Impact of the grinding process on the granulometric properties of triclinic alite

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Abstract. Four major clinker minerals, alite, belite, tricalcium aluminate and tetracalcium aluminate ferrite are crucial for cement properties. This work deals with alite as the most important clinker minerals. Alite is affected by the milling process technology more than other clinker minerals. It contains micro-cracks, which are formed during fast cooling, and is therefore less resistant to grinding than other clinker minerals. The paper deals with the influence of length and the technology of the milling process in 3 types of laboratory mills on the particle size and distribution, agglomeration and the change of the grain shape of the synthetically prepared triclinic alite.

1. Introduction

The most important part of the Portland cement is clinker, which is produced by burning raw meal in a cement kiln at 1450°C. The final properties of the clinker and cement do not directly determine the chemical composition but the mineralogical composition. The mineral composition of the clinker is the result of used raw materials and production technology.

Up to now, more than 25 minerals are known in Portland clinker. It is necessary to distinguish pure minerals from technical ones that are usually altered in the clinker by the presence of other components or impurities in the solid solution. The most important technical phases occurring in the clinker are alite (C_3S), belite (C_2S), tricalcium aluminate (C_3A) and brownmillerite (C_4AF) (according to Törnebohm) and their polymorphs [1-3].

Alite (Ca_3SiO_5, C_3S) is the dominant phase of Portland clinker, the amount of which is generally above 60%. It is essentially tricalcium silicate (C_3S) with a certain amount of Al_2O_3, MgO, Fe_2O_3 and other solids in its structure. C_3S occurs at temperatures above 1250°C and in Portland clinker is in an unstable subcool condition, because its stability field lies between 1250 - 1900°C [4].

Alite is characterized by significant polymorphism. Up to date, seven modifications have been identified in the aliquot, 3 triclinic (T1, T2, T3), 3 monoclinic (M1, M2, M3) and 1 trigonal (R) dependent on temperature and impurity content. Under laboratory conditions there is a stable modification of T1. It is simplest to prepare because it is produced by cooling the pure C_3S compound [5-6].

This work is based on the preparation of the pure triclinic phase of alite, with the aim of monitoring the influence of milling in laboratory mills on its grindability.

The grinding time is one of the most important parameters affecting the milling process. With the growing time of grinding, the material gets so refined that agglomeration and aggregation may occur, which means that when the material is grinded, the individual particles are distributed but subsequently very compressed. There is an electrostatic charging of the particle surface with opposite charges.

IOP Conf. Series: Materials Science and Engineering **385** (2018) 012044 doi:10.1088/1757-899X/385/1/012044

2. Materials and methods

The Wesselsky-Jensen method was used to prepare pure triclinic alite. For solid phase synthesis, a ventricular high temperature kiln with superkanthal heating elements was used. Solid phase synthesis was carried out in two steps at 1600°C in accordance with the Wesselsky-Jensen method. Phase composition control was performed by XRD analysis on PANalatical Empyrean (Cu-cathode λ = 1.540598 for Ka1).

The triclinic alite was adjusted to an entry specific surface area of 400 m^2/kg. To achieve a specific surface area, the material was milled at 500 rpm in a Fritsch Pulverisette 6 planetary mill. Blaine specific surface area was measured using a PC-Blaine-Star automatic device with a measurement cell capacity of 7.95 cubic centimeters. The measurement was performed three times to eliminate errors, and the resultant value was the average of the three readings.

Alite subsequently underwent grinding in three types of laboratory mills with dry and wet technology. The milling was done using the PULVERISETTE 6 planetary mill, the RS 200 vibratory disk mill from RETSCH and the McCrone Micronising mill. Fritsch planetary ball mill Pulverisette 6 in a bowl with the volume of 0.5 dm^3 was used. The bowl was filled by 25 grinding balls with 20 mm in diameter. The comminution of the material takes place primarily through the high-energy impact of the grinding balls. The grinding bowl, containing the grinding balls and the material to be ground, rotates around its own axis on the main disk whilst rotating rapidly in the opposite direction. Centrifugal force causes the ground sample material and the grinding balls to separate from the inner wall of the grinding bowl. The grinding balls then cross the bowl at high speed and further grind the sample material by impact against the opposite wall. The Vibratory Disc Mill RS 200 comminutes by impact and friction. The grinding set is firmly attached to the vibration plate with a quick-action lever. The plate with the grinding set is subjected to circular horizontal vibrations. The centrifugal force acting on the grinding rings in the dish results in extreme pressure. Impact and frictional forces acting on the sample produced analytical fineness in 1-3 minutes. The circular vibrations are produced by a frequency controlled 1.5 kW 3-phase motor.

Isopropyl alcohol was used as an inert liquid for wet milling. McCrone Micronising Mill is designed only for wet milling. 5 periods of milling were set at 1, 5, 20, 60 and 120 minutes. The milling in the planetary mill was set at the optimum speed for the alite 300 rpm and in a vibratory disk mill at 1200 rpm. The grinding times in the McCrone Micronising Mill were the same as in the previous two types of mills.

The particle distribution and fineness were determined using the Malvern Mastersizer 2000 laser granulometer.

The monitoring of grain shape and topography and the agglomeration process for the various milling technologies were determined using a scanning electron microscope TESCAN MIRA3 XMU.

3. Results

The quality control of the mineralogical composition was performed after the 1st and 2nd firing steps by XRD analysis, the scans of which is shown in figure1.

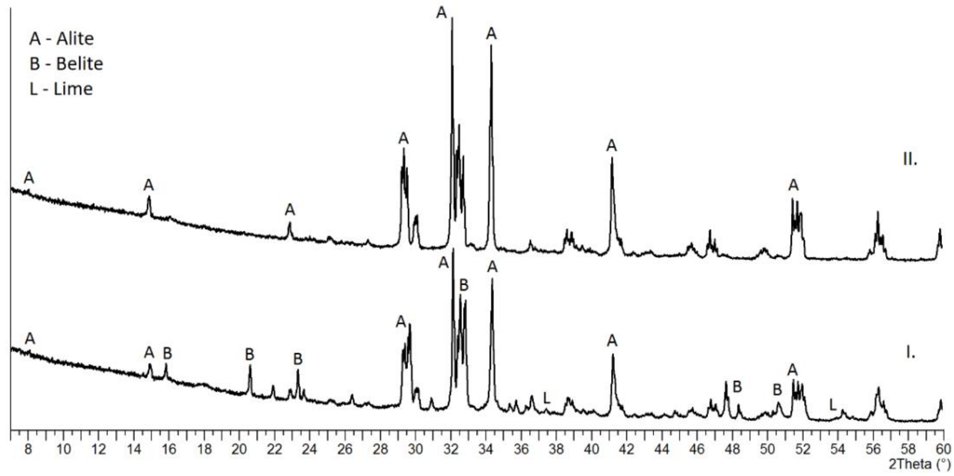
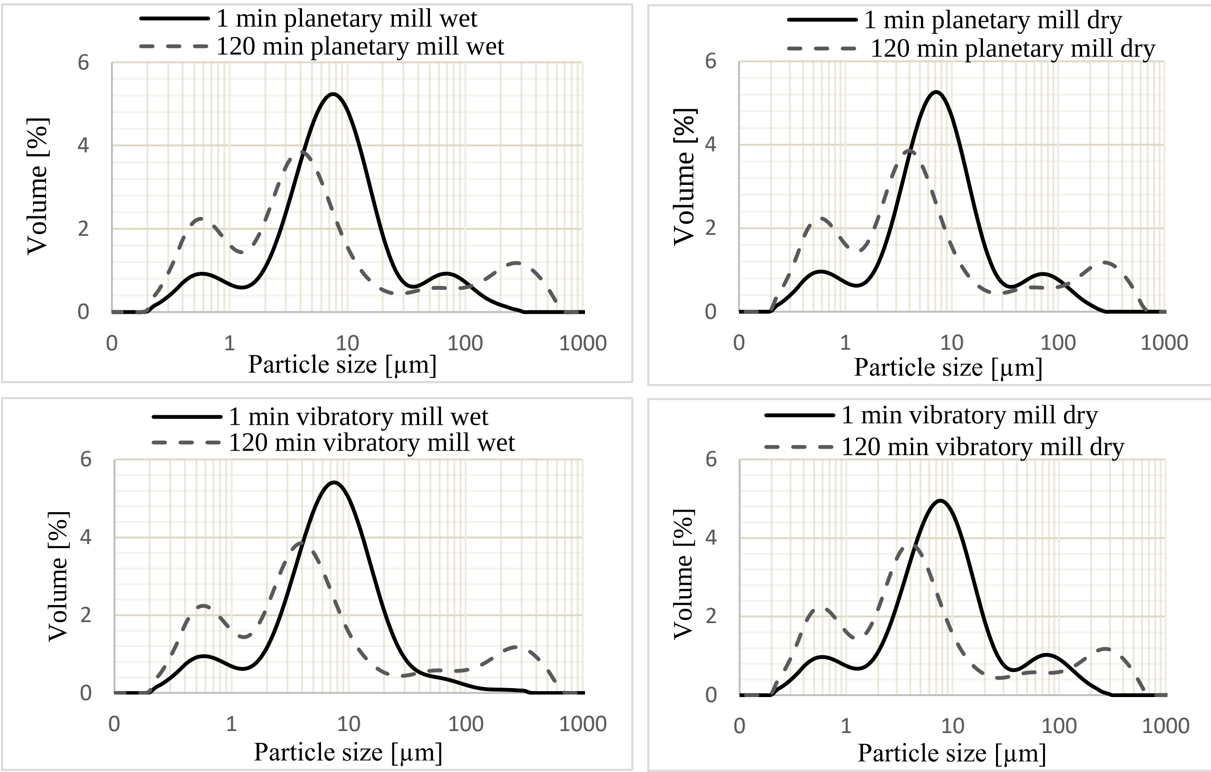


Figure 1. XRD patterns after first and second burning.

After the first firing, alite, belite and residual lime are identified in the diffraction record. After the second firing, this is a triclinic alite.

Comparison of the influence of the milling technology on the distribution and the particle fineness was done using laser granulometry. In the following graphs, the granulometry is compared at a milling time of 1 and 120 minutes for all three types of laboratory mills and milling technologies where the change in particle distribution and fineness is the most pronounced.



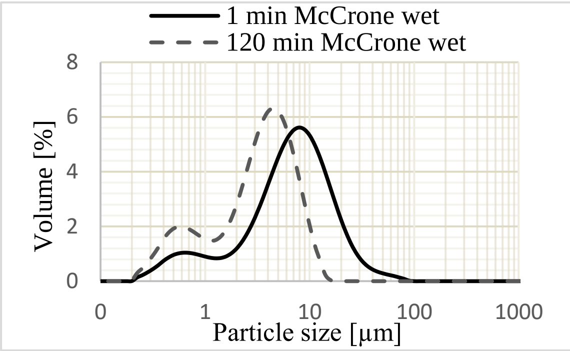


Figure 2. Particle distribution at milling time of 1 and 120 minutes for all types of mills and grinding technology.

Intensive milling in the vibratory and planetary mills results in the formation of large quantities of fine particles. These particles formed agglomerates which caused higher volume of particles above 100 µm. This phenomenon was more pronounced when grinding the material with dry technology.

Comparison of the particle distribution during grinding of material in all types of mills and milling technologies in 120 minutes is shown in figure 3.

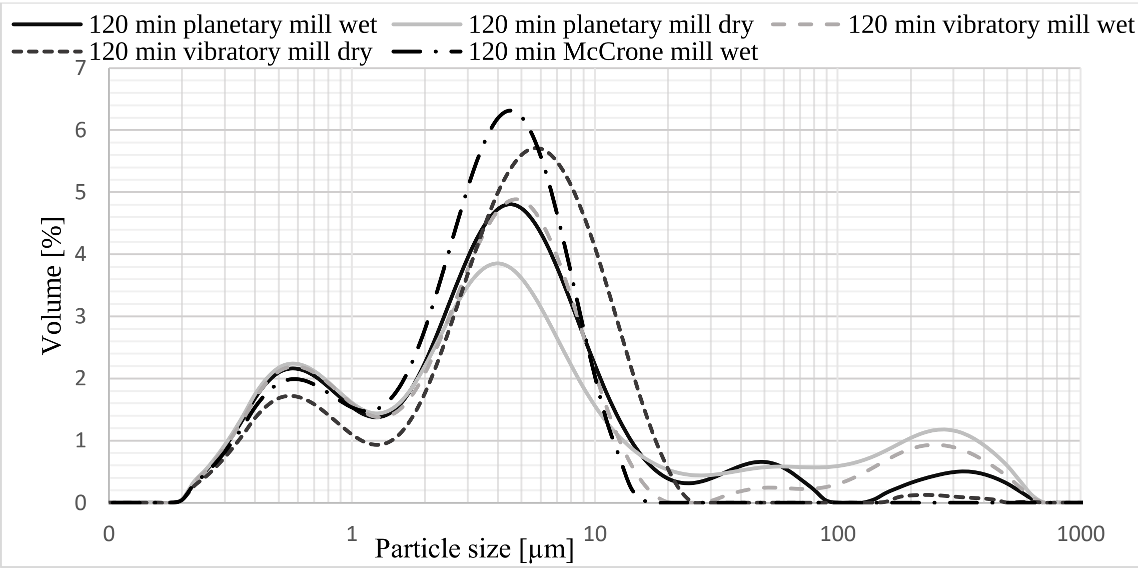


Figure 3. Particle distribution in 120 minutes.

The largest amount of very fine particles is produced by dry grinding in a planetary mill. The trend of the milling shows good grindability of the material, even the most pronounced increase in the volume of agglomerates which has been produced at the expense of fine particles up to 10 µm.

In wet grinding in a planetary mill, the amount of agglomerates is smaller than in the case of dry grinding, as it is to some extent suppressed by the liquid. In the area of very fine and fine particles, the wet milling trend in the vibratory mill is almost the same as in the wet milling in the planetary mill. At both mills, the formation of agglomerates, the amount of which in the case of the vibratory mill is greater.

With dry grinding in the vibratory mill, the smallest amount of very fine particles is observed, which is reflected by a relatively high amount of fine particles. We see only a slight increase in agglomerates, as there has been no significant increase in the amount of very fine particles that would tend to clump to the agglomerates in dry milling.

When grinding at McCrone mill, the material is well pulverized, increasing the amount of fine particles at the expense of the coarser portions without the agglomeration that is observed when grinding in other types of mills.

The influence of grinding on the grain shape was evaluated by electron microscopy. In figure 4 are images of material ground in each type of mills with dry and wet technology.

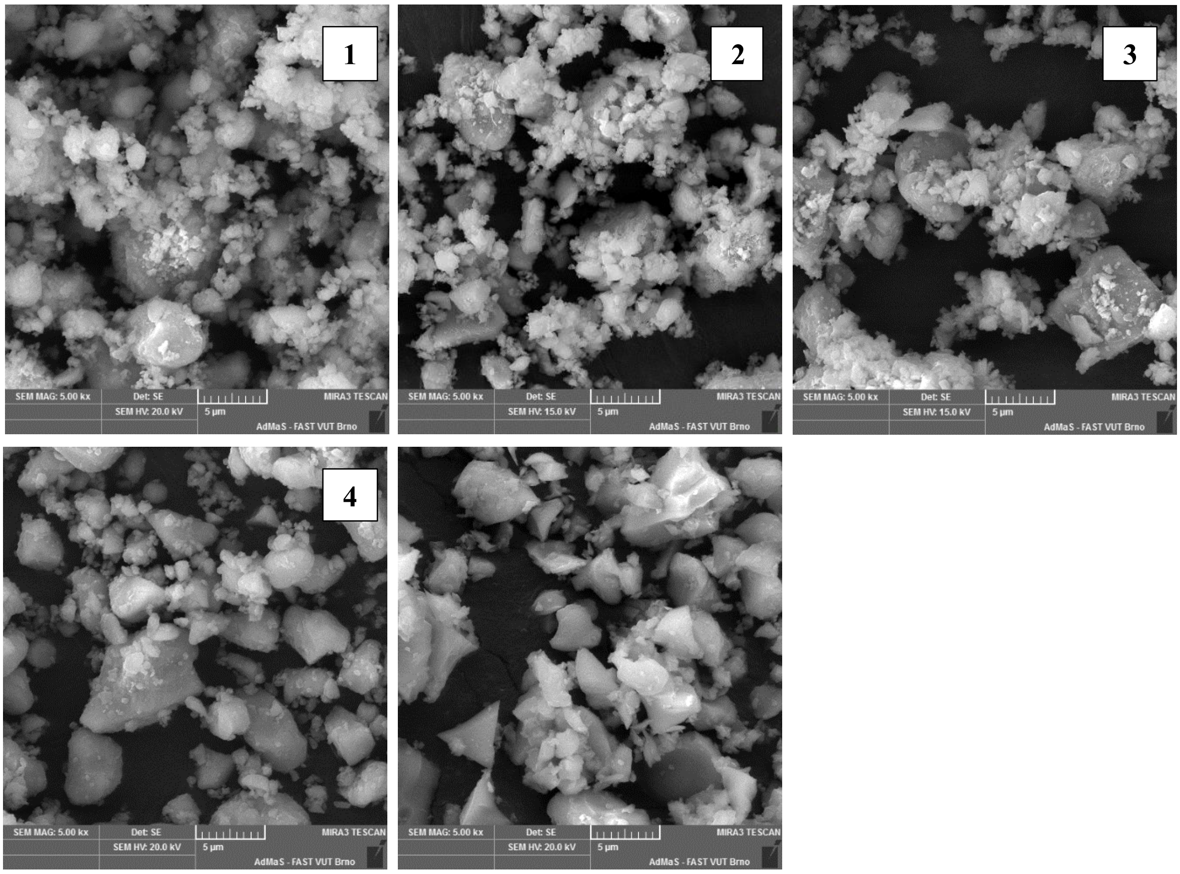


Figure 4. SEM images for dry milling planetary mill (1), wet milling planetary mill (2), wet milling vibratory mill (3), dry milling vibratory mill (4), wet milling McCrone mill (5).

In the image of dry grinding in a planetary mill, we see a considerable refinement of the material, a very large amount of very fine particles and massive agglomerates.

Wet grinding in a planetary mill, the agglomeration is less pronounced, the grain material is nicely rounded.

In the case of dry grinding in the vibratory mill, we do not see much of the material softening as in previous mills and milling technologies. Agglomeration is minimal.

In the image of dry grinding in McCrone Mill, we see that the grains are not isometric as seen in previous mills but are sharp-edged. Cleavage planes are visible on them. The amounts of fine particles are minimal agglomeration does not occur.

4. Discussion

The pure triclinic alite was prepared by the Wesselsky-Jensen method and subjected to various milling technologies in three types of laboratory mills.

Dry grinding in a planetary mill seems very effective in particle size reduction. The problem arises with a longer grinding time when a large amount of energy and very fine particles accumulate in the grinding capsule, which tend to stick together, and after 120 minutes of grinding clump into massive agglomerates, as confirmed by electron microscopy images.

Wet milling in a planetary mill, the agglomeration is suppressed to a certain extent in the liquid, but after 120 minutes of milling, agglomerates also occur, regardless of whether they are wet in the planetary or vibratory milled. The grinding efficiency in terms of particle size is in both cases substantially identical with the grinding parameters selected.

The material was milled at 300 rpm in the planetary mill and at the vibratory mill at 1200 rpm, indicating that the two grinding modes are comparable to one another.

The wet milling trend in the vibratory mill is therefore almost identical to the trend of wet milling in the planetary mill, with the exception that a larger amount of agglomerates is produced in the vibratory mill than in the case of a planetary mill. The reason for agglomeration in wet milling is the fact that when milling in a liquid and at high energy in a grinding capsule, the material is melted into very fine particles which are poured into themselves and after drying, tend to aggregate into agglomerates.

In the case of dry grinding in the vibratory mill, we observe the lowest amount of very fine particles, and thus a small amount of agglomerate which was confirmed again by electron microscopy. In this case, and for this material, the use of a vibratory mill in a dry medium appears to be the least appropriate.

McCrone-milled material does not tend to form agglomerates after 120 minutes. McCrone mill does not destroy the structure, but it mills a very small amount of material so it is not suitable for larger laboratory milling.

5. Conclusion

The greatest influence on the granulometric properties of triclinic alite has a dry milling in a planetary mill, which appears to be the most effective among all types of mills and technologies used. There is a very rapid refinement of the material. The problem occurs with long grinding times when very fine particles tend to clump to the agglomerates. In the case of selected grinding modes, specifically wet grinding, the efficiency and influence of the grinding is the same as for the vibratory mill in terms of its impact on the granulometry. It has been confirmed that McCrone mill is designed very well to prepare samples for XRD analysis.

Acknowledgements

This work was financially supported by project No. FAST-J-18-5432: "Preparation of alite polymorphs".

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