

Mechanical Activation of Construction Binder Materials by Various Mills

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Abstract. The paper deals with the mechanical grinding down to the nano powder of construction materials. During mechanical activation a composite binder active molecules cement minerals occur in the destruction of the molecular defects in the areas of packaging and breaking metastable phase decompensation intermolecular forces. The process is accompanied by a change in the kinetics of hardening of portland cement. Mechanical processes during grinding mineral materials cause, along with the increase in their surface energy, increase the Gibbs energy of powders and, respectively, their chemical activity, which also contributes to the high adhesion strength when contacting them with binders. Thus, the set of measures for mechanical activation makes better use of the weight of components filled with cement systems and adjust their properties. At relatively low cost is possible to provide a spectacular and, importantly, easily repeatable results in a production environment.

1. Introduction

Modern building materials technology tends to a constant reduction of the dimension of the materials. The increase in the specific surface binding powders can increase their surface area, respectively, increasing the area exposed to chemical hydration reaction when mixed with water. Milling binders - an essential process step consisting in mechanical grinding of raw mix. With increasing fineness increased activity binders, mechanical strength hardening. At the same time, it should be noted that for each binder set its own optimal fineness at which most fully use its properties. Needless high fineness is not always desirable because with increasing fineness of powder require more water to make a dough, which, in turn, leads to increased shrinkage and cracking during hardening.

Mineral binders - is finely crushed mineral powders, which form when mixed with water, plastic mass, which over time under the influence of physical and chemical processes passes in stone condition. This property is used for binders for producing the artificial stone materials (concrete, etc.). In this case, the mechanical process of natural raw materials is increasingly replaced by chemical - a simple, efficient and cost-effective.

The aim of this study sought to determine the effect of various industrial milling machines on the properties of composite cementations materials.



2. Results and Discussion

To achieve the goal have been developed composite binders obtained by co-grinding cement, hyperplastisizer, fly ash and limestone.

The problem of increasing the density and strength of the concrete in a large number of works of both Russian and foreign scientists [1-3]. It is known that one of the ways to improve the performance of concrete, reduced permeability parameters is the use of highly active additives of different composition and origin, both micro- and nanosized level, which contribute to process optimization of structure by initiating the formation of hydrated compounds. So in the work carried out previously, it has been proven effective use as an active mineral additives of nanostructured silica-modifier composition. In addition, the parameters studied the possibility of reducing the permeability of concrete by mechanical grinding of the components of the composite binder.

The properties of composite materials largely depend on the structure of disperse systems on which they are obtained [4]. The structural strength of the dispersed system, its stability and the behavior in the flow, the rate of destruction and restoration of the structure are interconnected. Conglomerate building material - concrete refers to a class of composites. As a concrete matrix substance, successively ambitious outline levels are the cement-sand stone, cement stone (microconcrete), cementing substance, neoplasms cementing substance, solid phase tumors, essence single structural element of tumors, which corresponds to a large-scale order from the macro- to the nanoscale structure [5]. Ordered structure of the composites due to the proportionality of scale levels of the structure - the corresponding properties of the composite at each scale level [6]. The achievement of high strength concrete contributes to a combination of factors: increasing density of systems by optimizing the composition of the grain; reducing the number of long cement matrix by reducing the water-cement ratio; filling the pores between the cement particles and to improve the rheology due to the effect of lubrication; formation of secondary products of hydration in the pozzolanic reaction with $\text{Ca}(\text{OH})_2$ for the introduction of concrete additives microfill effect [7].

To select the optimal method of grinding tests were carried out in a ball, vibration and vario-planetary mill.

Ball mill is a hollow rotating drum around its axis, which is about half-filled with crushing balls (percussion elements). As a result of the rotation, the balls rise in the upper part of the drum, and then under the influence of gravity fall down [8-10]. After one of the pivots is constantly fed material to be ground, and going through another bowl discharge (figure 1).

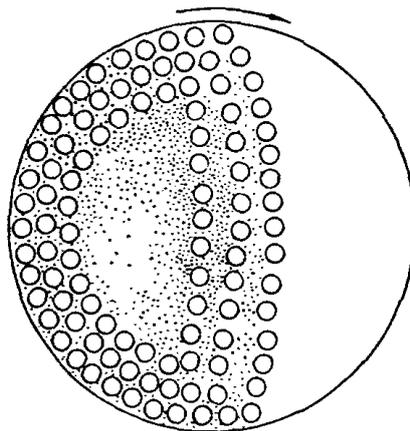


Figure 1. Operating principle of the ball mill

One of the features is a crushing blow to free the fact that the destruction of the material occurs at the weakest bond, structural defects in the joints of crystal grains, layers, etc. In the production of graded gravel or artificial sand is an undoubted advantage because the product is represented by

impact crushing grains of isometric shape with no internal defects with a small amount overgrinding product. At the same time, to obtain greater fineness, particle hardening that occurs with decreasing their size, it creates additional difficulties.

At some point, when the structural strength of each individual particle reaches its maximum, and its weight is negligible, free kick almost completely replaced by abrasion. Rotor centrifugal mill accelerator ceases to function as soon as the running and the swirler material airflows. Is interested in to the walls of the grinding chamber large particles are squeezed smaller, which, moving from the periphery to the center, are crushed only by mutual abrasion of turbulent flows.

Judging by the consumption of energy on the surface of the formation of a new unit of solid materials is one of the most inefficient ways of grinding.

The operating principle of a vibration mill (figure 2) based on the prompting vigorous grinding bodies, when instead of gravitational forces causing the drop of balls is used the inertia, centrifugal force, etc. [11-13]

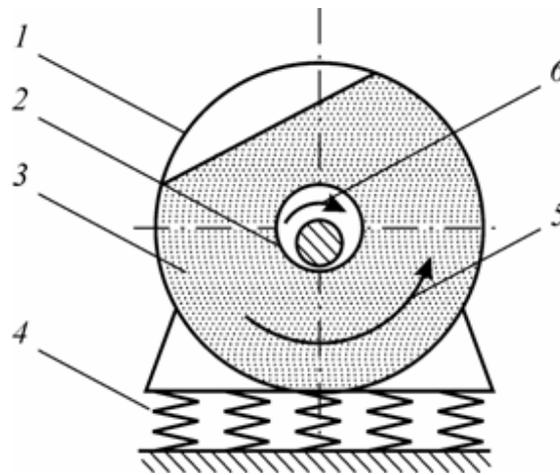


Figure 2. Operating principle of the vibration mill

1 - body of the mill; 2 - the eccentric (or unbalanced) shaft; 3 - ball boot from the material being ground; 4 - spring supports; 5 - the direction of the circulation load; 6 - the direction of rotation

Rotation of the shaft of the vibrator, and behind them of the mill housing causes the grinding media to be moved according to the magnitude of the eccentricity or the radius of the carrier. Energy transfer grinding load through the mill housing. Under the influence of inertia, centrifugal force, alternating loads balls inside the body move along a complex trajectory, pressed against the wall of the drum, hit against each other, as well as the particles of the crushed material, breaking, crushing and rubbing them.

For the production of fine materials, vibrating mills are more efficient than the ball. An impact grinding effect on the material in this case, a small but intense abrading, to achieve fineness

The vario-planetary mill speed grinding bowls and supporting disc can be set completely independently of each other. By varying the ratio, it can affect the movement and trajectory of grinding balls so that the balls hit horizontally on the inner wall of the grinding bowl (high impact energy), approach each other tangentially (high friction) or just roll along the inner wall of the grinding bowl (centrifugal mills) [14-16]. All intermediate stages and a play between the friction and blow pressure can be freely set (figure 3).

Accordingly, the grinding in vario-planetary mill is more energy-efficient compared to the ball and vibration mills. In addition due to the combined action of the drum and centrifugal drum and abrasive efforts, it is possible to achieve a highly dispersed powders.

Through comparison fineness of the claimed composite binder on different mills, revealed that the ball mill (1.1kW, 90 rpm) can be milled to 400 m²/kg, a further unit operation is uneconomic. Vibration Mill (2.2 kW, 1500 rpm) showed the ability to effectively grinding composite binding to a specific surface of 430 m²/kg (figure 4).

Due to the fact that according to the declared method of experiment planning interval varying specific surface 500-900 m²/kg, a ball mill and vibration is not able to meet these conditions.

Vario-planetary mill "Pulverisette 4" (9 kW) capable of providing grinding to a predetermined specific surface area (900 m²/kg).

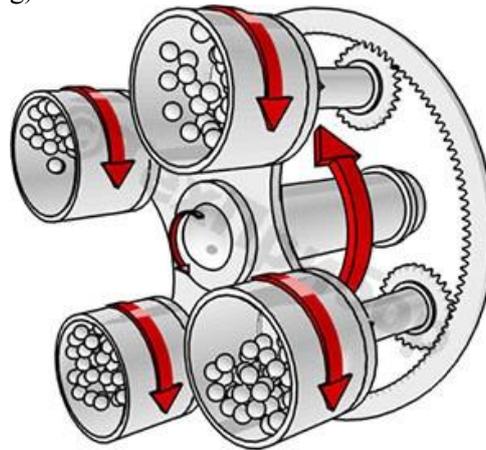


Figure 3. Operating principle of the vario-planetary mill

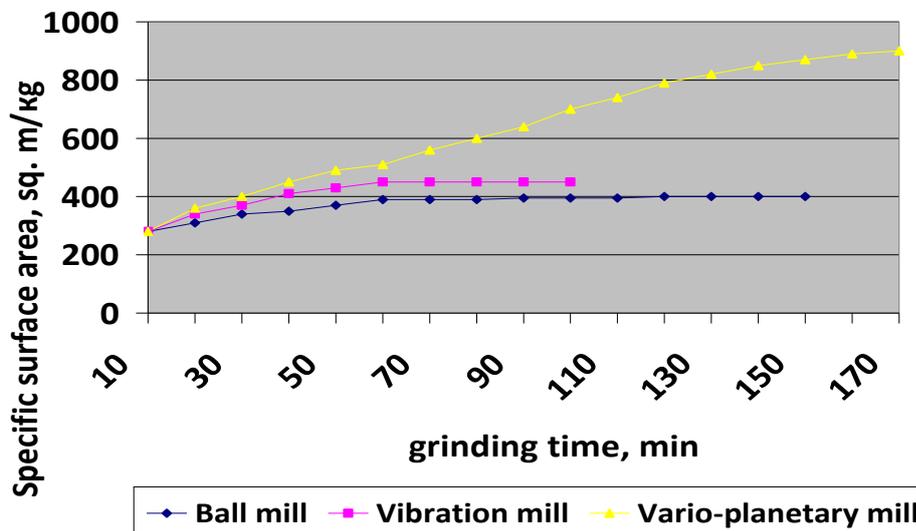


Figure 4. The dependence of the specific surface area of the composite binder of the time for any grinding mill

In order to determine the optimum particle size was produced intergrinding cement hyperplastisizer, ash and limestone to varying the specific surface area: 500, 550, 600, 700, 800, 900 m²/kg (table 1).

Table 1. The results of determination of compressive strength (MPa) of cement samples

Age of the sample, d.	The specific surface area of the composite binder, m ² /kg					
	500	550	600	700	800	900
3	46.1	47.4	47.2	46.0	45.6	45.5
7	50.3	54.2	54.1	49.1	48.6	48.4
28	68.1	77.3	70.2	65.8	55.0	65.0

It was found that the optimum surface area binder 550-600 m²/kg. Increased activity in excess of these values has a negative effect on the structure. Using a binder with increased activity significantly speeds up the process of setting setting the end of the mixture ends after 35-40 min., while the developing temperature 95-97°C. Fast setting raw prevents the formation of spherical particles uniformly distributed in the macro-structure of cement stone.

During mechanical activation a composite binder active molecules of cement minerals occur in the destruction of the molecular defects in the areas of packaging and breaking metastable phase decompensation intermolecular forces. The process is accompanied by a change in the kinetics of hardening of portland cement.

Mechanical processes during grinding mineral materials cause, along with the increase in their surface energy, increase the Gibbs energy of powders and, respectively, their chemical activity, which also contributes to the high adhesion strength when contacting them with binders.

Thus, the set of measures for a mechanochemical activation makes better use of the weight of components filled with cement systems and adjust their properties. At relatively low cost is possible to provide a spectacular and, importantly, easily repeatable results in a production environment.

Increased strength binders when administered in their composition finely additives besides hydraulic activity could also be explained by the formation of fine grains more nucleating additives in the contact zone of cement. "Microfiller effect" can not be explained only by the formation of additional nucleation, as their direct effect is to accelerate the initial stage of the chemical hardening. The basis of "micro filler effect" are both chemical processes of interaction of cement hydration products and the physico-chemical phenomena, such as the effect of the surface energy of the particles of fine additives.

In the presence of mill ground additives in concrete is hardened the contact zone between the cement stone and aggregate. In portland cement concrete without nanoadditives contact area is usually less dense than the cement paste, and includes a large number of plate-like crystals of calcium hydroxide, whose longitudinal axis is perpendicular to the surface of the aggregate. Consequently, it is more susceptible to the formation of microcracks in the tensile forces arising from the changes in the normal conditions of temperature and humidity. Thus, the contact area due to its structure is weakest in the concrete and therefore has a great influence on its toughness. Introduction of fine additives greatly reduces capillary porosity contact zone due to a sharp reduction in the total content of Ca(OH)₂.

The positive effect on the microstructure of the contact zone is achieved by introducing a relatively small amount of fine ground active mineral additives, such as fly ash. The cementitious systems containing the hydraulically active mineral additives, the formation of hardening an additional quantity CSH of by the interaction Ca(OH)₂ with active silica or aluminosilicate filler. The consequence of these processes is the formation of additional phase contacts (contacts between fusion crystal hydrates) and the increase in the density of the cement stone, which determines the high strength cement system.

In addition, we should not forget that in addition to the introduction of cement mill ground supplements increase the specific surface of the cement also allows you to adjust the activity of the

binder. It is known that by grinding the same Portland cement clinker and thus altering the proportion of particles 5-20 microns in the total mass of the cement powder can be prepared portland cement grades 600, 700 and 800 and very rapidly hardening cement.

It was found that the combined effect of mechanical and chemical activation (the presence of limestone particles) increases the pozzolanic activity of acidic ash. Analysis of the microstructure showed that the particles of ash and limestone formations completely surrounded by the gel. Individual particles are bonded together to form clusters. This cement matrix characterized by the presence of needle-like lesions, length of 2 μm and a diameter of about 0.2 microns (figure 5).

Thus, from fine limestone additive is a chemical way to improve the activity of ash and sand. It has a catalytic effect on the reaction activity of the surface of ash and sand during machining in vario-planetary mill. Furthermore, the introduction of limestone increases the alkalinity of the concrete, resulting in a greater formation of cement hydration products in a unit time.

The possibility of increasing the impermeability of the concrete due to the varying amount and type of additives, fineness, and synthesis parameters, allowing you to create materials for multilayer walling with a compressive strength of up to 100.9 MPa, with low permeability under real operating conditions. Intergrinding cement hyperplasticizer, acidic fly ash, and limestone in an amount of 55%, 40% and 5% respectively accelerates the synthesis of neoplasms, linking allocated at alite hydration of CaO in calcium hydrosilicates of different basicity. Thus optimizing the microstructure of cement paste, you can get an astringent activity of 77.3 MPa.

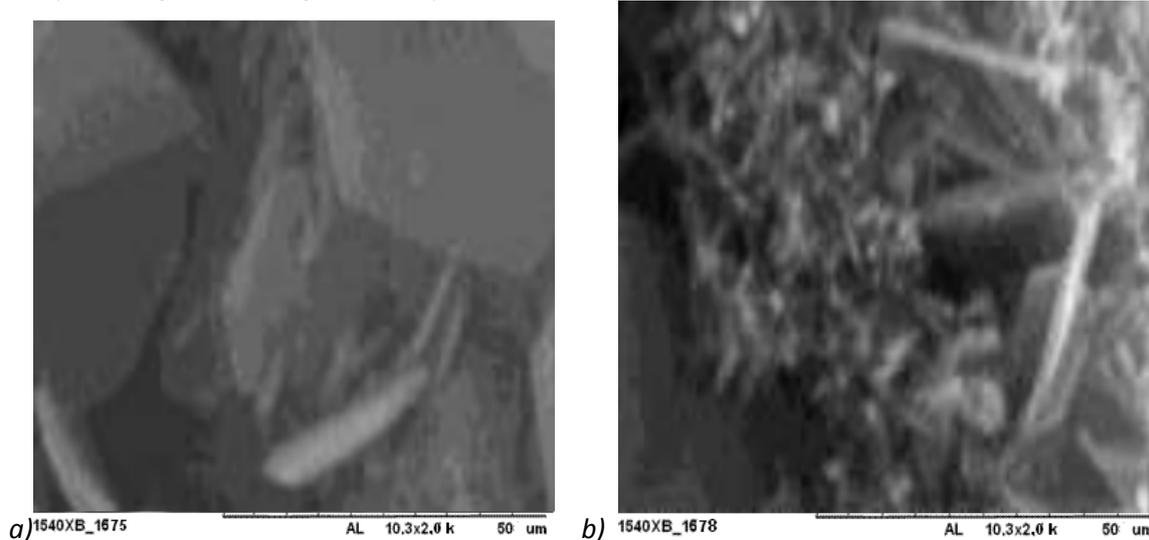


Figure 5. The micrographs neoplasms: *a* - cement stone without additives; *b* - cement stone on the basis of the composite binder

3. Conclusion

It was proposed the mechanism explaining the effect of the use of cement-ash binder in conjunction with hyperplasticizer and limestone in the a mechanochemical activation in the vario-planetary mill: by mechanical grinding is an increase in the reactivity of the cement-ash binder, hyperplasticizer combined with limestone increases the density of tumors, and the adhesion of the binder with filler to provide increased impermeability of concrete.

It was designed the principles of optimizing the structure of fine-grained concrete on the nanoscale by using nanosized composite binder; at the micro level through the creation of high-density packaging filler; at the macro level through the introduction of steel and basalt fiber. It is possible to develop a wide range of fine-fiber-reinforced concrete with a water vapor permeability to 0.021 mg /

(m-h-Pa), permeability to W14, breathability to 0.0253 cm³/s, the water absorption by weight to 2.5%, gas permeability, effective diffusion coefficient of 1.34·10⁻⁴ cm²/s and high strength characteristics.

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