Powder Technology 197 (2010) 87–90

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

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

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ARTICLE INFO

*Article history:*
Received 21 January 2009
Received in revised form 22 June 2009
Accepted 30 August 2009
Available online 8 September 2009

*Keywords:*
Modeling
Milling
Specific surface area
Minerals
Chalcopyrite

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:

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

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 $\alpha$ 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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doi:10.1016/j.powtec.2009.08.025

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:

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

or:

$$S = a + b e^{-mt} + c e^{-nt}. \tag{11}$$

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:

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

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

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].

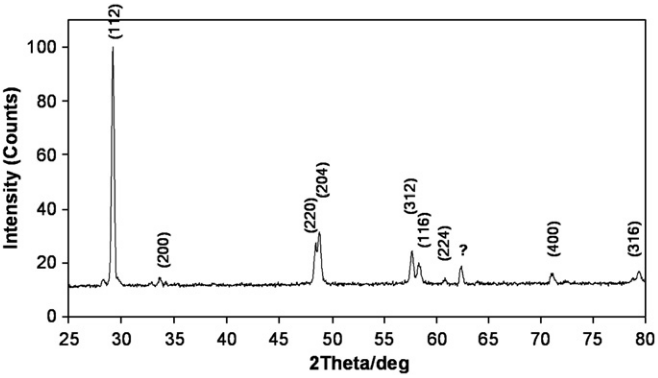

**Fig. 1.** X-ray diffraction pattern of natural chalcopyrite mineral.

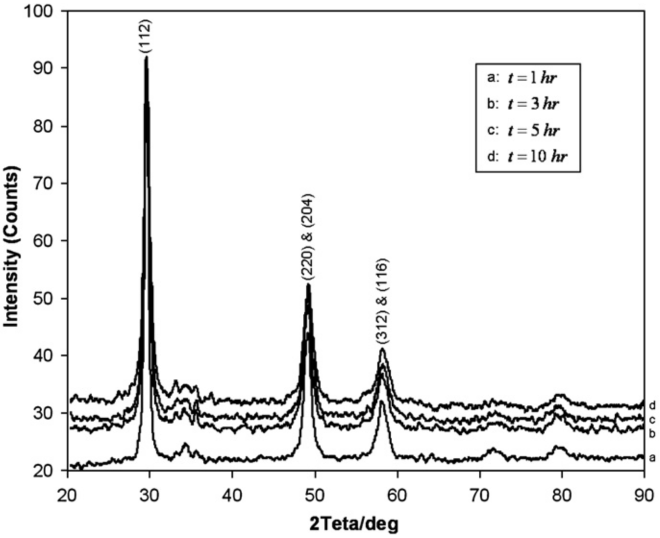

**Fig. 2.** Evolution of X-ray diffraction pattern of mechanically activated chalcopyrite with milling time.