 - A$, where S_0 is the initial surface area. The constant k_2 in Eq. (2) represents the surface increment in unit time and α characterizes the rate of aggregation process. The retardation of formation of new surface observed in both categories may be due to the aggregation of fine particles as reported for several mechanically activated sulfides [13].

Eq. (1) is obviously unable to describe the variations of SSA of the second category. On the other hand, expression (2) was obtained by mere fitting [14]. Thus, attempts have been made in the present study to

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develop a mathematical model with a physical basis that could explain either of the above mentioned trends of SSA of a mineral powder during an intensive milling process, e.g. mechanical activation.

2. Derivation of the model

It has been recognized by various studies that in an intensive grinding process, at first the primary particles crush, then some of them agglomerate; and finally, some of the agglomerates disintegrate back into the crushed particles. Analogous to a system of chemical reaction acting in series, these phenomena can be expressed by the following scheme:Primary particles → Crushed particles ⇄ Agglomerated particlesor simply:

$$P \xrightarrow{k_1} C \underset{k_3}{\overset{k_2}{\rightleftarrows}} A \tag{3}$$

Here, k_1, k_2 and k_3 refer to the crushing, agglomeration and disintegration rate constants, respectively. Accordingly, if S_P, S_C and S_A are correspondingly the total surface area of P, C and A, the relevant rate equations in terms of the changes of surface area could be written as follows, assuming that all processes are first order:

$$\frac{dS_P}{dt} = -k_1 S_P \tag{4}$$

$$\frac{dS_C}{dt} = k_1 S_P - k_2 S_C + k_3 S_A \tag{5}$$

$$\frac{dS_A}{dt} = k_2 S_C - k_3 S_A \tag{6}$$

If the initial amount of S_C and S_A is zero, solution of Eqs. (4)–(6) gives:

$$S_P = S_P^0 e^{-k_1 t} \tag{7}$$

$$S_C = \frac{k_3 S_P^0}{k_2 + k_3}(1 - e^{-(k_2 + k_3)t}) + \frac{(k_1 - k_3)S_P^0}{k_2 + k_3 - k_1}(e^{-k_1 t} - e^{-(k_2 + k_3)t}) \tag{8}$$

$$S_A = S_P^0(1 - e^{-k_1 t}) - \frac{k_3 S_P^0}{k_2 + k_3}(1 - e^{-(k_2 + k_3)t}) - \frac{(k_1 - k_3)S_P^0}{k_2 + k_3 - k_1}(e^{-k_1 t} - e^{-(k_2 + k_3)t}) \tag{9}$$

where, S_P^0 is the initial surface area of P. The internal surface area of agglomerates is not accessible for the molecules of adsorbate [13], so the observed SSA of a mineral under milling, S, can be written as follows:

$$S = \frac{S_t}{m_t} \approx \frac{S_P + S_C}{m_P + m_C + m_A} = \frac{k_3 S_P^0}{m_t(k_2 + k_3)} + \frac{S_P^0}{m_t}[1 + \frac{(k_1 - k_3)}{(k_2 + k_3 - k_1)}]e^{-k_1 t} - \frac{S_P^0}{m_t}[\frac{k_3}{k_2 + k_3} + \frac{k_1 - k_3}{k_2 + k_3 - k_1}]e^{-(k_2 + k_3)t} \tag{10}$$

or:

$$S = a + be^{-mt} + ce^{-nt}. \tag{11}$$

Here a, b, c, m and n are constants. It is worth noting that this model satisfies the following limiting conditions:

$$S_0 = \lim_{t \to 0} S = a + b + c \tag{12}$$

$$S_\infty = \lim_{t \to \infty} S = a. \tag{13}$$

To find the coordinates of the maximum (if any), it must be $\frac{dS}{dt} = 0$, then:

$$t_{\max} = \frac{1}{n - m}\ln(-\frac{cn}{bm}) \tag{14}$$

$$S_{\max} = a - c\,(-\frac{cn}{bm})^{\frac{n}{m-n}}(\frac{n - m}{m}). \tag{15}$$

In order to evaluate the validity of proposed model given by Eq. (11), intensive milling experiments on a natural chalcopyrite mineral were conducted and the results have been presented and analyzed in the following sections of the paper.

3. Experimental

Milling experiments were done on a natural chalcopyrite concentrate originated from Mazra-e mines, south-east Iran. X-ray diffraction of the concentrate (Fig. 1) showed a mineralogical analysis of about 96 wt% $CuFeS_2$ together with around 4 wt% gangue minerals. BET surface area of the concentrate before milling was determined to be 0.3678 m^2/g. Details of the material and procedure were given elsewhere [15].

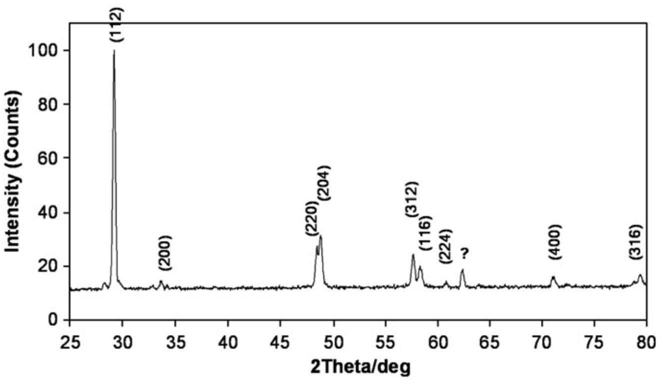

Fig. 1. X-ray diffraction pattern of natural chalcopyrite mineral.

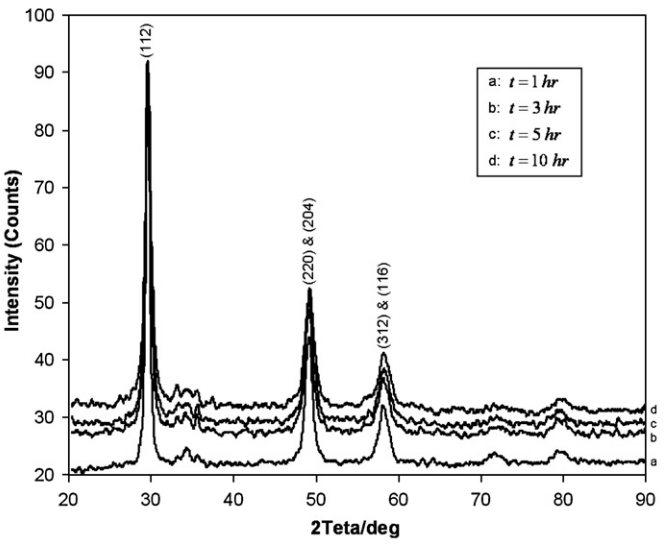

Fig. 2. Evolution of X-ray diffraction pattern of mechanically activated chalcopyrite with milling time.

Table 1
Changes in BET surface area of the milled chalcopyrite samples with grinding time.

t (hr)	0	0.25	0.5	1	3	5	10
S (m^2/g)	0.368	1.707	2.745	3.162	3.181	3.632	3.752

Intensive milling experiments were carried out in a laboratory 4-cup planetary ball mill (Fara-pajouhesh, Iran) from 15 min to 10 h with a fixed conditions (ball to powder weight ratio: 10:1, rotation speed: 600 rpm, rotation mode: direction reversal every 15 min, environment: dry milling, air atmosphere, room temperature). The characterization of the milled products was performed by a D8-ADVANCE X-ray diffractometer (Bruker, Germany) using Cu-k$_\alpha$ radiation, as well as a Gemini 2375 nitrogen adsorption BET analyzer (Micromeritics, USA).

4. Results and discussion

Selected XRD patterns of the mechanically activated chalcopyrite sample are shown in Fig. 2. It can be seen that the sample did not undergo any sensible changes in crystal structure during high-energy milling, as no shift has happened to the XRD peaks. Nevertheless, some line broadening and reduction in height of the diffraction peaks due to disintegration and plastic deformation as well as rising of the background intensity owing to the formation of amorphous material are observed.

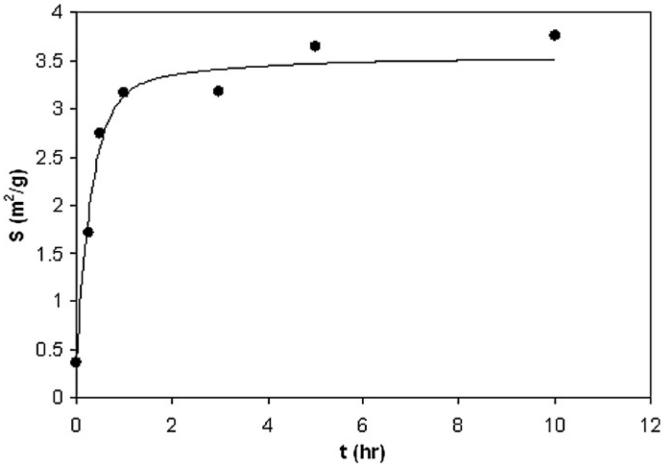

Fig. 3. Fitness of the proposed model to SSA data of the present study; $r = 0.989$.

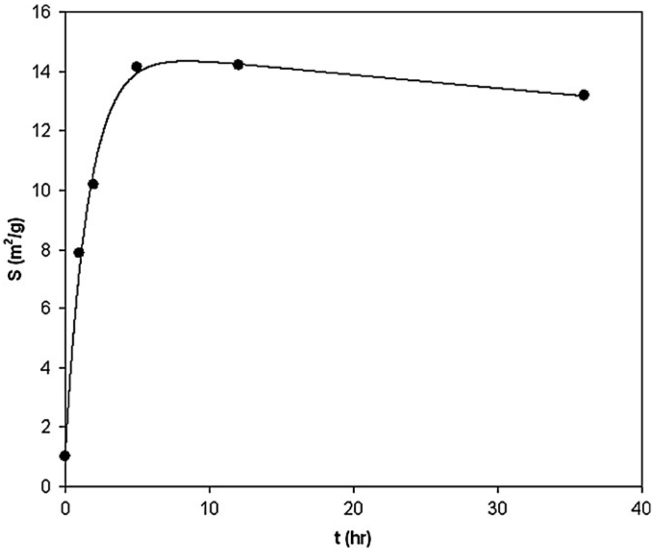

Fig. 5. Fitness of the model in the present study to SSA data for dry grinding of molybdenite [17]; $r = 0.998$.

Experimental results regarding the change in BET surface area of the milled chalcopyrite samples with milling time are given in Table 1. It is apparent that the SSA of the natural chalcopyrite increases during the milling process. The increase is substantial at short milling times. For instance, surface area reaches to about 6.5 times of the initial value after 30 min milling. However, the rate diminishes gradually and the BET surface area shows negligible changes at higher grinding times and approaches to a constant maximum value. This is the characteristic behavior of category I of SSA trend discussed earlier in this paper.

Using Eq. (11) derived in this paper and applying a non-linear regression analysis to the experimental data, parameters a, b, c, m and n in the proposed model can be obtained, which leads to the following equation:

$$S = 3.515 - 2.823\,e^{-3.016\,t} - 0.361\,e^{-0.399\,t}. \tag{16}$$

The SSA values determined in the present study as a function of milling time together with a plot of the derived model (Eq. (16)) are shown in Fig. 3. A good fit (expressed by the value of the correlation

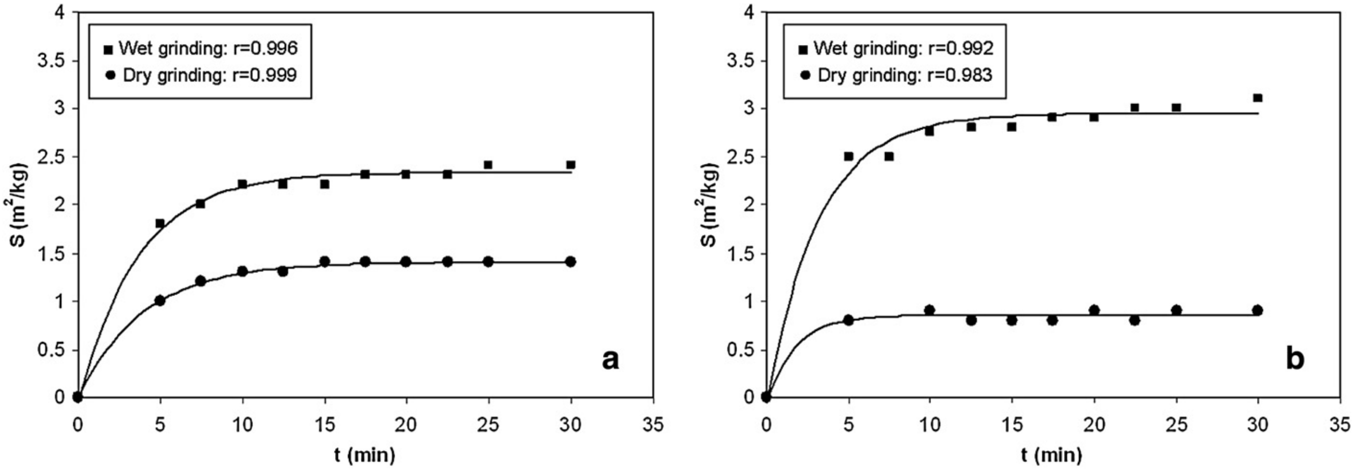

Fig. 4. Fitness of the model in the present study to SSA data [16] for mechanical activation of (a) galena and (b) chalcopyrite.

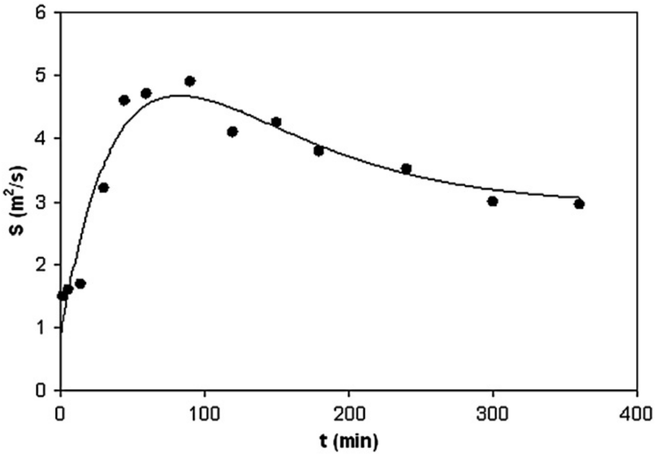

Fig. 6. Fitness of the model in the present study to SSA data for planetary grinding of chalcopyrite [13]; $r = 0.962$.

coefficient, *r*) is observed between the proposed model and experimental data.

Available data in the literature on the variations of SSA with milling time for different sulfide minerals may be necessary for further verification of the derived model. Data for changes of SSA during dry and wet mechanical activation of galena (PbS) and chalcopyrite ($CuFeS_2$) in a planetary mill [16] are shown in Fig. 4 as an instance for SSA variations of category I. To give an example for category II, the results of high intensity dry milling of molybdenite (MoS_2) in a planetary ball mill [17] are depicted in Fig. 5. The curves fitted to data using our model are also represented in these figures. Excellent agreements are observed between the model and the experimental data. With regard to Fig. 5, values of $t_{\max}$ and $S_{\max}$ can be calculated according to Eqs. (14) and (15). This would respectively give 8 min and 14.5 m^2/g that are comparable to the practical values.

Another example would be SSA changes of a chalcopyrite sample under planetary milling [13] as displayed in Fig. 6. Again, calculated values of $t_{\max}$ and $S_{\max}$ (83 min and 4.7 m^2/g, respectively) are very close to the actual data. These examinations, on the whole, provide sufficient confirmation on the applicability of the proposed model, irrespective of the mineral substance or milling device and conditions. Moreover, it was shown that the model developed in the present study could satisfy both two trends of the SSA with the milling duration mentioned in section one.

6. Conclusion

A mathematical model has been developed to describe the changes in the specific surface area of a substance during intensive milling processes. Validity of the proposed model has been verified by the results of experiments performed on a natural chalcopyrite mineral as well as the available data in the literature relating to a range of minerals and milling conditions. It was concluded that the model fits various experimental data with a very good accuracy. Considering the importance of surface area of mineral powders in mineral processing operations, the model would find wide applicability in predicting the behavior of an intensively milled mineral through mechanical activation pretreatment processes.

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