Effect of Different High-energy Grinding Technologies on Granulometric and Crystallographic Properties of Portland Cement

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Abstract. *The present article deals with the effect of different high-energy grinding technologies through available laboratory mills on Portland cement's granulometric and crystallographic properties. Two types of commonly available laboratory mills were selected, namely the planetary mill and the vibratory mill. The type of laboratory mill used, the grinding environment, and the grinding time were monitored. The planetary laboratory mill with 10 mm in diameter grinding steel balls proved to be more efficient in the scope of material reduction, which effectively reduces the material, especially during wet grinding of the material. The agglomeration effect is significantly reduced, which is a big advantage of method of wet grinding.*

Keywords

High-energy milling, laboratory mills, Portland cement.

1. Introduction

In the current era of environmental measures, it is important to look for ways to save energy in production processes. A large part of the energy in the production of cement is consumed in the grinding of Portland clinker. For several decades, research has been carried out on the topic of making the grinding process more efficient. Although the topic of the effect of grinding on Portland clinker is relatively well researched from the point of view of macrostructure, it is also necessary to focus on the microstructure and monitor the effect of grinding on the crystalline lattice of the ground material [1-2].

Grindability is one of the important properties of a material that is monitored in a wide range of industries. This is the ability of the material to disintegrate into smaller particles due to mechanical work. From an economic point of view, material that can be milled well is more suitable for the preparation of powder raw material [3-5].

One promising technology in milling is high-speed milling technology. The concept of high-energy or high-speed grinding is not precisely defined anywhere in the literature. It has all the basic properties in common with grinding in the classical sense, such as refinement of grain size, increase in surface area, the opening of grains, etc. In contrast to classical grinding, high-energy grinding (and also high-speed grinding) produces certain phenomena (effects) that are not observed in ordinary grinding. And it is to these effects that a certain part of the expended energy is converted, which in normal grinding is converted to heat without benefit [6-10].

Mechanochemical activation enables much more efficient use of energy, spent on the treatment, i.e., grinding of the substance. The effect of mechanochemical activation makes it possible, for example, to improve chemical reactions in the solid-state during grinding in high-speed grinding devices [14-15].

This paper examines the effect of two different high-energy grinding technologies on the crystallographic properties of the main clinker mineral Portland cement. One of the mills used will be a vibratory mill. It belongs to the group of devices with free storage of grinding bodies, the movement of which is not only dependent on gravitational forces. This type of mill is used for both dry and wet environment and for very fine grinding to a particle size of up to 10 µm. The second type of laboratory mill will be the planetary mill. It uses the principle of centrifugal acceleration, not gravity, which is used in commonly used ball mills. The planetary mill produces a high mechanical activation, already after a relatively short period of grinding. The energy density in this mill is 100-1000 times higher than that of commonly used mills [16]. The article also examines other influences such as the milling time and milling conditions on the granulometric properties and shape of the grains of the milled material.

2. Materials and methods

2.1. Characteristics of materials

Portland clinker (Hranice a.s., Czech Republic) and energogypsum (Precheza a.s., Přerov, Czech Republic) were used as the main raw materials. The clinker was crushed in a jaw crusher to a grain size of 4 mm. Energogypsum was dried at a temperature of 40 °C for 30 min. The resulting Portland cement was composed of 95% Hranice Portland clinker and 5% energygypsum. Material was analyzed by X-ray powder diffraction (XRD) and X-ray fluorescence (XRF). The XRD analysis was performed using a Panalytical Empyrean diffractometer (Malvern Panalytical Ltd., Almelo, Neetherland). The Panalytical HighScore 3 plus software was used to identify the individual phases. The ICSD (released in 2012) was used for a qualitative analysis of the diffraction patterns. Quantification was performed by the Rietveld method with a fundamental parameters approach.

The XRF analysis was performed using a PANalytical Axios 2.4 kW sequential wave dispersive spectrometer with Rh anode (Malvern Panalytical Ltd., Almelo, Neetherland). The acquired data was evaluated using the SUPERQ V4.0 software. The resulting values represent the average of three independent measurements.

2.2. The effect of grinding on the granulometric properties of cement

The cement was ground in the following two types of available laboratory mills. A laboratory planetary mill (PULVERISETTE 6, Fritsch, Idar-Oberstein, Germany) and a laboratory vibratory disc mill (RS 200, Retsch, Haan, Germany) were used. In a planetary mill, the cement was ground at 400 rpm for 80 min. Samples were taken for analysis at 1, 3, 5, 10, 20, 40, 60, and 80min. Grinding took place in steel grinding capsules with a volume of 500 ml using two different sizes of grinding steel balls: 10 mm in diameter (weight for one grinding was 300 g) and 20 mm in diameter (weight for one grinding was 100 g).

Grinding in the vibratory mill took place again for 80 min and, as in the previous case, samples were taken at times 1, 3, 5, 10, 20, 40, 60 and 80 min. Grinding in the planetary and vibratory mill took place in both dry and wet environments. In the case of wet grinding, acetone was used.

Samples of variously ground cement were subjected to analysis to determine the specific surface area by means of Blain's apparatus. Blaine-specific surface area was measured using a PC-Blaine-Star automatic device with a measurement cell capacity of 7.95 cubic centimetres. The measurement was performed three times to eliminate errors and the resultant value was the average of three readings.

2.3. Effect of grinding on the size of crystallites

Calculation of the crystallite size is based on the measurement of the full width of half maximum (FWHM). The FWHM values were obtained in the program HIGHSCORE PLUS for selected diffraction lines. The crystallite size was evaluated only for selected peaks on suitably selected crystallographic planes having a major crystallographic direction. Peaks were selected that were sufficiently high, had little overlap with other peaks, and at the same time they covered the chosen crystallographic plane directions. The crystallite size was evaluated by the modified Scherrer equation:

$$L = \frac{K.\lambda}{\cos\theta} \cdot \frac{1}{\beta} = \frac{1}{\cos\theta} \cdot \frac{K\,.\,\lambda}{\sqrt{B^2 - b^2}} \tag{1}$$

L is crystallite size, K is the Scherrer constant (0.94), λ is wavelength of X-ray radiation (1.540598), θ is diffraction angle, B is FWHM, b is FWHM of used standard (LaB_6).

2.4. Effect of grinding on grain shape

The effect of milling on grain shape was evaluated through SEM analysis by the scanning electron microscope TESCAN MIRA3 XMU. Samples were prepared using a colloidal graphite solution in isopropyl alcohol and a rotary pump pumped by a carbon sputter.

3. Results and discussion

3.1. Characteristics of materials

The chemical composition of the raw materials used, and the mineralogical composition of the resulting cement are shown in the following tables.

Tab. 1: Chemical composition of Portland clinker Hranice [%].

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	other
clinker	65.3	20.3	5.2	5.0	1.1	1.1	0.1	1.9

Tab. 2: Chemical composition of energygypsum [%].

	$CaSO_4.2H_2O$	H_2O	$CaSO_3$	TiO_2	SiO_2	Al_2O_3	Fe_2O_3	other
gypsum	84.0	11.0	2.4	1.2	0.6	0.4	0.3	0.1

Tab. 3: Mineralogical composition of Portland clinker Hranice [%].

	C_3S	C_2S	CaO	C_4AF	C_3A*	C_3A**	B	Calcite	G
clinker	71.2	8.7	0.0	8.7	3.0	1.7	1.2	1.8	2.8

*cubic, **orthorhombic, B-basanite, G-gypsum.

According to the results of mineralogical analysis, Portland cement Hranice contains a high amount of alite. The mineral alite is found in the monoclinic modification, specifically M1. Therefore, crystallinity will be assessed only on alite as the dominant phase, because other clinker minerals are represented in small amounts and their crystallinity would be very difficult to assess.

3.2. The effect of grinding on the granulometric properties of cement

The input specific surface area of cement was 230 m^2/kg. In Fig. 1, trends for grinding cement in individual types of laboratory mills in wet and dry environments are shown.

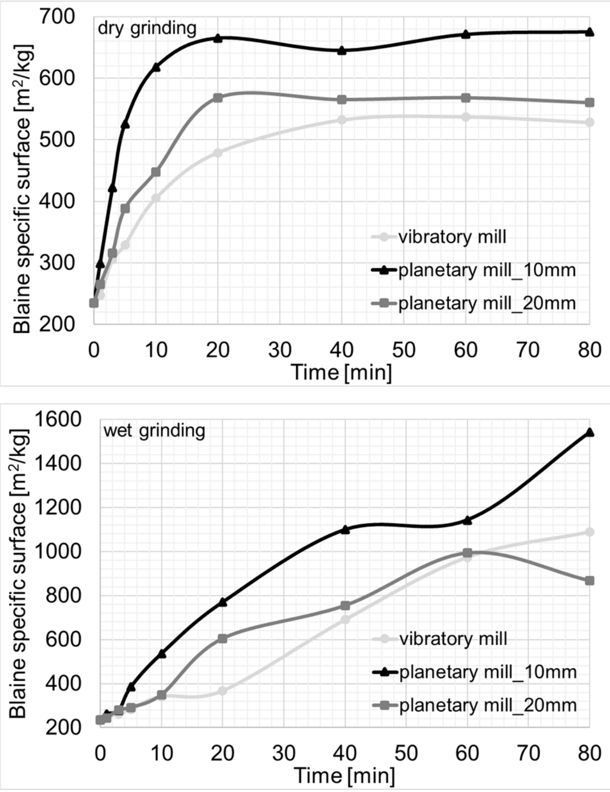

Fig. 1: Dependence of specific surface area on grinding time for individual types of mills and environment.

Dry milling

After just 20 minutes of grinding, the value of the specific surface reached 660 m^2/kg. When using 20 mm in diameter grinding balls, a value of 560 m^2/kg was achieved. The lowest specific surface values of only 480 m^2/kg were recorded after 20 minutes in the vibratory mill. As can be seen from the progress of grinding, a longer time no longer had a significant effect on the increase in the specific surface of the cement. The values remained approximately constant for further grinding time up to 80 minutes.

Wet milling

During wet grinding, the highest specific cement surface values were achieved again by grinding in a planetary mill with 10 mm in diameter grinding balls. After 80 minutes of grinding, a specific surface of 1470 m^2/kg was achieved. With 20 mm in diameter balls, only 990 m^2/kg was achieved after 80 minutes of grinding. For the vibratory mill, the value of the specific surface was determined to be 1090 m^2/kg after 80 minutes of grinding. During wet grinding, the influence of agglomeration is significantly reduced, therefore the specific surfaces increased throughout the grinding period for both types of mills. The grinding limit was probably reached after 60 minutes by grinding in a planetary mill with 20 mm in diameter of grinding balls.

In both methods of grinding in dry and wet environments, the highest fineness of cement was achieved in a planetary mill with 10 mm grinding balls.

Based on the development of grinding fineness, it can be concluded that higher specific surfaces can be achieved with wet grinding than with dry grinding. During wet grinding, the agglomeration effect is significantly reduced, which is a big advantage of this method of grinding. However, high surface area values for wet milling can be misleading, as the accuracy of the Blaine apparatus decreases at high surface area values around 1000 m^2/kg.

On the other hand, during the dry grinding the material accumulates between the rings and thus dampens the grinding efficiency. During wet grinding the suspension spreads spontaneously over the entire grinding area and grinding is thus more efficient

3.3. Effect of grinding on the size of crystallites

Due to the complexity of the lattice, it was difficult to select crystallographic planes that would clearly copy the major crystallographic direction, and which would also be reflected in the diffraction pattern by distinct isolated peaks. For this reason, distinct crystallographic planes determined by Miller indices „ hkl “41-1 were selected.

The following Tab. 4 shows the crystallite size values calculated based on Equation 1.

Tab. 4: Calculated crystallite size [Å] values for types of mills and milling environments.

Time [min]	Dry milling			Wet milling		
	PM 10mm	PM 20mm	VM	PM 10mm	PM 20mm	VM
1	947.2	936.7	852.7	897.2	1038.8	916.5
3	916.5	1091.0	980.2	926.5	968.9	980.2
5	878.8	869.9	957.9	887.9	887.9	968.9
10	743.8	790.7	957.9	763.2	763.2	957.9
20	628.5	731.5	820.4	686.3	686.3	869.9
40	509.0	697.0	812.8	697.0	697.0	869.9
60	445.1	651.3	776.7	651.3	651.3	828.3
80	316.6	569.3	713.8	569.3	569.3	783.6

PM-planetary mill, VM-vibratory mill

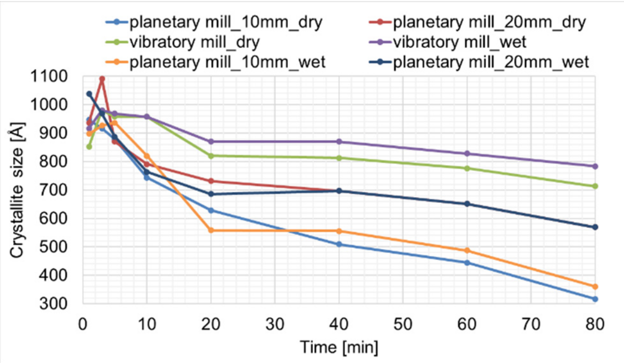

Fig. 2: Graphic representation of the dependence of crystallite size on grinding time.

3.4. Effect of grinding on grain shape

As part of the evaluation of the effect of grinding on grain shape, grinding in a planetary mill with 10 mm in diameter balls was compared with grinding in a vibratory mill. Dry and wet grinding were compared. The images taken were magnified 10000×.

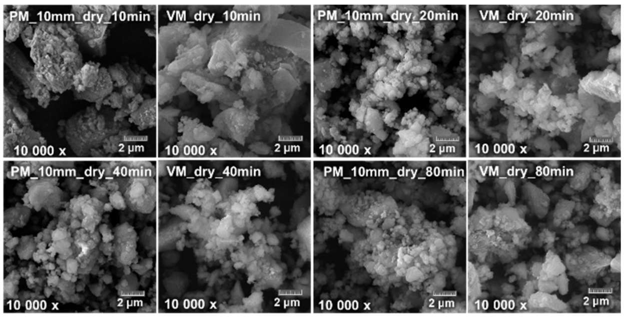

Fig. 3: SEM images of comparison of grinding in a planetary and vibratory mill in dry grinding after 10, 20, 40 and 80 minutes.

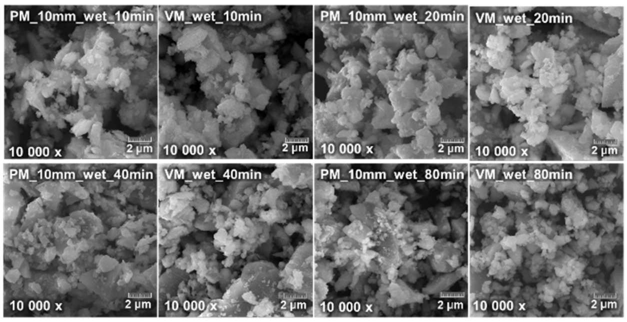

Fig. 4: SEM images of comparison of grinding in a planetary and vibratory mill in wet grinding after 10, 20, 40 and 80 minutes.

The difference between the influence of the planetary and vibratory mill on the shape of the grains is already observable after 10 minutes of grinding, where in the case of vibratory mill, the particles are larger than in the case of grinding in a planetary mill. Even at advanced times of grinding, a planetary mill grinds more intensively and creates more agglomerates than a vibratory mill.

In the case of dry grinding, the difference between the used grinding technologies is already obvious after 10 minutes of grinding. In vibratory grinding, the ratio of larger grains in the order of units of micrometres prevailed over smaller particles, while in the case of grinding in a planetary mill, the ratio of smaller particles already prevailed. From the 20th minute onwards, agglomerates clump together for both technologies. At each grinding time when images were taken, the planetary grinding technology appears to be more efficient.

In the case of wet grinding, the differences between the technologies used are not that significant. In both cases, however, a decrease in the formation of agglomerates can be observed, which is one of the characteristics of this grinding method.

4. Conclusions

The main objective of this article was to assess the influence of different grinding technologies on the granulometric and crystallographic properties of Portland cement. Not only the type of laboratory mill used but also the grinding environment and grinding time were monitored. The planetary laboratory mill with 10 mm in diameter grinding steel balls appears to be the most efficient mill in the scope of material reduction, which effectively reduces the material especially during wet grinding of the material. During wet grinding, the agglomeration effect is significantly reduced, which is a big advantage of this method of grinding.

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