Mechanoluminescence of quartz particles during grinding in a stirred media mill

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Abstract

The development of mechanoluminescence-based method for monitoring of size reduction processes in stirred media mill is described. Quartz particles are used as feed material that consists of aggregates and primary solid particles. Analysis of breakage in such system is problematic because it is very difficult to distinguish aggregates from primary particles. On the other hand, only stressing of primary particles between mill beads causes the mechanoluminescence impulses. Consequently, the use of mechanoluminescence can be very useful to characterize breakage in aggregates/primary particles system. The distribution of mechanoluminescence impulses depending on amplitude is measured at different grinding times and stirrer speeds. The obtained impulse number distribution can be described by means of two power functions with different exponents by low and high amplitudes. The first power function reflects the mechanical loading of fine primary particles. The second one corresponds to breakage of coarse particles. The impulses caused by stressing of fine primary particles are found to be suitable for dynamic characterization of size reduction in such system.

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1. Introduction

Mechanoluminescence (ML) is a type of luminescence induced during any mechanical stressing of solids. For example, ML can be excited by grinding, crushing, compressing, and rubbing of solids. Nearly one-half of all inorganic solids of both crystalline and noncrystalline structures exhibit the phenomenon of ML [1]. ML is often used to measure the velocity of crack propagation in solids or to image cracks structure [2,3]. The use of ML to characterize grinding has been reported in several articles [4–8]. Kürtén and Rumpf [8] have reported about a fairly good correlation between power consumption and intensity of ML during the grinding of sugar or ZnS/Mn. Later, the same correlation for quartz particles is reviewed [4,6,7].

However, the application of ML as tools for studying processes in grinding machines is often problematic because of decreasing total light outcome with reduction of particle size. Furthermore, the interpretation of obtained results is very complex since the ML of single particle with size of few microns is not exactly investigated. On the other hand, ML is very attractive for various applications in the context of fine grinding monitoring:

(a) The operating conditions can influence the particle breakage behaviour and, correspondingly, the distribution of created light impulses. The breakage mechanism depends on operating conditions such as the stress intensity, frequency [9] and particle size. Therefore, if the breakage mechanism remains the same, the type of function that described the light impulses distribution does not vary with breakage conditions and particle size as well. In this context, the breakage mechanism of fine particles can be tested by means of ML.

(b) It is often difficult to distinguish what kind of process takes place in the grinding device: grinding of primary
particles or disintegration of the aggregates or agglomerates. Aggregates consist of primary particles which are strongly bonded at their contact points by covalent or ionic bonds, e.g. crystallisation or sinter bridges. But weakly bonded primary particles by Van der Waals forces are called as agglomerates. Here we will use only one term—aggregates for both aggregates and agglomerates. The particle size measurement is usually based on the light scattering or particle motion under the influence of applied force. However, it is problematic to distinguish aggregates from primary particles by use of the light scattering or the particle motion under applied force. On the other hand, primary particles and aggregates build from this primary particles exhibit different behaviour under applied mechanical stressing. Mechanical stress applied to solid particles leads to the fracture of particles and intensive light emission. In case of aggregates, the applied stress leads mostly to cracking of the solid bridge bonds between primary particles. It occurs due to shear stress between mill media [9]. The breakage energy of aggregate is low compared with the energy necessary to break primary particle of the same size. As a consequence, the ML is not so intensive by stressing of aggregates and its contribution to the total ML is not significant. This factor can be used to distinguish what kind of process is responsible for size reduction in the grinding device—disintegration of aggregates, e.g. fractures of solid bridge bonds between primary particles or bulk fracture of particles.

Therefore, the objective of the research described in this paper is to develop and to test ML-based method for monitoring grinding processes in stirrer media mills.

2. Mechanoluminescence of quartz

Quartz is a piezoelectric material that exhibits a strong luminescence caused by mechanical loading. This is a reason for intensive use of quartz for studying of luminescence-related phenomena. Pacovich [4] and Streletsky et al. [5] reported about the study of luminescence of quartz induced due to grinding in lab scale vibration mill. Their mechano- and photoluminescence spectra are found to be similar. Both spectra exhibit two peaks of luminescence intensity. First peak (blue) reached its maximum at the wavelength of 475 nm and the second one, (red) at the wavelength of 650 nm (Fig. 1).

Consequently, it is possible to distinguish two types of active chemical radicals. The first one, two-coordinated silicon atoms (≡Si–O–)2Si: is responsible for red luminescence and the second one, silylene (≡Si–O–)2Si* is responsible for blue luminescence. Both types of radicals are located in the optical active centres with surface number concentration of about 10^15 m^-2 estimated by means of electron paramagnetic resonance spectroscopy [12].

The intensity of light emitted from single particle being stressed is a function of time. The curve of light impulse (intensity versus time) reflects the particle behaviour under applied stress. There are two different kinds of optical impulses (respectively time behaviours) that appear during the dry mechanical treatment of quartz particle in the grinding device. Optical impulses of first type have a symmetric shape with lifetime about 10 ms. The impulses of second type have an asymmetric shape and short lifetime about 1 ms [4,6].

Impulses of first type are more intensive in blue wavelength range. Usually, symmetric impulses are caused by plastic deformation and creation of microcracks (Fig. 2). An intensive quenching of symmetric impulses occurs

![Fig. 1. Typical mechanoluminescence spectrum of quartz [4].](image1)

![Fig. 2. Light radiation by single particle stressing.](image2)
rapidly in the gas environment. As a rule, the impulses of the second type (asymmetric) accompany the creation of new surfaces. The intensity of these impulses in the red spectral range is larger than in the blue one.

3. Experimental

3.1. Experimental setup

ML of quartz particles was monitored on the lab-scale stirred media mill produced by Netzsch. Grinding chamber was filled with about 2 mm zirconium dioxide ceramic beads. The filling rate of this grinding media (bulk volume related to the net volume of the grinding chamber) was 0.7. The revolution number of the stirrer was varied from 1500 to 2500 rpm which corresponds to the range of stirrer tip speed between 3.16 and 5.2 m/s. Fig. 3 shows the schematic diagram of the measurement technique. The temperature of water suspension with quartz particles was kept constant at 18 °C.

The wall of the grinding chamber was made from quartz glass. Quartz exhibits optical transmission for UV radiation and high resistance to abrasion. The design of optical system allows the recording of ML impulses from a small volume of the grinding chamber only. The characteristic size of this volume is comparable with the diameter of the grinding media. Hence, the change of optical transmission during the grinding does not influence the results of measurement. Sampling of ML impulse was carried out by use of the photosensor module H6779. This sensor exhibits a high sensitivity in visual and ultraviolet wavelengths range. The data acquisition was performed by use of the ME-3000 PCI board. This board provides the data sampling with the rate up to 300 kHz. The visual programming language HP-VEE was applied for data processing.

Milled quartz—product SP6 with 99.9% silica contents was used as a feed material. Feed particles were produced by means of dry grinding of the quartz sand in the ball mill. During the dry grinding in the ball mill, intensive creation of defects and optically active centres occurred. Due to mechanical activation, a great number of aggregates were formed. As a result, the feed material contains a great number of pre-existing aggregates and solid particles with optically active centres.

3.2. Signal processing

Data acquisition (logging) was carried out with the sampling rate of 300 kHz during the period of 0.33 s. As a result, the time sequence of 10 000 samples was obtained. The form of obtained ML impulses was asymmetric like the one observed in the case of dry grinding [4,6,7]. During the grinding in the stirrer media mill, the intensive quashing luminescence takes place in the liquid environment of particles. As a result, amplitudes of ML impulses had the low level that was comparable with noise signal of the photosensor. However, there is an approach to improve the signal-to-noise ratio. The method is based on the fact that the characteristic time of ML impulses is usually three to four times longer as duration of noise impulses. Consequently, the short initial impulses were eliminated by use of the digital filter. After applying the digital filtration, the signal-to-noise ratio was significantly improved. The thresholds of the digital amplitude discriminator were subdivided into $k=16$ classes. The impulse amplitude was normalized with respect to lower amplitude $A_{16}=27$ mV. Finally, the number of impulses $N(A_k)$ with normalized amplitude larger than amplitude $A_k$ was counted. Another important characteristic of impulse amplitude distribution—number of impulses $n_i(A_k)=N(A_{k+1})-N(A_k)$ in the amplitude interval $A_{k+1}-A_k$ was computed. The density of impulse number (DIN) $n$ is expressed by:

$$n = \frac{\delta N}{\delta A} = \frac{N(A_{k+1}) - N(A_k)}{A_{k+1} - A_k}$$

To achieve statistical validation of measured data, the measurement was repeated hundred times for each fixed grinding time. Before start and after the end of grinding, a test calculation of noise impulses (without particles in the mill) was carried out. If the difference between numbers of noise impulses was larger than 20% at the lowest applied amplitude, the results of measurement were not accepted and the measurement was repeated. The resulting ratio of signal-to-noise impulse number was more than 10 at lowest applied amplitude of impulse. At other amplitudes, the noise impulses disappear.

4. Results

4.1. Impulse number distribution and breakage of particles

The normalized density of impulse number $n$ varies versus amplitude from 1 to $2 \times 10^{-4}$ (Fig. 4) that corre-
sponds to the range of normalized amplitude of impulse $A$ from 1 to 28.42. The density of impulse number $n$ was found to be independent of stirrer tip speed. A grinding time of 9 min was chosen for representation of this distribution. It seems reasonable to assume that the obtained function $n(A)$ reflects different behaviours of particles under applied mechanical stressing:

(a) the first part of the dependence at low impulse amplitudes reflects the mechanical stressing of fine particles

(b) the second part at high impulse amplitudes (higher than critical amplitude $A_c=10$) and low density of impulse number corresponds to the breakage of coarse particles [4,6].

The line $n(A)$ in Fig. 4 can be fitted with the function:

$$\ln(n(A)) = a \ln(A) + C$$

with the exponent $a$ of amplitude function

(a) $a_1 = -(6 \pm 0.2)$ for $A > A_c$

(b) $a_2 = -(2.5 \pm 0.04)$ for $A < A_c$.

An exponent $a_2 = -(2.5 \pm 0.3)$ was found in case of grinding quartz particles in the jet mill [6,7].

It is worth to note here that breakage rate is depending on particle size [13]. Hogg and Cho [10] have reported about similar effects of particle size on specific rate of breakage. According to Ref. [10], the specific rate of breakage for quartz particles could be simulated using an exponent dependence on the particle size. This exponent is increasing from 1.0 in the coarse size range to 2.0 for the submicron particles.

The particle size distribution can be used to find the critical amplitude $A_c$ that corresponds to change of exponent $a$. It is known, that the curve of fragment distribution obtained during grinding is influenced by the microprocess of size reduction [11]. Fig. 5 represents the evolution of size volume fraction with the grinding time measured by the Mastersizer (Malvern Instruments). A strong bimodal size distribution was observed. There are two sub-collectives or sub-populations of the total population:

(a) sub-collective of fine particles with size smaller than 2 μm and

(b) sub-collective of coarse particles with size larger than 2 μm

This bimodal size distribution is typical for disintegration of aggregates. The mode with $d_c=0.6$ μm corresponds to the sub-collective of fine particles and depends only weakly on time. The resulting fine particles have almost the uniform size distribution and only the total fraction of these particles is increasing with time, see increasing area below the left peak of Fig. 5.

It makes sense to conclude, that the critical amplitude $A_c=10$ (Fig. 2) corresponds to a split size $d_c$ (about 2 μm) between the two sub-collectives. Both the split size $d_c$ and the critical amplitude $A_c$ do not depend on the grinding time. The sub-collective of elementary fine particles already existed in aggregates as bonded constituents. Size distribution and other properties of these particles are dependent on the type of dominant breakage mechanism in the ball mill and, more importantly, on the properties of the quartz sand that was used for production of the feed material. These solid particles appear to be pre-existing in the material that is ground. During the wet treatment in the stirrer media mill, the fine particles are so to say “liberated” from that parent aggregates. The mechanical properties of fine particles are different from the ones of primary coarse particles. Consequently, fine and coarse particles exhibit a different deformation or breakage behaviour under stress in stirrer media mill. That leads to the difference between exponents in observed distribution of impulse number.

### 4.2. Evolution of impulse number with time

It was mentioned above that the ML is not intensive by stressing of aggregates and breakage of solid bridge bonds.

![Fig. 4. Normalized density of impulse number (DIN) reflects the fracture and attrition of solid quartz particles.](image)

![Fig. 5. Evolution of total volume fraction of solid particle and aggregate sub-collectives with time. It is impossible to distinguish primary particles from aggregates that have the same size.](image)
Consequently, the breakage of aggregates makes no significant contribution to the total ML. This factor provides a useful way to study the disappearance kinetics of these aggregates. It can be expected, that the disappearance rate of pre-existed dry aggregates has a considerable effect on the size distribution at the beginning of wet grinding in the stirrer media mill. Fig. 6 represents the measured particle volume fraction at the different stirrer tip speeds and fixed grinding time of 1 min. The feed material is always the same. However, a great difference in particle volume fraction distribution is registered just in the first minute of grinding process.

The observed characteristic time of size reduction is estimated to be about a few minutes. This time is too short compared with the time that is necessary for effective grinding of the primary solid particles. It can be concluded that Fig. 6 demonstrates the disappearance of aggregates that is very significant at the beginning of the grinding process.

On the other hand, the disappearance kinetics of aggregates can be reflected by the dependence of the impulse number versus time. Fig. 7 shows the impulse number at the normalized amplitude 1 versus time. One can see that the impulse number is a maximum at the beginning of process and then decreases exponentially.

Additionally, at larger operation times the impulse number \( n(A, t) \) is proportional to \( \exp(-k(A) \cdot t) \), where \( k(A) \) is an impulse disappearance constant. Consequently, the increase in number of fine particles (see Fig. 6) with time requires an existence of two sub-collectives of fine particles that can be distinguish according to their optical properties. The “light” particles hold their ML properties up till current measurement time. However, all the “dark” particles have lost their ML properties after stressing.

5. Discussion

5.1. Disappearance kinetics of aggregates

It is reasonable to assume that the number of impulses at given normalized amplitude \( A \) is proportional to the stress frequency of particles with size \( d_i \) that corresponds to amplitude \( A \). According to Ref. [9], the stress frequency (SF) can be expressed as

\[
SF = uc(d_i)f(d_i)
\]

where \( c(d_i) \) is number concentration of particles with size \( d_i \) and \( f(d_i, \ldots) \) is function of \( d_i \) and process parameters such as diameter and filling ratio of the grinding media. In the case of fixed operating parameters, the impulse number may be represented by

\[
n_l(A_i, t) = kuc_l(d_i)f(d_i)
\]

where \( k \) is constant and \( c_l(d_i) \) is the number concentration of “light” particles. The relative number of “dark” particles is low at the beginning of grinding process. On the other hand, at the beginning of process the operating time is too short to change the structure of parent aggregates. In this case, the structure of aggregates remains similar for all stirrer speeds and \( c_l(d_i) \) is proportional to the volume fraction of fine particles. Therefore, the relationship represented by Eq. (5) can be tested at the beginning of process (Fig. 8). It can be

\[
\text{Fig. 8. The fraction of low amplitude impulses versus volume of fine particles by different speeds of stirrer. Operating time } t = 1 \text{ min.}
\]
seen that impulse number $n_1$ normalized with respect to stirrer speed $u$ is proportional to volume fraction of “elementary” particles. Taking into account the exponential decreasing of impulse number versus time and Eq. (5), the impulse number can be expressed as

$$n_1 = (A, t) = kuf(d) \int_0^t c(d, \tau)\exp(-k_1(A)(t-\tau))d\tau \quad (5)$$

where $\delta c = \dot{c}(d, \tau)d\tau$ is the change of number concentration of “elementary” particles with size $d$ in the fine sub-collective (below $d_c=2 \, \mu m$) during the time interval $d\tau$. It might be expected, that the disappearance of aggregates is the first-order process similar to the size reduction of aggregates obtained by the sintered alumina particles [11]. Consequently, the increasing ratio of fine particles number concentration is given by

$$\dot{c}(d, \tau) = k_p n_{p,\text{max}} \exp(-k_t \tau) \quad (6)$$

where $k_p$ is a constant which characterizes the disappearance of the aggregate and $n_{p,\text{max}}$ is proportional to the number of fine particles in the mass unit of feed material.

By substituting $\dot{c}(d, \tau)$ from Eq. (6) in Eq. (5), we obtain for the impulse number

$$n_1(A, t) = kuf(d)n_{p,\text{max}}(d) \frac{k_p}{k_p - k_t} \left[\exp(-k_t t) - \exp(-k_{p,\text{max}})\right] \quad (7)$$

If the operating time $t$ is high and $k_p \gg k_t$, then the Eq. (7) can be simplified as follows:

$$n_1(A, t) = kuf(d)n_{p,\text{max}}(d)\exp(-k_1(A)t) \quad (8)$$

Eq. (8) can be rewritten as

$$\ln \left[\frac{n_1(A, t)}{ku} \right] = B(A) - k_1(A)t \quad (9)$$

with

$$B(A) = \ln \left(f(d)n_{p,\text{max}}(d)\right) \quad (10)$$

If the impulse number reaches its maximum at the time $t_{\text{max}}$ then we obtain from Eq. (7)

$$k_p \exp(-k_{p,\text{max}}) - k_t \exp(-k_{t,\text{max}}) = 0 \quad (11)$$

If the $k_t$ is already determined from Eq. (9) then Eq. (11) can be used for numerical calculation of the disappearance constants of aggregates $k_p(A)$. Those values are found to be from 0.2 to 1/min.

5.2. Particle size distribution

A term $B(A)=\ln(f(d)n_{p,\text{max}}(d))$ in Eq. (9) can be found as function of amplitude $A$ by means of linear fitting the data according to Eq. (9) and taking $t=0$. The initial condition $t=0$ corresponds to the start of grinding. As mentioned earlier, the particle size distribution $n_{p,\text{max}}(d)$ of feed material used in all tests is the same. Therefore, the dependence $B(A)=\ln(f(d)n_{p,\text{max}}(d))$ remains the same regardless of the stirrer speeds (see Fig. 9). The weak reduction of $B$ at stirrer speed of 3.68 m/s can be explained by media segregation in the mill. Generally, the link between particle size and impulse amplitude allows to measure the size distribution of primary particle in a collective which consists of both aggregates and primary particles.

On the other hand, the dependence $B(d)=\ln(f(d)n_{p,\text{max}}(d))$ can be obtained due to direct calculation from any known size distribution and parameters of grinding process [9]. This provides the use of equation $B(d)=B(A)$ to found the relationship $d(A)$ between particle size $d$ and impulse amplitude $A$. It can be carried out exactly if $B(A)$ reaches its maximum value at any fixed amplitude $A_m$ that corresponds to the size $d_m$ of maximum value $B(d_m)$. However, the amplitude $A_m$ was not reached by our measurements because of the range of ML impulse amplitudes used in this work was limited by the sensitivity of the photosensor.

6. Conclusions

The mechanoluminescence (ML)-based method of process characterization can be used for investigation of size reduction in stirrer media mills. The results obtained by the analysis of ML impulses are generally similar to those obtained by means of other methods. For example, the difference between specific rate of breakage for primary quartz particles in fine and coarse sub-collective is verified by the analysis of impulse number distribution. The impulse number is found to be proportional to the stress frequency.

Generally, the size distribution of primary particles in a collective, which consists of aggregates and primary
particles, can be calculated from impulse number distribution. This allows the on-line monitoring of size reduction of primary particles in such collectives. However, due to limited range of impulse amplitudes, it will be shown in a future work. Other interesting application of ML is the research of disappearance kinetics of aggregates. The impulses caused by stressing of fine primary particles are found to be suitable for this purpose as well.

List of symbols

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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>( A )</td>
<td>normalized impulse amplitude</td>
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<tr>
<td>( A_c )</td>
<td>critical impulse amplitude</td>
</tr>
<tr>
<td>( d )</td>
<td>particle size in ( \mu \text{m} )</td>
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<tr>
<td>( k )</td>
<td>proportionality constant between stressing frequency and impulse number</td>
</tr>
<tr>
<td>( k_1 )</td>
<td>impulse disappearance constant in ( \text{min}^{-1} )</td>
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<td>( k_p )</td>
<td>constant that characterized the disappearance of aggregates in ( \text{min}^{-1} )</td>
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<tr>
<td>( N(A_k) )</td>
<td>number of impulses with the amplitude greater than ( A_k )</td>
</tr>
<tr>
<td>( B(d(A)) )</td>
<td>logarithms of stressing frequency of feed particle divided by stirrer tip speed</td>
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<tr>
<td>( n(A_k) )</td>
<td>number of impulses in the range of amplitudes between ( A_{k+1} ) and ( A_k )</td>
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<tr>
<td>( n_\text{p, max} )</td>
<td>parameter which is proportional to the number of primary particles in the mass unit of feed material in ( \text{m}^{-3} )</td>
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<tr>
<td>( u )</td>
<td>circumferential speed of the stirrer tip in ( \text{m/s} )</td>
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<tr>
<td>( t )</td>
<td>grinding time in ( \text{min} )</td>
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Greek symbols

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<tr>
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<tbody>
<tr>
<td>( \alpha )</td>
<td>exponent of power function</td>
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References