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Particle size distribution and structural changes in limestone ground in planetary ball mill

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ABSTRACT

The dry grinding of limestone in a planetary ball mill was investigated as a function of the diameter of the grinding balls and the revolution speed of the mill. The tests were carried out with the same feed size (75 × 250 μm) at variable times up to 240 min. The analyses of the mean particle size, the specific surface area and the dispersion in size distribution showed that the grinding rate slowdown when ~50% of the particles became smaller than 20 μm. Among the grinding conditions investigated here, that one set with 10 mm balls, 200 rpm and 60 min showed to be suitable to achieve mean particle size smaller than 10 μm. The scanning electron microscopy was useful to explain the decrease in the grinding rate by the effect of agglomeration of fines lying on partially broken particles. The agglomeration was attributed to the increase in particle surface energy that was promptly associated with the creation surface defects and bulk distortions detected by electron paramagnetic resonance (EPR) spectroscopy. The X-ray diffracting peaks of dolomite and other accessory minerals (talc, quartz and biotite) present in the limestone decreased with prolonged grinding. Differential thermal analysis revealed that the activation energy related to $MgCO_3$ decomposition in dolomite decreased with the grinding time increasing and a simple relation was found between the energy deposited by the mechanical action and the specific surface area of ground particles.

1. Introduction

The industrial uses of natural carbonate rocks are numerous and diversified. In building constructions, limestone ($CaCO_3$) and dolomite-bearing dolostone ($CaMg[CO_3]_2$) are used in the production of aggregates, dimension stones, cements and lime (CaO). In agriculture, they are employed as natural ground particles in soil correctives and fertilizers. Limestone and dolostone are integral ingredients to soda–lime silicate glasses, serving to assist in fluxing the melt while enhancing the durability of the product. They are also employed as fillers in paper, paint and polymer industries and play an important role in flue gas desulfurization and metallurgical fluxes. Finely ground limestone can be added to ceramic glazes or bodies as source of lime. Chemical composition and particle size distribution are chief specifications when limestone and dolostone are employed as fillers and fluxes. For instance, the top size of ground limestone for papermaking should be lower than 5 μm and the impurity content should be lower than 1% (Sinton, 2006; Varela et al., 2006; Sampaio and Almeida, 2008). These specifications are difficult to be achieved simultaneously using tumbling ball mills due to the high energy consumption to produce ultrafine particles and the subsequent contamination with iron. For ultrafine particles (<10 μm), the use of mills delivering a huge amount of energy for particle breakage, such as vibratory-, jet- and planetary-mills, has been considered an alternative for mineral processing (Osawaru and Orumwense, 1992; Wellenkamp, 1999; He et al., 2004).

In the so called planetary mill, a number of two or four bowls filled with the grinding balls are equidistantly installed on a supporting disk. The bowls and the disk are simultaneously and separately rotated at a high speed in opposite directions. The high speed of rotation of the bowls and the revolution speed of the supporting disk generate extremely high centrifugal forces acting on the balls. This results in, as an attrition effect, the grinding balls running along the inner wall of the bowl, and as an impact effect, the balls impacting strongly against the opposite wall of the bowl and against one another (Mio et al., 2002). The grinding may occur in dry or in suspension with the aid of liquids in order to minimize the agglomeration effect between ground particles (Hasegawa et al., 2001). Besides ultrafine grinding, high-energy milling has been successfully used for mechanochemistry in the process of numerous materials in laboratory-scale and industry (Mio et al., 2004; Baláž and Dutková, 2009). Transformations in the crystalline structure of industrial minerals due to the mechanical action of ultrafine grinding were already detected in kaolinite (Aglietti et al., 1986a, 1986b), gypsum (Zhang et al., 1996), talc (Mio et al., 2002) and anorthoclase (Sánchez et al., 2004).

As far as we know, even though the kinetic of breakage of carbonate rocks has been studied at different grinding conditions (Austin and Bagga, 1981; Choi et al., 2001; Teke et al., 2002; Matijašić et al., 2009),

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no attempts were done to look at surface distortions and bulk changes in ground particles of limestone. In addition, although the decrease in grinding rate has been attributed to the adhesion of ground particles between each other (Tavares and Kreischer, 2004; Mio et al., 2004; Sánchez et al., 2004), the circumstances under which agglomeration occurs were not yet related to surface or bulk distortions induced by high-energy milling. To tackle these problems, the aim of this study is to investigate structural alterations resultant from the mechanical action of grinding as well as particle size distribution and particle morphology of limestone ground at different conditions in a planetary ball mill. For this, size distribution and particle morphology were analyzed in order to characterize the grinding rate and the start-up of the agglomeration process. Electron paramagnetic resonance (EPR) spectroscopy, X-ray powder diffraction and differential thermal analysis were used to characterize surface defects and structural changes created in the mineral constituents of the limestone as a function of the grinding time. In addition, efforts were done to discuss the decrease noticed in the grinding rate with the agglomeration between ultrafine and coarse particles and the increase in the concentration of electron-trap centers measured by EPR spectroscopy. The intensity of Mn^{2+} hyperfine lines due to Ca–Mn substitution in calcite lattice and the activation energy due to thermal decomposition of $MgCO_3$ in dolomite were useful to show the effect of the mechanical action on the structural changes generated in ground limestone.

2. Experimental

In this study approximately 8 kg of limestone blocks originated from the country rocks of the Brejuí scheelite mine located in the district of Currais Novos (Rio Grande do Norte, Brazil) were used. Sample preparation occurred in two rounds as follows. The blocks were crushed with jaw and roll crushers until all particles being <1.7 mm. The crushed particles were ground in a porcelain ball mill in order to obtain particle sizes between 75 and 250 μm. After homogenization, 25 aliquots of 40 ml (~60 g) were obtained in each round of preparation. Two aliquots of each round were used to determine the initial particle size distribution by means of dry sieving. The nominal diameters d_{10}, d_{50} and d_{90}, corresponding to the apertures related to 10, 50 and 90% of passing material, respectively, were determined. Table 1 shows the mean values of d_{10}, d_{50} and d_{90} and the parameter d_{90}/d_{10} adopted as an indication of the size distribution heterogeneity.

The mineral constituents of the limestone were determined by X-ray powder diffraction (XRD) using two aliquots of the material with particle size <75 μm. XRD patterns were obtained with a *Rigaku-Ultima* diffractometer, Cu-Kα (40 kV, 20 mA) radiation, goniometer step of 1°/min and 2θ scanning from 2° to 80°. The qualitative analyses of the XRD patterns were performed by using a search software and the COD database (Gražulis et al., 2009). Besides calcite, it was identified the occurrence of dolomite, talc, quartz and biotite. Diffraction patterns of ground limestone were obtained in the same conditions. The full-width at half-maximum (FWHM) of the main diffraction peaks of each mineral was calculated.

The grinding experiments were carried out in a planetary mill, model *Fritsch Pulverisette 5* (revolution radius: 123 mm; rotation/revolution ratio (relative): 2.19; nominal power: 1300 W), with tempered tool-steel bowls (inner diameter: 75 mm; volume: 250 ml) and balls with diameters of 5, 10, 20 and 30 mm. The number of balls was fixed as a function of the charge volume that was fixed in 21 ml for all grinding media except when 30 mm balls were used. In this case, the volume of the feed was increased in the same proportion as the charge volume occupied by two balls (28.3 ml). Additional data for the grinding media is shown in Table 2. The first round of experiments was carried out varying the ball diameter, keeping the revolution speed constant (150 rpm), and varying the grinding periods from 7 to 240 min. For grinding times ≥60 min, a break of 5 min was adopted after each 30 min of grinding followed by the inversion of the direction of the revolution speed. Later, the tests were performed with different revolution speeds (100, 200 and 300 rpm) using grinding balls of 10 and 20 mm and varying the grinding periods from 7 to 120 min. For 300 rpm, the grinding period did not exceed 60 min. All tests were carried out in dry with the bowls rotating in the counter direction against the revolution disc.

The particle size distributions were measured by using a laser granulometer model *Malvern Mastersizer 2000*. The measurements were carried out in dry using the Scirocco 2000 accessory. Each ground aliquot was measured three times and the nominal diameters d_{10}, d_{50} and d_{90} were calculated. The specific surface area (S) of each size distribution was calculated by the equipment based on the assumption of the equivalent spherical volume and considering the optical properties and density of calcite (2.7 g/cm^3). The particle morphology was analyzed by scanning electron microscopy (SEM) using the *FEI Quanta-200-FEG* microscope. The images were obtained in low-vacuum with secondary (SE) and backscattering (BS) electrons without coating. Microanalyses by electron dispersion spectrometry (EDS) were carried out at several positions in ground samples.

The electron paramagnetic resonance (EPR) spectroscopy was carried for limestone ground with balls of 10 mm at 150 rpm. The samples (100 mg) were placed into fused quartz tubes with inner diameter equal to 2 mm. The measurements were carried out in a *Bruker EMX 10-Plus* spectrometer operating at the X-band (~9.83 GHz) provided with a high sensitive cylindrical cavity. Initially, the magnetic field was swept from 1000 to 5500 G. For specific magnetic field intervals, the signal was recorded as a function of the microwave power ranging from 0.002 to 63.25 mW. Then, the EPR intensity was recorded at room temperature by sweeping the magnetic field from 3400 to 3550 G setting the parameters as follows: microwave power: 2 mW; modulation amplitude of the magnetic field: 2.5 and 1 G; modulation frequency: 100 kHz; time constant: 5.12 ms; conversion time: 25 ms; receiver gain: 5×10^2; number of scans: 5. The peak-to-peak intensities of EPR signals were measured in non-saturated conditions. The EPR spectra were obtained before and after the samples being irradiated with a dose of 5 kGy of γ rays. The irradiation was carried out in a γ-cell irradiator (^{60}Co) with a dose rate of 5.43 kGy/h approximately.

Structural investigations were completed with differential thermal analysis (DTA) carried out in aliquots of approximately 1.2 g from limestone ground with balls of 10 mm at 150 rpm. The measurements were carried out with a BP-RB-3000 equipment from 25 up to 1000 °C operating at a heating-rate equal to 10 °C/min. The analyses were carried out in ordinary atmosphere using alumina as reference material. The peak temperatures related to the thermal decomposition of dolomite and calcite were indentified and the (non-calibrated) enthalpy differences were estimated by integrating the area of the endothermic events. At low pressure experiments, the enthalpy difference is an approximation for the activation energy (E) required to the thermal decomposition.

Table 1
Particle size characteristics of the feed.

Round	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)	d_{90}/d_{10}
1	84	145	244	2.9
2	76	136	205	2.7

Table 2
Overview of the grinding media used in the experiments.

Ball size (mm)	Number of balls	Filling rate (%)	Total contact surface (mm^2)
5	321	8.4	25,211
10	40	8.4	12,566
10 and 20	24 and 2	8.4	10,053
20	5	8.4	6,283
30	2	11.3	5,655