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Changes of surface and volume properties of calcite during a batch wet grinding process

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Abstract

An experimental study on the ultra-fine wet grinding of calcite in a batch stirred bead mill is reported. The evolution of the size distribution and of the specific surface area of the particles versus grinding time was measured revealing that an agglomeration phenomenon takes place during the comminution process. The X-ray diffraction profiles versus milling time did not show any polymorphic phase transformation but an intensity reduction and a broadening of diffraction peaks. The size distributions can be properly fitted by a linear combination of statistical log-normal laws, taking the agglomeration of particles into account. The analysis of rheological properties of the ground suspensions revealed a plastic thinning behaviour which can be described by the Hershel–Bulkley equation.

Keywords: Comminution; Wet grinding; Stirred bead mill

1. Introduction

Grinding is one of the most used processes allowing the production of very fine particles. Many industrial applications are concerned by ultra-fine wet grinding processes. Examples of applications are fillers for paper or plastic, coatings, pigments, ceramics for abrasives and structural applications, pharmaceuticals, agro-chemicals, etc. However, the prediction and the control of the ground product properties are still difficult, especially relating to ultra-fine grinding processes.

Comminution includes all the processes allowing a size reduction or an increase of the specific surface area of particles. But, other physico-chemical properties are modified [1–4]. Indeed, during a fragmentation step, the stress energy is converted into elastic energy applied to the lattice lacks (vacancies, dislocations, grain joints, etc.), which gives rise to cracking. Additionally, plastic deformations also occur. During prolonged mechanical treatments, the further dissipation of energy generates the alteration of superficial and structural properties of materials and some phenomena can occur such as superficial amorphization of crystallised solids, polymorphic phase transformations, surface activation or changes in surface properties and mechano-chemical solid-state reactions. Even moderated mechanical treatments can influence the superficial energising of minerals that is put in evidence by adsorption isotherms of molecules having a strong affinity with the solid. Thus, various physical and physico-chemical aspects of a grinding operation have to be known. They depend on the minerals and mill characteristics, the energy applied to the system, the temperature and the pressure of the environment. Different studies have been developed for several materials on these points [1–12].

Calcium carbonate was chosen as test material for this study. It is a salt, widely used in the ground form, in paints, food or pharmaceuticals industries and as filler in the papermaking process; it permits the production of a brighter paper with a greater resistance to yellowing and ageing. Moreover, used as a part of the coating of the paper, it provides larger opacity, printability, ink receptivity and smoothness to the paper. It is also used as filler in plastic industries to improve heat resistance, hardness, colour fastness or stability of the materials.

Concerning calcite, bibliography reports a decrease of the reactivity during mechanical treatments and an increase of the energising heterogeneity [4,5]. Moreover, a polymorphic phase transformation of calcite into aragonite was observed, however, this is restricted to the dry grinding processes [8–12]. The lack of this in wet operations is allocated to the dissolution of the amorphous surface layer or the restructuring of the disrupted layer. It was also observed that carbonates have a strong tendency to agglomerate

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Nomenclature

d_i	mean class diameter relative to class i (μm)
d_{50}	mean diameter (μm)
D_l	limit diameter (μm)
f_{LN}	mass density size distribution
$F(x)$	mass cumulative size distribution of particles of size less than x
g	acceleration due to gravity ($m\,s^{-2}$)
h_i	weight fraction of the sub-population i
i	index of each sub-population
k	constant of Boltzman ($J\,K^{-1}$)
K	viscosity coefficient of the Herschel–Bulkley law ($Pa\,s^n$)
n	flow behaviour index
SSA	specific surface area ($m^2\,g^{-1}$)
T	temperature (K)
v_i	relative volume in class i (%)
x	particle size (μm)
x_g	geometric mean size of the distribution (μm)

Greek symbols

γ°	shear rate (s^{-1})
ρ_l	liquid density ($kg\,m^{-3}$)
ρ_s	particles density ($kg\,m^{-3}$)
σ_g	geometric standard deviation (μm)
τ	shear stress (Pa)
τ_0	yield value (Pa)

during dry and wet grinding operations [3,13,14]. The agglomeration of fines, intensively produced during the batch operation, disturbs the size reduction process and modifies the properties of the ground suspension.

The aim of the paper is to analyse the effect of the ultra-fine wet milling process on the properties of ground calcite particles and suspensions in order to control the quality of the final product. Analysis of the evolution of particle size distribution versus grinding time was conducted, with particular attention paid to the aggregation and agglomeration phenomena taking place during the batch grinding operation. Thus, the changes during wet grinding of the properties of fragments and the rheological behaviour of the ground suspensions were carefully analysed.

2. Material and experimental devices

Batch grinding experiments have been carried out in a Drais Perl Mill. It is a laboratory agitated bead mill with a grinding chamber of 0.8 l. A double jacket ensures the cooling of the grinding chamber. A stirrer, constituted of four perforated discs fixed on a driven shaft, provides the energy required for the size reduction of calcite to the grinding medium. The agitation speed is controlled by a pulley arrangement giving four different speeds comprised between 2130 and 4370 rpm. In this study, the agitation speed was fixed to 2130 rpm in order to limit the wear of the beads. The grinding medium was composed of spherical silicate zirconium beads. The size of the grinding media used in stirred mills is usually between 200 and 4000 μm [15], but it is known that the smaller the beads size, the finer the fragments will be. So, fairly small beads with a size comprised between 400 and 600 μm were chosen for this study. In the same way, it is possible to adjust the filling volume of beads at a value, usually comprised between 70 and 85% [15]. The filling volume of beads was fixed at 80%, which was found to be the optimum value for this device, with respect to the time required to reach the limit size. Moreover, a temperature probe (PT 100) allows the temperature evolution of the suspension to be followed during the grinding process.

Precipitated pure calcite (>99%, Merck) corresponding to the rhombohedral crystalline form of the calcium carbonate was taken in this study. A SEM photo presented in Fig. 1a shows that the initial powder is constituted of calcite particle agglomerates. The agglomerates have a mean diameter of about 30 μm. The powder has a density of $2710\,kg\,m^{-3}$, a specific surface area (BET) equal to $0.54\,m^2\,g^{-1}$ and a hardness in the Mohs scale of 3.

In wet comminution processes such as those performed in agitated bead mills, the solid concentration of the suspension varies generally between 10 and 60 wt.%. In this study, an intermediate value of 30 wt.% of calcite in distilled water was taken.

Concerning the operating procedure, the suspension and the grinding media were simultaneously introduced in the grinding chamber, and the temperature in the double jacket fixed at 10 °C. The grinding run was then started, and the temperature of the suspension set. At fixed time intervals, the mill was stopped and sample taken. The size analysis and the characterization of the rheological behaviour were done immediately after stopping the mill to avoid a modification of the structure of the suspension.

3. Characterization of the particle properties

As mentioned in Section 1, not only the size distribution of particles is modified during a comminution step but also other properties of the material such as the specific surface area, the structure or the fragments shape. Some of these properties have been characterized in the present paper in order to analyse the effect of the grinding process on the quality of the ground particles.

3.1. Structure and purity

A powder diffractometer (CPS 120 INEL) was used for the structure characterization. The X-ray diffractograms were obtained using Co Kα radiation (at 50 kV and 30 mA). The measured line profiles were highly reproducible.

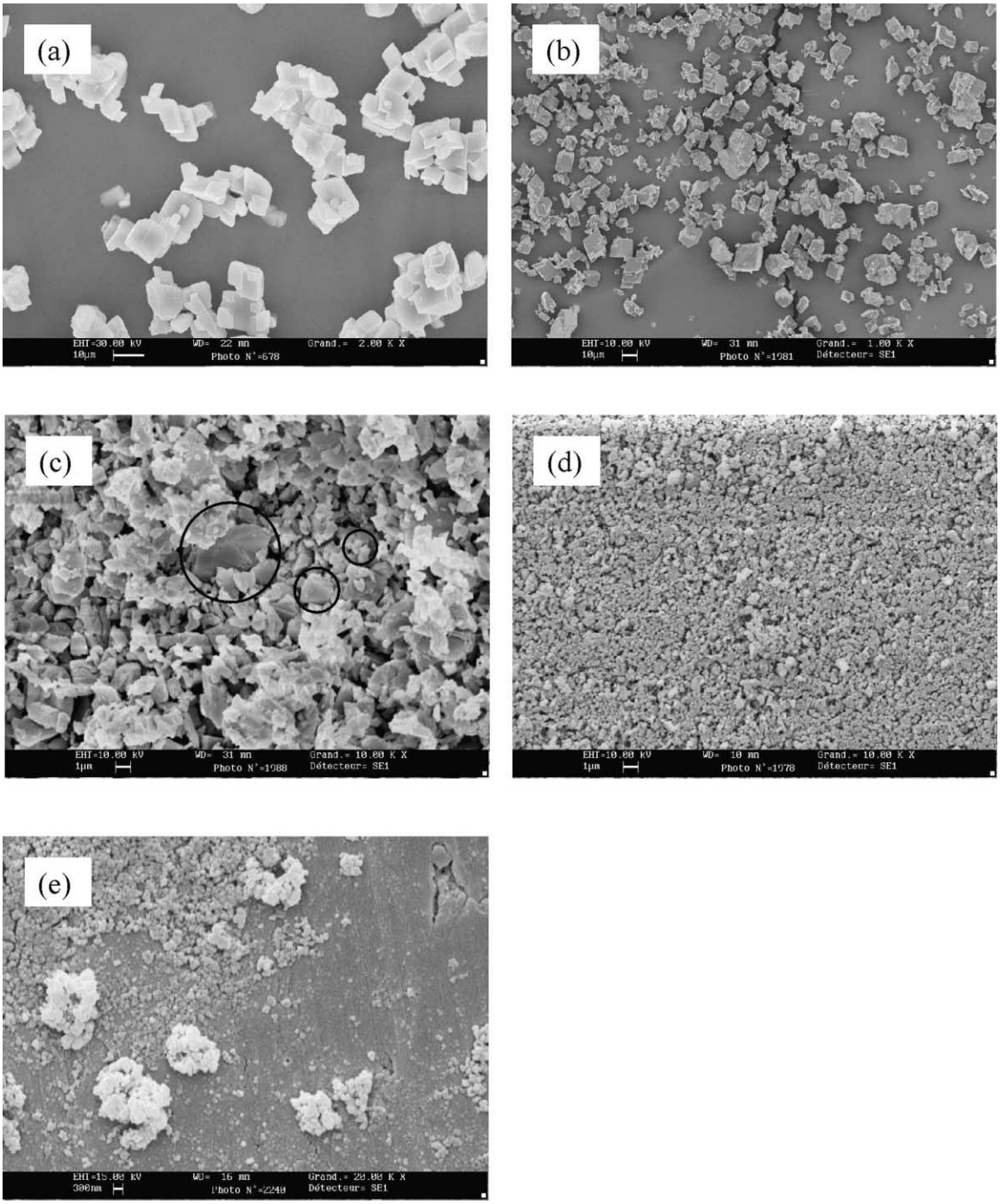

Fig. 1. Scanning electron micrographs of: (a) unground calcite; and calcite ground during (b) 10 s, (c) 3 min, (d) 10 min, (e) 45 min.

The diffractogram of the original powder (Fig. 2a) proves that the precipitated powder is only composed of pure calcite. In order to analyse the effect of grinding on the structure, the diffractogram of the original sample, and the one of the material taken after 60 min of wet milling were compared (Fig. 2). The change induced by grinding may be observed looking at the line broadening, the reduction of peaks intensity and the shifting of reflections. It is well known that a polymorphic phase transformation from calcite into aragonite may occur during prolonged dry grinding operations [8–12] where high pressures and a lattice defaults accumulation induce a restructuring of the lattice of calcite or of the newly formed aragonite. The lack of polymorphic transformation in wet grinding operations is usually explained by the cooling and the lubricating effects of the aqueous medium. Results of Fig. 2 confirm that no polymorphic phase transformation occurs for the run presented in this study.

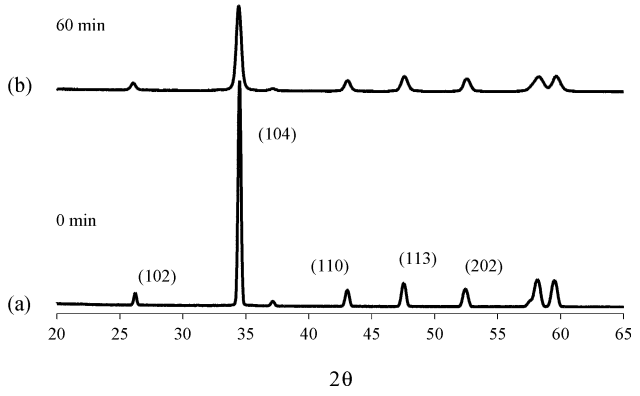

Fig. 2. X-ray diffraction profiles of: (a) untreated calcite and (b) calcite ground during 60 min.

Moreover, the diffraction intensities decrease versus grinding time and this is more pronounced for the (1 0 4) crystal lattice face. The integral breadth of the peaks also increases. Such an evolution has been reported in the literature by various authors [3,6,7]. Different interpretations have been made relating to runs performed in water or air. Indeed, the shape and the breadth of X-ray diffraction profiles, depend either on the crystallite size and lattice defaults or on an amorphization of the material. However, the amorphization aptitude of ground materials depends on milling conditions and seems to occur only in dry environments. Conversely, solids submerged in water possess at their surface, a layer of the medium that can allocate the shear strain [4]. In these conditions, the solid breaks following the initial discontinuities without an increase in the number of microstrains. Moreover, even if an amorphous layer is formed at the surface of the solid, it may be dissolved if the operation takes place in a medium such as water.

A chemical analysis of the ground product has also been performed in order to identify a possible pollution of the suspension by the grinding media, during the comminution process. An Inductively Coupled Plasma JY 24 was used and a quantitative analysis of the chemical composition in Si and Zr elements of the particles ground during various times was performed. Table 1 does not put in evidence a significant change of the Si and Zr concentrations with the grinding time. The concentrations remain relatively constant and are of the same order as those measured in the initial particles.

Table 1
Chemical concentration of Si and Zr elements in samples ground at different times

Grinding time (min)	Si (ppm)	Zr (ppm)
0	0.69	13.9
2	0.61	15
10	0.70	14.5
15	0.57	9.07
30	0.51	10.3

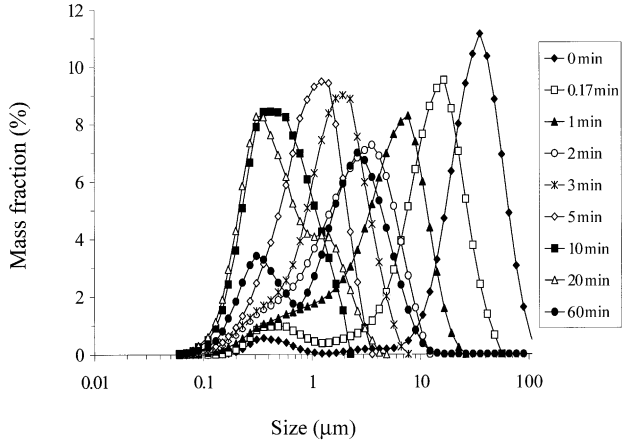

Fig. 3. Evolution of the experimental size distributions versus grinding time.

3.2. Evolution of the particle size during grinding and temperature control

The particle size distributions have been measured by means of a laser sizer (Malvern Mastersizer S) based on light diffraction. The ground suspensions were analysed after a suitable dilution in water without any surface active agent and without ultrasonic device in order to determine the state of agglomeration of the pulp in the mill. The analysed suspensions were highly stirred in order to disperse the fine particles. The full size distributions were firstly measured and the median diameter was then derived from the sizer results.

3.2.1. Evolution of the size distribution and of the median size

The evolution of the size distributions versus grinding time is shown in Fig. 3. The initial distribution is multimodal and puts into evidence the existence of three sub-populations. The mode of the coarser population is about 30 μm and shifts from the right side to the left during grinding. A second peak with a lower frequency can be observed at around 4 μm on the initial distribution. However, from the first few moments, these two populations merge into a spread one. The peak of the finer population is centred at 0.3–0.4 μm, with a mode which remains relatively constant during the milling process. After 5 min, the three peaks converge into a single peak whose mode decreases until reaching that of the finer population described previously. Finally, at the end of the run, another sub-population appears at approximately 1–2 μm, resulting probably from an agglomeration of fine particles.

Fig. 4 shows the evolution of the median diameter of the particles versus time. The size decreases rapidly during the first 10 min and then appears to slow down. After reaching a value of 0.45 μm, the median diameter increases, due to the agglomeration of the fine particles. After 45 min, the median size approaches a constant value, resulting probably of

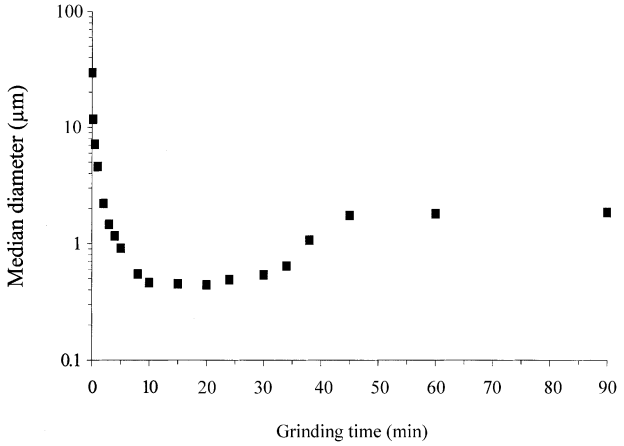

Fig. 4. Evolution of the median diameter versus grinding time.

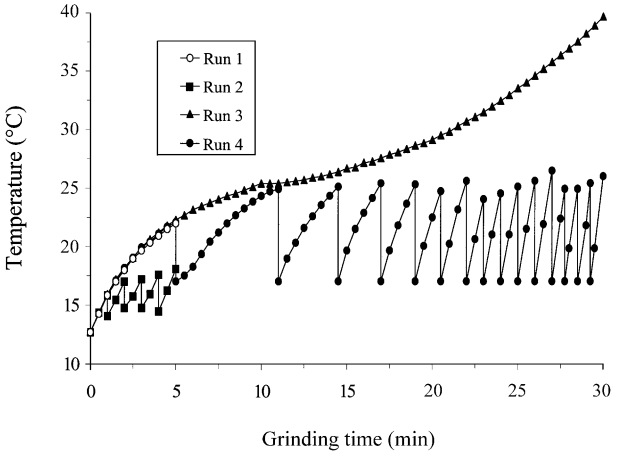

Fig. 5. Profiles of the temperature of the suspension versus grinding time.

an equilibrium between the fragmentation and the agglomeration processes.

3.2.2. Effect of the temperature control on the size distribution

It is well known that in grinding processes, the whole energy transmitted by the mill is not used for the size reduction, and, consequently, the temperature of the suspension may increase significantly during the process, in particular, when the particle size is very small. During the run presented above, an important increase of the temperature has been observed, and this may have an influence on the size evolution. This increase is due to the fact that the surface area of the chamber is not sufficient to evacuate the heat produced during batch grinding. Thus, the effect of the temperature variation during the experiment has been studied. For this purpose, the standard grinding chamber of the Drais Perl Mill has been replaced by a chamber which allows to put a temperature probe directly into the grinding chamber. Thus, the temperature can be measured in situ without stopping the mill. The probe was introduced in the middle of the chamber.

Four runs have been performed (with or without any control of the temperature) fixing the same operating conditions. To avoid a large increase of the temperature, the mill has been stopped at different times and started again when the temperature had decreased. The overall duration was 5 min for the first two runs and 30 min for the last two ones. The conditions of the runs are presented in Table 2, and the temperature profiles are illustrated in Fig. 5.

Fig. 6 presents the size distributions obtained after these four experiments, and shows that the temperature does not have a significant influence on the size of the particles.

3.3. Morphology

An LEO 435 VP Scanning Electron Microscope was used to observe the morphology of the ground particles. In order to try to observe the evolution of the structure of the suspensions versus grinding time, a drop of the suspension was dried immediately after grinding under a halogen lamp of 1000 W. The sample was then broken and plated by a gold layer, with the aim to observe the "heart" of the suspension.

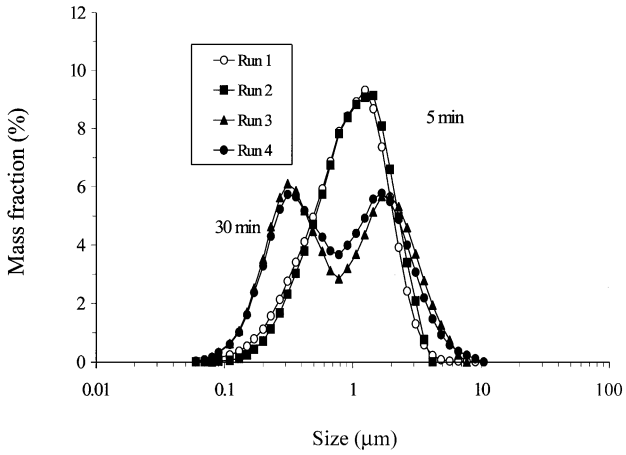

Fig. 6. Influence of the control of the temperature on the size distribution.

Table 2
Conditions for batch grinding runs in order to determine the influence of the temperature on the size distributions

	Run 1	Run 2	Run 3	Run 4
Run duration (min)	5	5	30	30
Grinding procedure	Without stopping the mill	Stopping the mill	Without stopping the mill	Stopping the mill
Maximum temperature of the suspension (°C)	22	18	40	26

Fig. 1 illustrates the evolution of the particles morphology versus grinding time. As indicated previously, before grinding, the powder is composed of agglomerates constituted by rhombohedral crystals of calcite (Fig. 1a). These agglomerates are nearly totally dispersed after 10 s of milling (Fig. 1b).

Then, the particle size quickly decreases with increasing grinding time, as illustrated in Fig. 1c after 3 min of comminution. Three types of fragments can be observed: some fragments with a relatively important size and a characteristic cubic shape, more numerous irregular smaller fragments and fines. Agglomerates made of fine particles or resulting from the coating of fine particles on coarser fragments can also be observed. The agglomerates are easily identifiable on the SEM photos due to their brightness since they present a great number of facets comparative to fragments.

For longer grinding times, the state of the suspension drastically changes leading to an increase in the consistency of the pulp which becomes more and more viscous. The SEM photo of Fig. 1d reveals that the suspension is fully aggregated and composed of only two kinds of particles: very fine fragments and agglomerates, whose the presence is confirmed after 45 min of grinding in Fig. 1e.

3.4. Specific surface area

The specific surface area of the samples taken after different grinding periods was first determined using the BET method with nitrogen gas as the adsorbate. The instrument employed was a NOVA 1000—QUANTA CHROME. The specific surface area deduced by the BET method (SSA BET) may be expressed by the product of adsorbed gas molecules by their surface divided by the mass of the sample. In the case of open agglomerates, the BET method allows to measure the whole surface area of the unit particles constituting the agglomerates. This value was compared to that deduced from the granulometric measurements (SSA LS), defined by

$$\mathrm{SSA\,LS} = \frac{6\sum v_i/d_i}{\rho_\mathrm{s}\sum v_i} \tag{1}$$

where v_i is the volume of particles belonging to size class i, d_i the mean diameter of particles of class i and ρ_s the solid density.

Values of the specific surface area obtained by both methods have been reported in Fig. 7. During the first minutes of grinding, the specific surface areas are similar but then, a deviation occurs, which increases with grinding time until constant values are reached. The linear increase of the SSA determined by the BET method proves that the breakage process still occurs until about 60 min. The difference between the two SSAs indicates that an agglomeration phenomenon takes place after a few minutes of milling and increases in importance. This result agrees with the evolution of the mean diameter of particles, as described in the previous section, which remains constant at around 0.45 μm and, increases then for longer grinding times (Fig. 4).

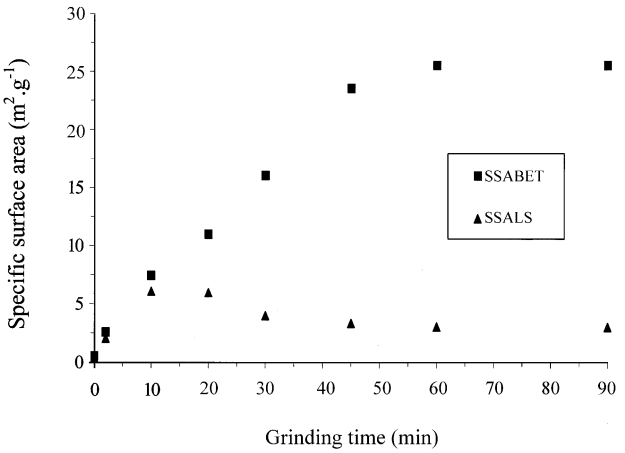

Fig. 7. Evolution of the specific surface area versus grinding time.

4. Modelling of the grinding kinetics

The main objective of this section is to express the grinding kinetics, in relation to the fragmentation mechanism, which could be used for process modelling, simulation and control. A kinetic model has been established taking into account not only the fragmentation step but also the agglomeration phenomenon which occurs during the comminution process.

Different methods have been presented in the literature to predict the size distribution. In particular, many statistical laws with two or three parameters or a combination of several laws have been applied to describe the size distributions in milling processes [16–18]. Experimental graphs of Fig. 3 and SEM photos of Fig. 1 clearly show the presence of several sub-populations of particles in the mill. Consequently, it has been tried to predict the experimental size distributions by combinations of various statistical laws (normal, log-normal, Rosin–Rammler). These preliminary trials have underlined that a combination of log-normal laws was appropriate for modelling grinding kinetics of calcite in the agitated bead mill.

The log-normal law is represented by the equation:

$$f_\mathrm{LN}(x) = \frac{\mathrm{d}F}{\mathrm{d}\ln x} = x\frac{\mathrm{d}F}{\mathrm{d}x} = \frac{1}{\ln\sigma_\mathrm{g}\sqrt{2\pi}}\exp\left[-\frac{(\ln x - \ln x_\mathrm{g})^2}{2(\ln\sigma_\mathrm{g})^2}\right] \tag{2}$$

where the geometric mean size x_g is defined by

$$\log(x_\mathrm{g}) = \frac{\sum \log(x)\,\mathrm{d}F}{\sum \mathrm{d}F} \tag{3}$$

and the geometric standard deviation σ_g is given by the expression

$$\log(\sigma_g) = \sqrt{\frac{\sum(\log(x) - \log(x_g))^2 \, dF}{\sum dF}}$$

The global equation of the evolution of the size distribution can be written as

$$\frac{dF}{d\ln x} = \sum_{i=1}^{n} h_i \frac{1}{\ln \sigma_{g_i} \sqrt{2\pi}} \exp\left[-\frac{(\ln x - \ln x_{g_i})^2}{2(\ln \sigma_{g_i})^2}\right] \quad (5)$$

where n is the number of sub-populations considered in the model, and h_i the weight fraction of the sub-population i.

It can be noted that if a larger number of log-normal laws are used for modelling, the results are in better agreement with the experimental data than if fewer log-normal laws are combined. Nevertheless, the number of laws must have a physical signification for the grinding process and considerations have been based in this study on the qualitative characterization of the particles morphology performed by SEM analysis.

The mean size, the weight fraction and the standard deviation of each law have been determined at each grinding time using a non-linear least-squares method. Their evolutions are presented in Figs. 8–10, respectively. A logarithmic scale has been used in order to have a full evolution as clear as possible of the data from 10 s to 90 min of milling.

Initially, as indicated in Section 3.2.1, mother particles are composed of three sub-populations: coarser particles with a mean size of 30 μm, intermediate population at 3.6 μm (called intermediate particles 1 in Fig. 8) and finer particles at 0.35 μm.

During the first 2 min, the size and the fraction of the first population decrease rapidly, due to fragmentation of the largest particles. On the other hand, the mean sizes of the two smaller sub-populations do not evolve significantly, whilst their proportions increase. These sub-populations are progressively supplied by the fragmentation products of coarser particles.

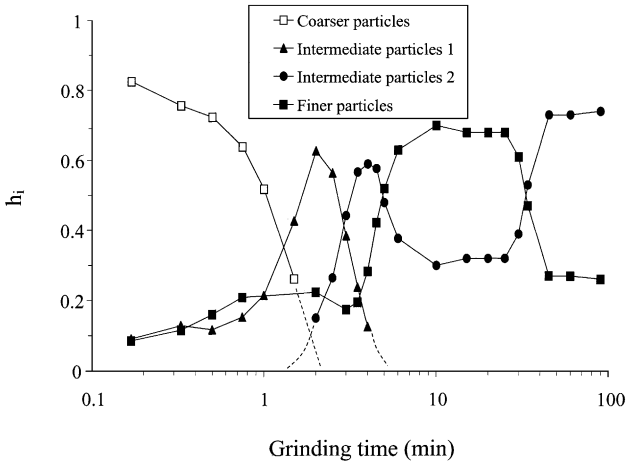

Fig. 9. Evolution of the sub-population fractions versus grinding time.

At 2 min, these coarser particles have totally disappeared. However, another sub-population (named intermediate particles 2 in Fig. 8) appears at 1.4 μm, which may be composed of fragments from intermediate particles 1 and agglomerates of fine particles. This is confirmed by SEM photos presented in Fig. 1. The agglomeration phenomenon seems to occur rapidly in the process, when the concentration of fines becomes significant. These three populations are observable between 2 and 4 min. During this period, the size of intermediate particles 1 decreases, whilst that of the two other populations levels off. The fraction of intermediate particles 1 also decreases, until this sub-population disappears. Concerning intermediate particles 2, their proportion becomes more significant due to an increase of the quantities of fragments and agglomerates with time. As for the finer particles, their fraction initially decreases and subsequently increases, in relation to the combination of a production of fines after

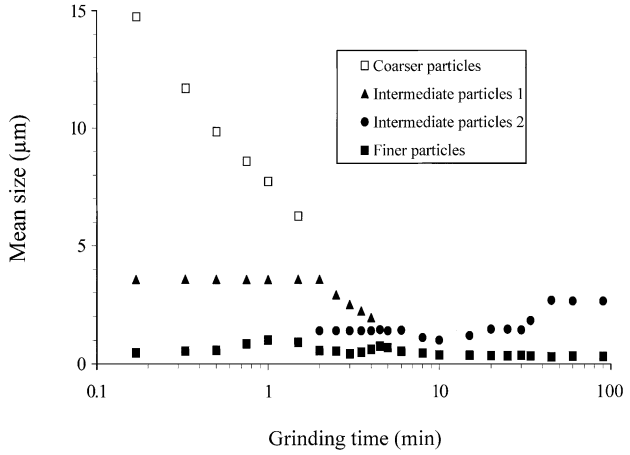

Fig. 8. Evolution of the mean sizes of the sub-populations versus grinding time.

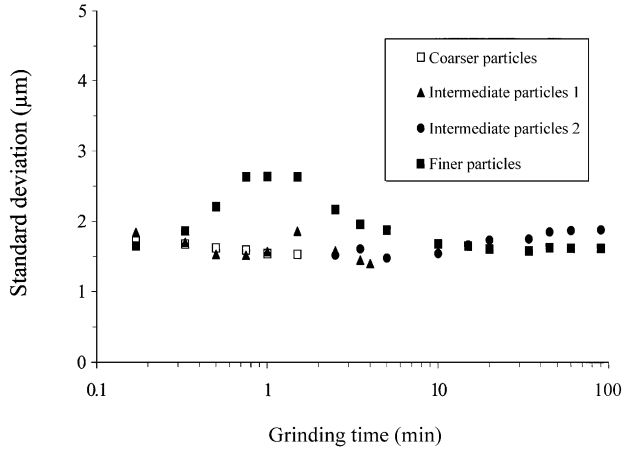

Fig. 10. Evolution of the standard deviations of the sub-populations versus grinding time.

fragmentation, and their disappearance resulting from agglomeration.

Finally, after 4.5 min, only two laws are necessary to fit the size distributions. These laws represent the two remaining populations: fine particles and intermediate particles 2. The mean size and the fraction of these ones initially decrease, then increase slowly after 10 min. In parallel, the proportion of fines increases until 10 min and decreases slightly then. This evolution may be explained by the fact that, as indicated previously, the sub-population of intermediate particles 2 is composed of small fragments and agglomerates. The fragments are progressively broken to produce fines. After a breakage of all the fragments, only agglomerates and fines remain in the mill (10 min). Then, the large fraction of fines leads to their progressive agglomeration. For grinding times higher than 30 min, the fraction of agglomerates becomes predominant over that of the fine particles, and their mode increases to reach a limit value after about 45 min of milling.

Moreover, standard deviations of the coarser particles and of the intermediate particles 1 decrease (Fig. 10), which proves that the size distribution becomes more narrow. In addition to that, the standard deviation of the finer particles increases during the first moments of grinding and then decreases to reach a constant value. Finally, the standard deviation of the intermediate 2 population seems to stay relatively constant during 10 min of grinding before slightly increasing and stabilizing for long grinding times.

A comparison between experimental and calculated size distributions at different times is presented in Fig. 11. Whatever the time considered, the size distributions are well predicted by the proposed kinetic model.

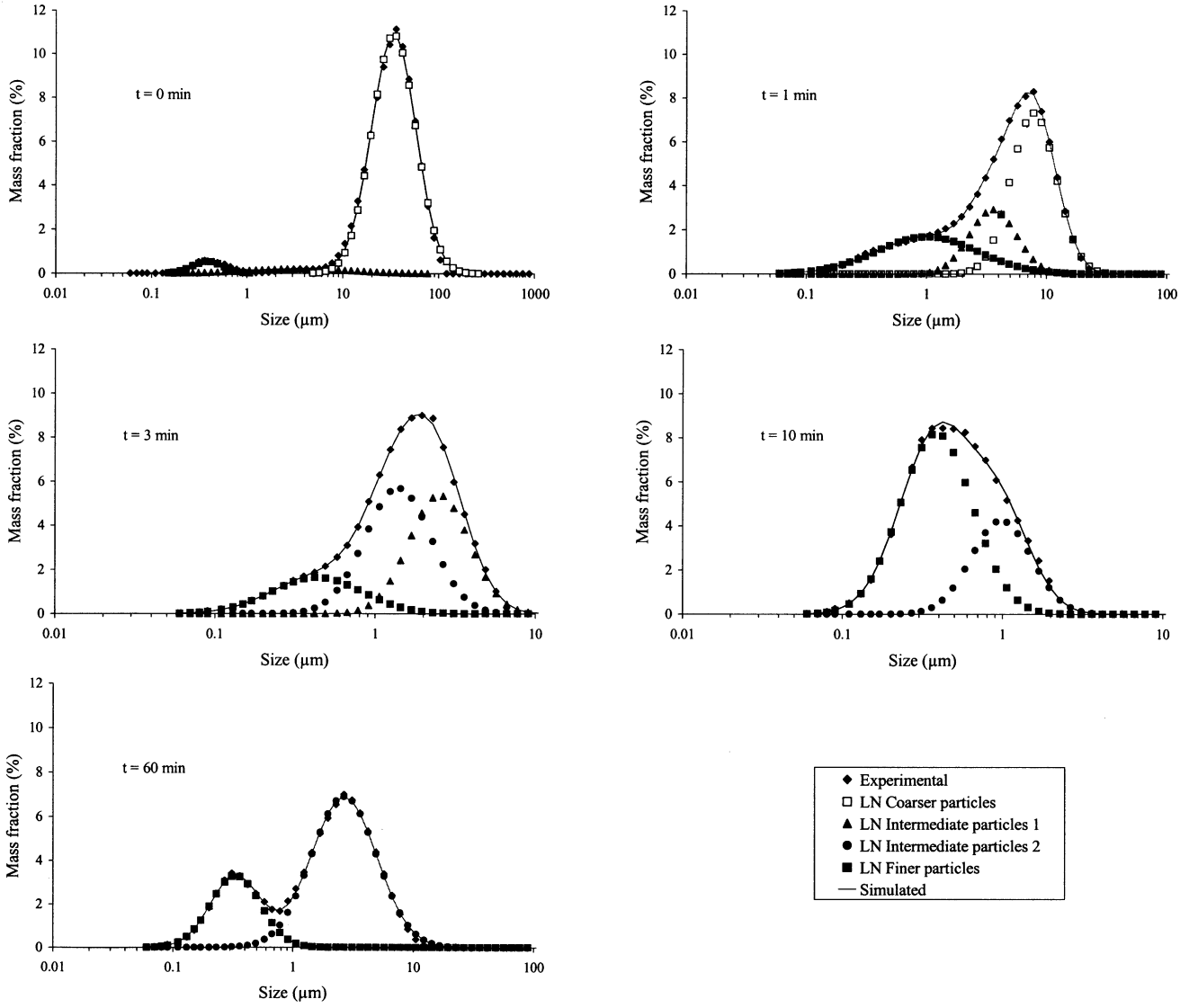

Fig. 11. Comparison between experimental and simulated data at different grinding times.

5. Rheological behaviour of the ground suspensions

The flow properties of suspensions depend on the properties of the liquid phase (viscosity, density, etc.) and of the dispersed phase (particles size distribution, shape, surface characteristics, volume concentration, etc.) [19–22].

When the particles are similar to the solvent molecules, depending on their size, the Brownian movement governs their motion. However, when the particle size enhances, the amplitude of this movement decreases, and the particles can then move under gravity forces (sedimentation). A limit size, D_l, governing the type of movement, is deduced as

$$D_l = \left(\frac{12kT}{\pi(\rho_s - \rho_l)g}\right)^{1/4} \quad (6)$$

If the particles size is lower than D_l, the suspension is seen as colloidal and the particles are subjected to the Brownian movement. Then, the interaction forces between particles govern the state of the suspension. Several particle–particle interactions are concerned, the combination of these defines the DLVO theory. If the attractive forces of Van der Waals type are predominant over the repulsive electrostatic forces, the system is flocculated and the suspension is composed of aggregates.

If the particles size is higher than D_l, the amplitude of the Brownian movement decreases and the particles move under the effect of gravity forces (sedimentation). The limit diameter calculated for calcite in water at a temperature of 20 °C is equal to 1.33 μm. Looking at the experimental size distributions presented in Fig. 3, one can see that, whatever the grinding time, the limit diameter always belongs to the size distribution, indicating that sedimentation can occur. However, the number of particles, with a diameter lower than this limit value, logically increases versus milling time and correct rheological analysis should be possible after a few seconds of grinding.

The aim of this part is to characterize the rheological behaviour of the suspension of calcite in water and to understand the phenomena which take place during the milling operation. Indeed, the viscosity of the suspension greatly influences the size reduction of the particles, and its evolution with grinding time modifies the hydrodynamic in the grinding chamber and so the quality of the final product.

Rheological experiments were performed on a TA Instruments CSL^2 500 rheometer to characterize the rheological behaviour of ground suspensions. This apparatus is a rotating rheometer working at imposed shear strains. The cone and plate geometry was used with a cone of 40 mm diameter and a 3.59° angle which was found to be the geometry giving the best measures. The shear rate could range between 0.14 and 646 s^{-1}. The temperature was fixed at 20 °C. The rheological measurements were performed 5 min after stopping the mill to limit the aggregation of fines. A pre-shearing step with a shear rate of 100 s^{-1} was applied during 10 s in order to obtain results independent from the deformation of the sample when it was put in place and from the pre-existent structure of the suspension formed during the time lapse between sampling and analysis. Preliminary tests were performed to ensure that the pre-shearing treatment did not destroy the sample. The curve, giving the shear stress, τ, versus the shear rate, γ°, has been established point to point. Analysis were performed setting the shear rate at a chosen value, and measuring the corresponding shear stress. The shear stress initially increases then tends towards a constant value at steady state. The value of the shear stress thus obtained corresponds to the true answer of the suspension when stressed at an imposed shear rate. The measurements were done for different shear rates in the available range and the curve τ (γ°) plotted. For all measurements, the volume fraction of the particles was equal to 0.136.

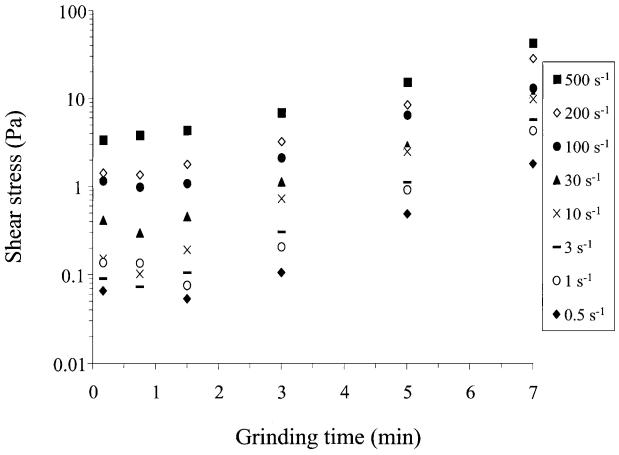

Fig. 12. Evolution of the shear stress versus grinding time for given shear rates.

Firstly, the evolution of the rheological behaviour of the ground suspensions can be seen in Fig. 12 for different shear rates. The shear stress and hence the apparent viscosity increase exponentially with grinding time, at a given shear rate. This evolution corresponds to the drastic modification of the pulp consistency observed during the milling operation, reaching a state similar to that of a paste. A part of the water constituting the continuous phase may be trapped in the bosom of the aggregates structure, and hence, it is no more available to promote the sliding of aggregates and particles between themselves.

The previous results have been reported in Fig. 13, where the shear stress has been plotted as a function of the shear rate for different grinding times. Fig. 13 shows that the shear stress increases with the shear rate whatever the grinding time considered. The suspension seems to have a plastic thinning behaviour which can be described by the Herschel–Bulkley law, defined as

$$\tau = \tau_0 + K\gamma^{\circ n} \quad (7)$$

The flow behaviour index, n, is less than 1, indicating that the suspension behaves as a shear softening fluid. Experimental

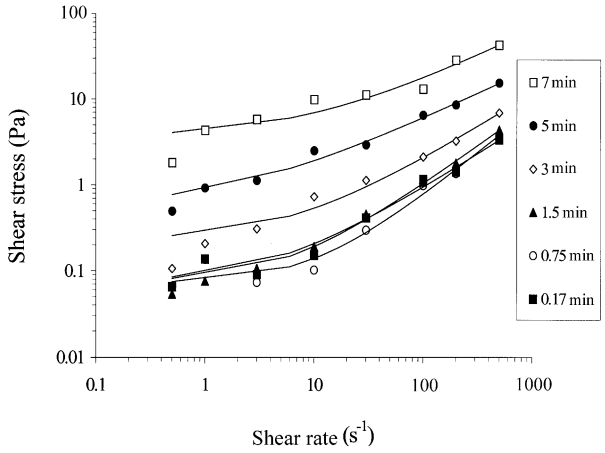

Fig. 13. Evolution of the shear stress versus the shear rate relative to experimental (symbols) and simulated (lines) data for given grinding times.

and simulated results are in good agreement as shown in Fig. 13. The increase of the viscosity coefficient, *K*, versus grinding time seems to indicate that the structure of the suspension is modified during the comminution process. The yield value, τ_0, characterizes the aggregation state of the particles in the suspension. It corresponds to the energy required to separate the particles overcoming the interaction energy due to Van der Waals forces. While the shear rate is low, the shear stress stands equal to the yield value. For higher values of the shear rate, the consolidated structure is broken and the suspension can flow. Indeed, when the particle–particle force is attractive, the rheological behaviour of the suspensions corresponds to that of a plastic fluid, which illustrates an aggregation of the particles remaining under high shear rates. Thus, the flow of the suspension does not correspond to a shifting relative to individual particles but between aggregates [21], and the qualitative state of aggregation is dependant of the attractive forces of Van der Waals. Unfortunately, the yield value of the suspensions could not be quantified experimentally in this study since shear rates lower than $0.1\,s^{-1}$ could not be applied with this apparatus.

Moreover, Fig. 13 puts in evidence a difference between suspensions ground for less or more than about 2 min. The samples are mainly composed of coarse particles, for short grinding times, while there is the formation of aggregates of fine particles then. During the fragmentation operation, the particles size greatly decreases versus milling time (Fig. 4), whilst the specific surface area increases (Fig. 7). The increase of the number of very fine particles with a high specific surface area may be considered as one of the main factors responsible for the increase in the yield value: the smaller the particles, the more aggregated they will become. Moreover, the particle agglomeration phenomenon takes place in the early stages of the process as concluded in the previous sections related to the fragmentation kinetics and the powder characteristics.

6. Conclusion

Experimental characterization of calcite ground in a batch wet comminution process has shown that an agglomeration phenomenon takes place under shear, due to the increase of the amount of fines produced during the process. The state of agglomeration can be deduced from the specific surface area data, comparing the results obtained from the BET method allowing the determination of the specific surface area of the individual fragments and those deduced from the laser sizer analysis. The size distributions of ground particles have been correctly fitted by a linear combination of log-normal laws. This kinetic model has been established considering several sub-populations of fragments and agglomerates whose presence has been confirmed by SEM photos of samples taken after various periods of time. From the rheological characterization, it was led to the conclusions that ground suspensions exhibit a plastic thinning behaviour, and that their structure is modified during the process. The increase of the number of fine particles versus grinding time seems to be the cause of this evolution of the suspension, promoting aggregation and agglomeration phenomena.

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