

Processing of Building Binder Materials to Increase their Activation

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Abstract. The paper deals modern physical methods of activation of building powder 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. Activated concrete has a number of features that are used as design characteristics of structures and are due to the structure of the activated binder and its contacts with concrete aggregates. These features also have a significant impact on the nature of the destruction of concrete under load, changing the boundaries of its microcracks and durability.

1. Introduction

It is known that to obtain high-quality new-generation concrete it is necessary to provide it more dense monolithic structure. This requirement is achieved by observing certain techniques and rules:

- extremely low water-cement ratio [1];
- increased requirements for the quality of concrete aggregates [2-3];
- application of modifying additives, providing obtaining a dense structure of concrete [4];
- especially careful mixing and compaction of the concrete mixture [5].

In this paper, studies have been carried out on the activation of binder. 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 [6-7]. 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 purpose of study is to determine the influence of methods of mechanical and chemical activation to the properties of composite binders.

2. Results and Discussion

Activation of cement-water suspensions, mortar and concrete mixtures is a variety of physical, chemical and complex physical and chemical methods of exposure, both to individual components and to their compositions. Activation leads to intensification of the processes of structure formation, modification of the structure and properties of composites. The activated state of a substance is a certain critical intermediate state, through which a process that passes through time passes. One of the promising areas of practical application of activation in the building materials industry is the joint use of mechanical and chemical methods for processing binders in order to increase their useful properties.

Activation leads to an increase in the specific surface of astringents, a change in the surface structure of particles, an appearance of physical defects in sublattices and lattices of minerals that accelerate the elementary interactions of the surface layer with water. There is reducing of the time to achieve cement strength and to ensure a more complete use of the chemical energy of the binder. Activated concrete has a number of features that are used as design characteristics of structures and are due to the structure of the activated binder and its contacts with aggregates of concrete. These features also have a significant



impact on the nature of the destruction of concrete under load, changing the boundaries of its microcracks and durability. The established fundamental difference in the nature of the destruction of activated concrete is the formation of an extensive pre-destruction zone and the explosive release of compressive stress energy. The concrete based on the activated binder has a homogeneous structure, which reduces the concentration of stresses on the boundary between the aggregate and the cement stone, so the deformation of such concrete under load takes quite a long time without micro-fractures. The purpose of mechanical chemistry is to use or prevent those chemical reactions that are caused or accelerated by mechanical activation. Part of the mechanical energy supplied to the solid during activation is assimilated to it in the form of a new surface, linear and point defects.

It is known that the chemical properties of crystals are determined by the presence of defects in them, their nature and concentration. The mechanical activation of the mixture is numerically equal to the total change in the free energy of the system under the action of mechanical forces. One of the main provisions of mechanical activation is that there can be mechanical activation without a grinding, but can not be a grinding without an activation. From this it follows that, first, it is impossible to separate grinding and activation. Any grinding is activation, because by influence of external forces the energy reserve of the ground substance increases, at least due to an increase in the surface energy. Secondly, any grinding machine is a mechanical activator. The most complete achievement of the joint mechanical and chemical activation of the binder is possible in a vario-planetary mill. In a vario-planetary mill, the rotational speeds of the grinding jars and the support disc can be set completely independently of one another. By varying the gear ratio, the movement and trajectory of grinding balls can be influenced so that the balls strike horizontally on the inner wall of the grinding jar (high impact energy), approach tangentially (high friction) or simply roll over the inner wall of the grinding jar (centrifugal mills). All intermediate stages and combinations between pressure friction and impact can be freely installed (figure 1).

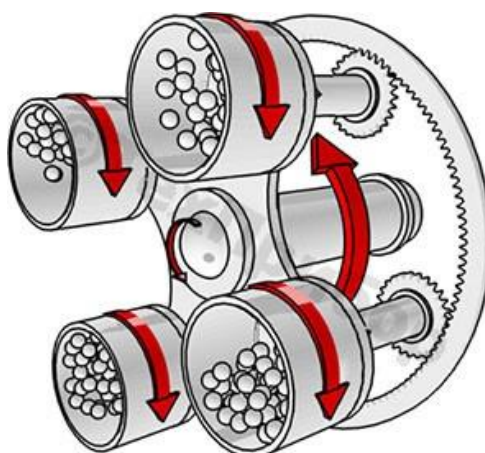


Figure 1. Operating principle of a vario-planetary mill

Grinding by any apparatus gives the activation of the processed material more or less. The effect of mechanical activation of components of a concrete mixture consists in the transition of the passive (inactive) surface of both astringent and inert materials to a chemical active state, which is expressed in an increased ability to react during subsequent technological operations. The increase in the specific surface area of the cement, its reactivity (activity) has a significant effect on the formation of the structure of the concrete, the rate of hardening and its strength characteristics. Using of activated cement makes it possible to form a denser and more uniform structure of concrete, which allows one to obtain a sharp increase in the one-day strength and increase it after 28 days of hardening (figure 2).

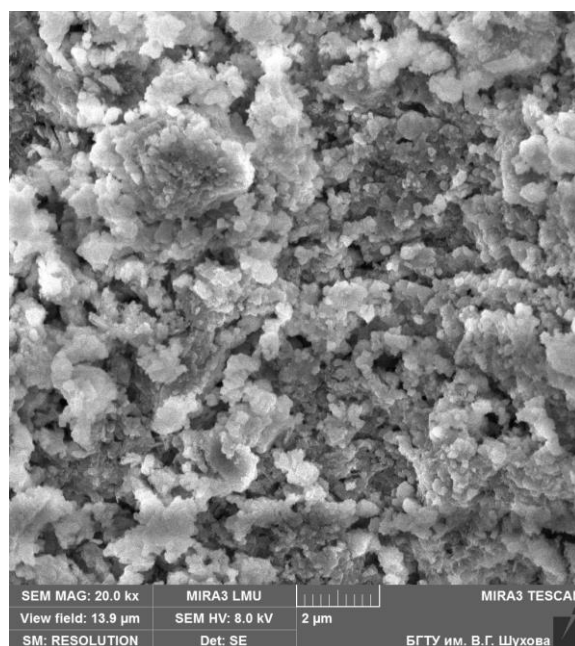


Figure 2. Microphotography of cement stone neoplasms based on an activated composite binder

Particularly relevant is the mechanoactivation of components for the production of foam concrete, polystyrene concrete, when the quality and stability of the characteristics of the constituents of the mixture is of particular importance. Increase in the activity of materials is achieved as a result of grinding, dispersing (grinding) in special energy-intensive grinding units (mills). One of the leading factors affecting the degree of structural change in minerals is the destruction method, determined by the type of shredder. Conventionally, several basic methods for grinding materials using energy-stressed fine grinding aggregates can be distinguished: grinding by crushing, abrasion and splitting (the free-blow method), and a combination of these methods. Activation of astringent and inert components of a concrete (mortar) mixture by the free-impact method and subsequent vibration activation in a turbo mixer-vibration activator makes it possible to save an expensive binder without reducing the strength characteristics of finished products and increasing their cost price, improve frost resistance, and improve resistance to all types of wear.

Scientists for several decades studied and developed the theory and practice of joint mechanical and chemical activation of solid materials [8-13]. This area of science and technology concerns the conduct of solid-phase reactions in grinding machines and contains a huge innovative potential. Solid-phase synthesis is attractive in that it provides a comparative simplicity of the process, the ability to conduct reactions in the absence of solvents, which is important from an environmental view point. Despite the destruction in the crystal structure and defectiveness, the chemical composition during activation does not change. Cement is a fine-grained powder with high specific surface area ($100\text{--}600\text{ m}^2/\text{kg}$). This causes intensive condensation on the cement grains of vaporous moisture and gases from the surrounding space. It is known that, in spite of the high specific surface area of the cement, their granulometric composition is far from uniform, and a significant part of the grains (40-50%) are larger than $50\text{--}60\text{ }\mu\text{m}$. In the process of increasing the strength of cement stone, the main role is played by a fraction of $3\text{--}30\text{ }\mu\text{m}$ in size. Grains of cement $40\text{--}60\text{ }\mu\text{m}$ or more remain unhydrated, and only after six months the thickness of the cement stone layer reaches $15\text{ }\mu\text{m}$. The incompleteness of the use of cement is aggravated by the difficulties in achieving an even distribution of water between the individual particles of the binder, which, due to adsorption and molecular bonding forces, are aggregated into flocules, which prevent uniform wetting.

Increasing in the specific surface is considered uneconomical, so it is rational to activate the binder during preparation of the concrete mixture. On the other hand, high rates of hydration of fine cement

fractions are associated not only with their high specific surface area, but also with the highest dislocation density and concentration of defects on the surface of fine cement particles. During increase defectiveness of the particles, a transition to a nonequilibrium state occurs, which leads to a decrease in chemical stability and the intensification of a whole series of physical and chemical processes, including the hydration activity of clinker minerals. This fact is explained by the fact that as a result of grinding the clinker, the grain surface contains a number of defects in the form of submicro- and micro- cracks. Destruction of cement grains at the beginning of hydration occurs and develops on defects, and is accompanied by dislocation movement. Speed of dislocation movement is determined by the physical and chemical nature of the surface of clinker minerals, the boundaries of their phases, and the content of impurity elements in crystals. In turn, crack growth is equivalent to a continuous distribution of dislocations in the volume of the solid phase. Clinker particles with defects are in a state of higher energy of interaction during hydration than structurally perfect minerals.

The activation of binders is also caused by an increase in temperature and pressure, the addition of special additives, chemical and mechanical dispersion of individual components and their mixtures, etc. The rate of most homogeneous reactions increases by a factor of 2-4 with a temperature increase of 10°C. Addition of surfactants and other chemical additives promotes the formation of additional crystallization centers and stimulates their growth. Using of chemical additives in construction shows that the largest share belongs to plasticizers and superplasticizers. They can significantly reduce the water requirement of the concrete mix (by 20% or more), and also reduce the consumption of binders and significantly improve the strength characteristics of concrete, to use when building concrete and reinforced concrete structures, cast self-compacting and non-dispersible concrete mixtures. The negative moment of application of such additives in concretes is their synergy with cement and a significant increase in the cost of the final product.

With the development of technologies, new opportunities appear to affect the structure and properties of water, there is the possibility of purposeful management of the process of structure formation and the properties of cement composites, which represent a complex hierarchical system including the nanoscale. Scientists are conducting studies on the modification of the mixing water by carbon fulleroidal nanoparticles [14-15] (figure 3).

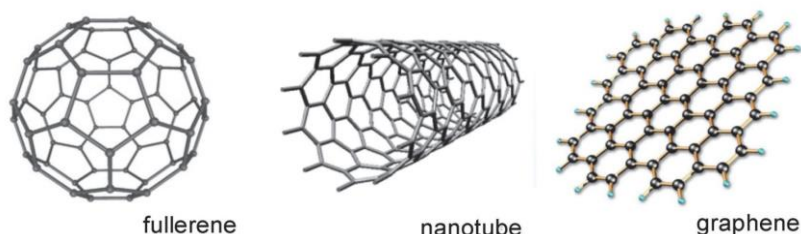


Figure 3. Carbon nanoparticles

The method of modifying (activating) mixing water allows, by reducing the cost of expensive components (cement and additives) to lower the cost of concrete, while the physical and mechanical properties of the final product do not deteriorate. Research is developing on electromagnetic activation methods aimed at intensifying the hydration of individual clinker minerals, regulating the basicity of hydrosilicates by applying an alternating or discrete constant electric field of a certain frequency [16-17]. Electromagnetic activation of binders compositions is less energy-intensive than joint mechanical and chemical activation, which is associated with an increase in the activity of components of astringent compositions. Interesting results were obtained by activating the cement test with high energy sources, aero hydro-dynamic radiators, and also with magneto-mechanical, electro-hydraulic and thermoelectric effects on solutions and concretes.

The technology of magnetic activation of mixing water has been developed for a long time, but it still does not find wide application in construction practice. One of the reasons for this is the problem of obtaining a stable level of water activation. This leads to variability in the manifested water properties and poor repeatability of the results. Magnetic treatment consists in passing the flow of water through a

magnetic field. Strength of products made using magnetic activated water, statistically significantly increases. Magnetic treatment of mixing water affects the hardening process: the setting speed and the plastic strength of the cement paste change, the sizes of the cement granules decrease, the hydration process becomes active. The mixing of concrete mixtures with magneto-activated water intensifies the processes of cement dissolution and hydration in the early periods of hardening and accelerates the release of smaller crystals, which leads to a decrease in porosity, an increase in density and frost resistance of concretes (figure 4).

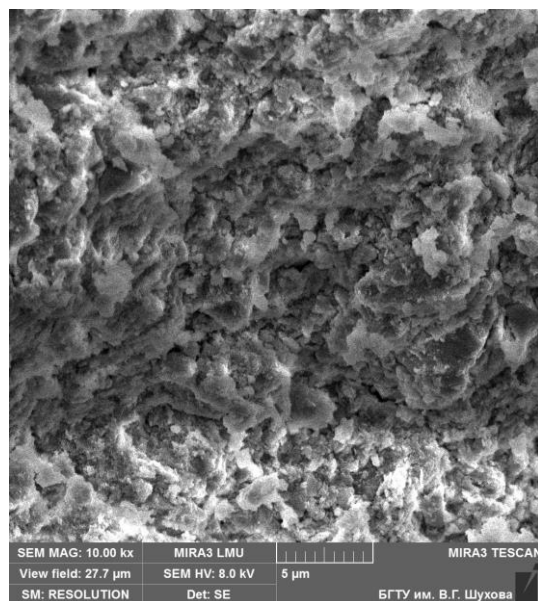


Figure 4. Microphotography of cement stone neoplasms based on magnetic activated composite binder

Among non-reactive methods of activation of building mixtures and their components, one of the promising is the treatment with high-voltage electric discharges. It is necessary to recognize the priority of electroactivation against magnetic activation, since the mechanism of influence of the first, at least at the phenomenological level, lends itself to logical interpretation. The study of the mechanism of the effect of the basic factors of a high-voltage electric discharge on cement-water systems and the influence of the discharge parameters on the physical characteristics of activated concrete with a view to reducing energy consumption showed that for the presence of the activation effect, it is necessary to observe the initial conditions:

$$E_{sp} \geq E_i,$$

$$E_{sp} \geq E_c,$$

where E_{sp} - specific electric energy introduced into the volume; E_i - energy that ensures ionization of the mixture; E_c - energy, which ensures the destruction of the crystal lattice of the cement conglomerate.

The ionization energy is the resultant value, the term of several components, the total value of which is sufficient for dissociative-associative phenomena to occur in the medium being processed. This facilitates the involvement of water layers located outside the electrical discharge channel to various oxidation reactions. Consequently, the initial impulse leads to a significant change in the ionic composition of the suspension and the appearance of polarized groups in the water. Mechanical dispersion of cement leads to an increase in its specific surface, morphological uniformity, increase in density and strength of concrete. Thus, the alternate execution of the first or second condition is forming two stages of the activation process. At the first stage of the processing, water-cement systems are activated by ionization, and in the second stage, the cement slurry is dispersed. As a result of electro-

impulse activation, the water of mixing and the cement slurry become chemically active, acquiring the state of the ionic solution, and can be used as an accelerator for hardening concretes. The selected processing regime, close to the critical one, helps increase the concentration of aqueous solution. As a result of electro-physical processing, the rheological properties of building mixtures benefit greatly and the strength characteristics of cement stone are increased.

System analysis of the structure gives a real picture of the change in density and porosity of activated concrete. As a result of active hydration processes, the amount and volume of pores is reduced. Cement stone has a more uniform morphological composition, in which particles with a smaller size predominate.

Recently, along with other areas, there has been an interest in the possibility of carrying out technological processes that require thermal activation under microwave (dielectric) heating conditions. Dielectric heating effect mainly consists in the absorption material energy microwave electromagnetic field (HF or UHF) band and converting this energy into heat. The thermal power emitted by the material depends on its dielectric characteristics and field parameters and provides a number of advantages over other thermal activation methods: high process speed, lack of heat carriers, dynamic temperature control, selective activation of individual components in composite systems, etc.

The activation of the cement dough also is by ultrasonic processing. It causes the effect of cavitation, the dispersion of solid particles, microcracks in crystals, which contributes to the dissolution of cement particles and their more complete hydration. Unlike high-frequency vibration, the relative increase in strength occurs with an increase in the water-cement ratio by ultrasonic action. Dense and strong crystal hydrate structure of cement stone is formed by influence of wave pressure arising in an acoustic field. Intensification of the hardening process of concrete is achieved by joint effect of an acoustic field with a frequency of 10-16 kHz and an elevated temperature. Cement paste can be preprocessed in an aero-hydrodynamic activator, followed by stirring with heating aggregates and pouring at 60-65°C. Thermo-acoustic activation of the concrete mixture is also possible with agitation in the heated state in mixers with acoustic radiators. The combination of activation with preheating allows about a 1.5-fold increase in the 28-day strength of concrete.

3. Conclusion

Activation leads to an increase in the specific surface of astringents, a change in the surface structure of particles, the appearance of physical defects in sublattices and lattices of minerals that accelerate the elementary interactions of the surface layer with water. There is a reduction in the time to achieve cement strength and ensure a more complete use of the chemical energy of the binder. Activated concrete has a number of features that are used as design characteristics of structures and are due to the structure of the activated binder and its contacts with concrete aggregates.

Despite the foregoing, the common drawbacks of all physical methods of activation are: the laboriousness of finding quantitative parameters characterizing the degree of activation of the aquatic environment in production conditions; the need to retrofit technological lines with special equipment for activation; the need for refinement, and in some cases, for reworking of technical normative documents and technological regulations, etc.

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