Effect of mechanical activation on the properties of Portland cement

S Ravaszová¹ and K Dvořák¹

¹ Brno University of Technology, Faculty of Civil Engineering, Veveri 331/95, 602 00 Brno, Czech Republic

Email: ravaszova.s@fce.vutbr.cz

Abstract. The paper deals with the mechanical activation of cement by grinding in a high-speed mill, and compares the parameters found with the commonly used grinding method in cement production, which uses grinding of cement by means of a ball mill. The aim is to verify the influence of the aging time of the ground material on the preservation of the mechanical activation effect and on the properties of the final product at different stages of hydration. It evaluates the physical-mechanical properties, the compressive and tensile strength after 1, 2, 7, 14 and 28 days, as well as the course of the hydration process. The evaluated results suggest the existence of mechanical activation, but this effect is very difficult to achieve and depends on many other factors.

1. Introduction

Mechanical activation is a complex process of changing the structure and thermodynamic state of solid particles. The principle of mechanical activation has been known for a long time. K. Tkacova and a team of authors [1] have been studying mechanical activation of materials for several years. In the publication by Sekulic et al [2], they consider mechanical activation as a phenomenon that can only be determined on a material of the same specific surface area and its resulting properties are evaluated. Z. Sekulic et al. ground Portland cement on different mills to approximately 400 m²/kg and then evaluated the resulting strengths depending on the type of mill. They attributed the added strength value, in their case an increment of 10 MPa at 28-day strengths, to the principle of mechanical activation [2].

The relationship and difference between fine grinding and mechanical activation was addressed in V. V. Boldyrev with S. V. Pavlov and E. L. Goldberg [3]. He divides the grinding process into coarse grinding, fine grinding, and mechanical activation. However, he admits that it is not possible to use such a simple scale, because of the more complex physical background of the whole grinding process. Mechanical activation can also take place simultaneously with fine grinding.

To achieve mechanical activation, two conditions must be met. The first condition is the particle size, which must be below the brittle-refractive transition. The second condition is that sufficient grain loading due to stress must be achieved [4–6].

It has long been shown [7] that a higher specific surface area of cement brings these benefits. The rate of hydration is higher with higher specific surface area of the cement. Thus, the smaller the particle size of the cement, the faster the formation of hydration products. The initial strength increases with increasing specific surface area of the cement. The final strengths will also increase as the specific surface area of the cement increases. The development of hydration heat will increase with increasing specific surface area of the cement. Finer cement has a positive effect on the workability of mortars and concretes.
At the same time, there are disadvantages. The price increases disproportionately compared to the increase in specific surface area. The amount of water mixed into mortars and concretes increases and the risk of water separation increases. More finely ground cements are subject to greater shrinkage, with a higher risk of cracking due to shrinkage. The shelf life of finely ground cement is shorter because finer ground cement is more prone to lumping and is more reactive, hence more sensitive to air moisture [7–9].

The aim of the paper is to investigate the mechanical activation of cement using a high-speed mill, and to compare the parameters found with the commonly used grinding method in cement production. A ball mill will be used as a commonly used mill in cement manufacturing technology. The aim is also to verify the influence of the aging time of the ground material on the preservation of the mechanical activation effect and on the properties of the final product at different stages of hydration. It is important to evaluate the resulting physical and mechanical properties and to evaluate the course of the hydration process.

2. Materials and methods

2.1. Grinding in a disintegrator (DESI 11)
The clinker (Cement Hranice a.s.) with gypsum (Precheza a.s.) was first ground in a ball mill (Brio Hranice with an OM20f plastering drum). The mill settings were not altered throughout the mill operation and the speed was kept at a maximum of 65 rpm. To achieve a final specific surface area of cement of 400 m$^2$/kg was proceeded in short grinding cycles of 5 minutes each time with control of the specific surface area by ZEB PC-Blaine Star device.

Since the grinding process in the ball mill ends with the discharge phase, during which the cover of the grinding drum is replaced by a perforated plate and the discharge time is set to 10 to 15 minutes, it had to be considered that the cement is still partially ground during the discharge. By checking the specific surface at intervals of 5 minutes, the average increment of the specific surface over the last cycles was determined and, accordingly, the grinding was stopped just before the desired specific surface area was reached when the cement started to discharge.

After the cement was poured, homogenization was carried out in a laboratory screw homogenizer for 40 minutes. To ensure even better homogenisation, the process was interrupted every ten minutes, the cement was emptied, and the homogeniser cleaned. This was done three times, i.e., after 10, 20 and 30 minutes. After thorough homogenisation of the cement, the output specific surface area was again verified on PC-Blaine-Star automatic device.

This pre-prepared cement was subjected to grinding on a high-speed mill. It was a disintegrator DESI 11 with two counter-rotating rotors with a speed of 12000 rpm. The power of the motors was 2 × 4.5 kW, with a grinding speed of 1 kg per minute. Three sets of new rotors were available for grinding on the high-speed mill. To carry out the aging experiment, it was necessary to carry out the actual grinding on 3 consecutive days. Therefore, a new set of rotors was used for each grinding, more precisely CR rotors with cubic teeth developed by FFservis. The samples of dimensions 20 × 20 × 100 mm was prepared from the ground cement in the disintegrator. The number of samples was designed to allow strength tests after 1, 2, 7, 14 and 28 days. To ensure the accuracy of the results, 3 samples then produced from each casting phase for each strength test. Prior to preparing the samples, a slurry test of normal consistency was performed to determine the optimum water coefficient.

2.2. Grinding in a ball mill (BRIO Hranice)
The grinding of cement in the ball mill was as close as possible to the grinding process in the disintegrator to ensure comparability of results. Again, the cement was pre-ground to a specific surface area of 400 m$^2$/kg. In this case, however, the preparation of the cement was partly different from that for the disintegrator. In the disintegrator preparation, the cement was prepared several days in advance. In the ball mill preparation, on the first day of grinding the cement was divided into three weights, one of which was ground directly to the required specific surface of 465 m$^2$/kg, and the other two weights were only prepared to a specific surface of 400 m$^2$/kg. These bales were then milled successively over the next two days to the required specific surface of 465 m$^2$/kg.

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After finishing the last part of the cement, the same number of samples was formed as in the case of grinding in the disintegrator. Thus, a total of 45 samples with dimensions $20 \times 20 \times 100$ mm was obtained from the ball mill grinding.

2.3. Preparation and mortification of the sample

The samples were made from cement putty, which was made from cement and water (keeping the same water coefficient to a slurry of normal consistency) and processed by hand with a whisk in a stainless-steel bowl.

The cementitious putty thus prepared was applied to the moulds and compacted in two layers using a vibrating table. The specimens were covered with plastic wrap and de-moulded after 24 hours. The first set of specimens was immediately tested for compressive strength. The remaining samples were stored at laboratory temperature immersed in water in a laboratory environment.

After the strength tests, the samples were always mortared for later investigation of the hydration process by DTA Thermogravimeter - Mettler Toledo DSC1 and X-Ray analysis by XRD PANalatical Empyrean, Cu - anode $\lambda = 1.540598$ for $K\alpha$1 radiation. The residue from the undercut strength test samples was hammered and ground in a laboratory planetary mill FRITCH Pulverisette 6 using isopropyl alcohol. The mill setting was the same each time, 500 rpm, for 105 seconds. The obtained mass was further filtered on a chemical filter assembly through a filter cloth and was washed three times with isopropyl alcohol. The resulting mortified samples were placed in a resealable bag and stored in a freezer. After all strength tests were completed, X-ray and DTA analyses were performed to map the hydration process of the mechanically activated cements.

3. Results and discussion

3.1. Grinding fineness

Table 1 contains the values of specific surface areas measured on the automatic Blain apparatus, which refer to the cement ground in the disintegrator and in the ball mill.

| Specific surface area [m$^2$/kg] | Aging of the sample | disintegrator DESI | ball mill Brio Hranice |
|----------------------------------|---------------------|-------------------|----------------------|
| O0*                             | 449                 | 452               |
| O1*                             | 464                 | 484               |
| O2*                             | 465                 | 462               |
| $\phi$ [m$^2$/kg]               | 459                 | 466               |

*marking of sample aging times (O: without aging; 1: one-day aging; 2: two-days aging)

When grinding in a ball mill, slight variations of the specific surface areas within the grinding batches are seen according to the aging. This is mainly because the values given are control measurements after homogenisation. Moreover, achieving a perfectly accurate specific surface area is not an easy task, if only because multiple measurements of the same sample show slight deviations in the order of units.

3.2. Physical-mechanical properties

The samples were tested for compressive strength. In the evaluation, the evolution of the strengths over time was monitored, as well as the comparison of grinding technologies. According to the assumptions of proving the effect of mechanical activation, the strengths of cement ground in a disintegrator should
be higher for the same specific surface area. The mechanical activation effect could also be reflected in increased strengths of cement without aging compared to cement with one- or two-days aging.

Figure 1. Comparison of compressive strengths of cements ground at different mills (without aging).

Figure 2. Comparison of compressive strengths of cements ground at different mills (one-day aging).

Figure 3. Comparison of compressive strengths of cements ground at different mills (two-days aging).

When comparing the strengths depending on the type of mill, the effect of grinding at different mills on the strengths of the cementitious putty was not demonstrated. For the cements without aging (figure
1) the values are comparable, the final strengths were higher for the cement ground on a ball mill. For the one-day aging (figure 2), the final strengths also came out higher for the cement ground in the ball mill. For the two-day aging (figure 3), the higher strengths were predominantly for cement from the disintegrator. Based on the results, it can be concluded that none of the grinding technologies seems to be more advantageous for achieving better physical-mechanical properties of cement.

3.3. Hydration process

The course of hydration was monitored mainly by X-ray diffraction analysis. DTA analysis was also performed to evaluate the portlandite increment. The evaluation of the X-ray analysis of the samples from the disintegrator can be seen in figure 4. Figure 5 then shows the evaluation of the samples from the ball mill.

![Figure 4](image1.png)

**Figure 4.** Hydration of cement ground in the disintegrator (P-portlandite; a-alite; B-brownmillerite; E-ettringite; C-cebollite Ca₅Al₂Si₃O₁₂(OH)₄).

![Figure 5](image2.png)

**Figure 5.** Hydration of cement ground in the ball mill (P-portlandite; a-alite; B-brownmillerite; E-ettringite; C-cebollite Ca₅Al₂Si₃O₁₂(OH)₄).

X-ray analysis confirmed that hydration was stable, so the lower strengths of cement ground in the disintegrator after 28 days were probably due to a defective set of samples or a factor other than the hydration process. From figures 4 and 5, the portlandite content increases with increasing strength, as best seen at 18 °2Θ. The intensity of alite, evident at one-day strengths, then decreases to disappear during hydration, like that of ettringite. Brownmillerite is only slightly visible, and the intensity does not change much during hydration.
Figure 6. Comparison of grinding technologies on the X-ray curves.

If we place the X-ray analysis outputs of the cement from the ball mill and the disintegrator side by side (figure 6), the curves are almost identical, even though the actual experiments were carried out many months apart. For comparison, the curves of the cements from the one-day strengths from the cement without aging were selected. We can notice only a slight difference in the portlandite intensities, as indicated in the graph. Cement ground in a ball mill has slightly higher portlandite intensity than cement ground in a disintegrator, but this is the only difference. The other peaks of portlandite did not differ between the grinding technologies.

Furthermore, the portlandite content was evaluated from the measured DTA analyses as a representative of the output hydration products. The following table 2 summarizes the results in percentages.

Table 2. Portlandite content in samples with stopped hydration process from different mills.

| days | aging | disintegrator | ball mill |
|------|-------|---------------|-----------|
| 1    | O0    | 7.45          | 5.17      |
|      | O1    | 6.94          | 5.27      |
|      | O2    | 6.8           | 5.62      |
| 2    | O0    | 7.59          | 6.18      |
|      | O1    | 7.74          | 6.39      |
|      | O2    | 7.36          | 6.23      |
| 7    | O0    | 8.06          | 6.89      |
|      | O1    | 8.34          | 7.11      |
|      | O2    | 8.12          | 7.09      |
| 14   | O0    | 9.13          | 7.25      |
|      | O1    | 9.08          | 7.52      |
|      | O2    | 8.98          | 7.23      |
| 28   | O0    | 9.64          | 8.67      |
|      | O1    | 9.61          | 8.54      |
|      | O2    | 9.52          | 8.61      |

From table 2, the cementitious putty prepared from ball mill cement has a lower portlandite content than the cementitious putty prepared from cement milled in the disintegrator, as calculated from the DTA analysis.
3.4. Effect of the specific surface area

In the following figure 7, which compares cement before and after milling in the disintegrator, the clinker minerals are apparently visible, and there is a very slight decrease in all the intensities shown. Sources [8] and [9] from the introduction stated that the effect of mechanical activation is evident from the increase in the amorphous phase and the decrease in intensities on X-ray analysis. Visually, we are unable to determine with certainty from figure 7 whether the mechanical-activation effect has occurred.

![Figure 7](image.png)

**Figure 7.** Result of X-Ray analysis of cement before and after grinding in disintegrator.

4. Conclusion

The cement ground in the disintegrator had an average specific surface area about 459 m$^2$/kg. For both compressive and flexural tensile strengths, the cement from the disintegrator showed the highest strengths after one day for the cement bodies without aging. However, in the further course of hydration this phenomenon disappeared.

The compressive strengths at 7, 14 and 28 days were compared with the grinding fineness of each aging, and it was found that as the hydration progressed, the strengths levelled off as a function of specific surface area, such that the finer the cement was, the higher the compressive strengths it exhibited, even with unintended small variations in specific surface area (approximately 10 m$^2$/kg). This phenomenon of differing initial strengths and subsequent comparison of strengths according to grinding fineness could be an effect of mechanical activation due to high-speed grinding in the disintegrator since it did not occur in the cement ground in the ball mill.

The highest compressive strength ever achieved was 94 MPa for cement ground in a ball mill with a one-day annealing. The 28-day strengths of the cement from the disintegrator were unusually low and given the normal hydration history of the cement under investigation, as demonstrated by X-ray analysis, this set of samples was deemed to have failed. It can therefore be assumed that if the set had been successful, the strengths of the cement from the disintegrator after 28 days would have been like those of the ball mill.

The DTA analysis allowed the calculation of the portlandite content, with the highest portlandite content at the one-day strengths, which corresponded to the cement without annealing strengths. The portlandite content was higher in the cement from the disintegrator than in the cement from the ball mill throughout the hydration time.

The results evaluated suggest the existence of mechanical activation, but this effect is very difficult to achieve and certainly depends on many factors. Harnessing this effect in practice is a challenging but not easy task. It would also be important to assess the potential increased energy costs associated with milling. It should be considered whether the increase in utility is effective enough.

Due to the nature of the mechanical activation of cement, the effect of ageing on long-term strength or durability needs to be further investigated. Because of the short-term nature of the mechanical activation effect, its effect could be better exploited in activation mixing, for example in precast concrete plants.
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