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Review

Review of methods for activation of binder and concrete mixes

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Abstract: Increasing the efficiency of dry construction mixtures (binders) and concrete mixes can be achieved through using of various activation methods. In addition to using of various chemical modifiers in the binder composition, the important point is the grinding of dry construction mixtures, magnetic activation of mixing water, treatment of cement mortar with electrical discharges, etc. This article is a scientific review on this important issue of building materials science. The simplest method of solid-phase activation is the grinding of binder composites. A comparison of various milling machines allowing mechanochemical activation to different degrees was made. The method of solid-phase activation is effective, but a more cost-effective method is liquid-phase activation, consisting in external energy impact on the mixing water containing the functional additive. When intensive mechanical action is carried out in a rotary pulsation apparatus, the destruction of polymolecules occurs with the formation of a large number of active groups that can promote the polymerization of organic molecules with the formation of polymer structures that are more complex than the original ones. Activation of binder and inert components of the concrete (mortar) mixture by the free-impact method and subsequent vibroactivation in the turbo mixer-vibroactivator makes it possible to save expensive binder without reducing the mechanical properties of the finished building structures and increasing their cost price, improve frost resistance, improve wear resistance. The increase in temperature and pressure, the introduction of special additives, the chemical and mechanical dispersion of individual components and mixtures thereof, etc., also lead to the activation of binders. Among the non-agent methods for activating building mixtures and their components, one of the promising ones is treatment by high-voltage electric discharges.

Keywords: mechanochemical activation; milling machine; magnetic activation; water modification; ultrasonic activation

1. Introduction

The use of single-component and multicomponent binders at the present stage is unthinkable without special preliminary preparation, called activation. As the activation of dry building mixtures and liquid-phase solution and concrete mixes, various physical, physicochemical and chemical methods of action are understood, both to individual components and to their compositions, leading to intensification of the processes of structure formation, modification of the structure and properties of composite materials [1,2].

The activated state of a substance is a certain critical intermediate state, through which a time process moves. One of the promising areas of applied use of activation in building materials is the use of mechanical and chemical methods of influencing binder systems in order to optimize their physicochemical and exploitation characteristics. Activation methods lead to the production of finer-grained particles, the modification of the surface structure of particles, the creation of physical defects in sub lattices and lattices of minerals that intensify the elementary interactions of the surface layer with mixing water. The time to reach the cement stone strength and to ensure a more complete use of the chemical energy of binders is reduced [3,4].

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 micro cracks and longevity parameters. The established fundamental difference in the nature of the destruction of activated concrete is the formation of an extensive pre-destruction zone and explosive release of compressive stress energy.

Concrete based on activated binder composition has a uniform volume structure; this reduces the concentration of stresses at the “filler-cement stone” boundary, so the deformation of this concrete under load for a long time is accomplished without micro-fractures [5].

According to the theory of P.A. Rebinder [6], the task of mechanochemistry is to apply, or vice versa, to neutralize those chemical reactions that are caused or intensified by mechanical action.

The aim of the study is to review modern methods of mechanochemical activation. Based on the formulated aim, the tasks of the study are:

- Structure existing methods of activation;
- To reveal the effectiveness of thermal, electrophysical and other types of activation;
- Describe the equipment and technology of modern activation methods.

2. Activation methods

The methods of activation of binder and concrete mixes are structured in Table 1.

Table 1. Methods of activation of binder and concrete (mortar) mixes.

Method	Technological features	Advantages	Disadvantages	Ref.
Chemical additives	Modification of formulations	Wide range of modified formulations	High price	[1,3,5,7–22,26]

Continued on next page

Method	Technological features	Advantages	Disadvantages	Ref.
Addition of surface active substances	Formation of additional crystallization centers and stimulation of growth of neoplasms of secondary generation	Compaction of cement stone structure	Limited range of applications	[6,13,27–30]
Grinding of binder by a mill	Different types of mills—ball, vibratory, vario-planetary, etc.	Simplicity	High energy costs	[4–6,10,12,21,24, 26,29,31–54]
Liquid-phase mechanoactivation	The mechanical effect produced by rotary-pulsating apparatus	The process of hydration occurs more fully, in addition, the mobility of the concrete mix increases	Small amount of the mixture charge per cycle	[30,55–57]
Magnetic activation of mixing water	Cycle magnetic water treatment	Energy efficiency	Expensive equipment	[23,25]
Hydrodynamic activation	Synergistically used are the physical and chemical processes occurring in the water flow: aeration, cavitation (cold boiling), collapsing, coagulation	There is a transfer of dissolved substances in water into insoluble substances and their removal	Relatively low efficiency	[1,4,5,18]
High-voltage electrical discharge treatment	The imposition on a water-cement system of a constant field of high intensity leads to phenomena of electrolysis of water and electrophoresis, i.e. of the motion of charged particles in an electric field	Significant change in the ion composition of the suspension and the appearance in the water of polarized groups	Technological complexity	[34]
Electrophysical activation	Electromagnetic action (sometimes followed by steaming)	Significant improvement in the elastic strength characteristics of concrete	High costs	[11,23,32]
Microwave (dielectric) heating	The absorption by the material the energy of the electromagnetic fields of the high-frequency or microwave range and the conversion of this energy to thermal	High speed of technological process	Expensive equipment	[19]

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Method	Technological features	Advantages	Disadvantages	Ref.
Thermal activation	Heating with subsequent cooling according to various schemes	A relatively simple and effective way	High costs	[2,17,18,32]
Ultrasonic treatment	Ultrasonic treatment causes the effect of cavitation, grinding of solid particles, micro cracks in crystals	Intensification of cement hydration processes	High energy costs	[12,19,25]
Thermoacoustic activation	The cement paste is pretreated in an aerohydrodynamic activator, followed by stirring with aggregates and heating before laying at 60–65 °C.	Strength increase 1.5 times	Complexity of processing	[32]

2.1. Chemical additives

Most often, the properties of concrete is modified by chemical additives. At the same time, optimal characteristics, such as strength, workability, etc., are achieved at a certain critical dose of the chemical modifier, after which the effect falls off [3,7–10]. However, the chemical industry produces a huge number of additives that allow to regulate the properties of concrete. Therefore, producers are not interested in applying new methods that have not received sufficient experimental justification for the influence of new methods on the durability of concrete.

There are works confirming the effectiveness of the use of suspensions based on chalk, the use of which in the amount of 10–40% of the mass of the cement allows to obtain high-strength and water-resistant concrete that has corrosion resistance to aggressive magnesia, high water resistance and frost resistance in comparison with equiprobable concrete [1,11–14].

The degree of influence of disperse additives on the general properties of composites can be explained by the following provisions. Composite materials are multicomponent and multiphase systems in which, when certain conditions are created, unique properties are formed that are not characteristic of individual components. In particular, the main structural feature of polymeric composite materials is their ability to form specific structures of filler and matrix particles, such structures can include fractal (cluster) structures. Their formation is a process of self-organization in the composite, with most of the energy transferred to the components of the composite spent on the formation and flow of complex physicochemical processes in a dispersed medium. The phenomenon of self-organization is mainly due to the excess of surface free energy in the disperse system. The phenomenon of self-organization in this system makes it possible to control the properties of the composite, and also to predict the change in its properties during the entire lifetime of such a system, this possibility appears as a result of high adaptive variability of the system [5,15–18].

After the discovery of cement stones with a compressive strength of more than 250 MPa, so-called densified-small-particles (DSP) composites (reinforced systems containing uniformly distributed nanoparticles) were proposed. These composites include special cements, microsilica, high-quality aggregates and microfibers. And the use of special technological methods at W/C = 0.12–0.22 made it possible to obtain a strength of 270 MPa, while concretes are characterized by high resistance to corrosion and abrasion [5,7,19–22].

In [9] it is the increase in the strong characteristics, waterproofness and frost resistance of concrete composites due to the use of a hyperplasticizer, dispersions of multilayered carbon nanotubes (fullerenes) in combination with highly disperse amorphous SiO_2, which form the crystalline hydrate formation formed in the course of their formation on the surface of fullerenes, the degree of hydration of Portland cement and the reduction of capillary porosity. The main difficulties in modifying composites by nanotubes are attributed to their tendency to agglomerate in a liquid medium, as well as chemical inertness with respect to the cement matrix. At the present stage of the development of science and technology, the search for the solution of the problem of the most effective way of introducing and distributing fullerenes in the volume of cement stone led some researchers to methods involving "growing" fullerenes on the surface of cement particles, joint grinding during mechanical activation with clinker powder, dispersion in mixing water due to ultrasonic or hydrodynamic cavitation. In the latter case, in view of the disaggregation of the solid phase in the liquid dispersion medium, the introduction of special surfactants is additionally required to ensure the stability of such a system. Such substances can be polycarboxylate hyperplasticizers, which are widely used in the production of concrete mixtures.

Returning to fullerenes, we briefly mention several ways to use them [19,23–26]:

1. "Top-down"—grinding, laser evaporation, etc.
2. "Bottom-up"—the preparation of fullerenes from molecular precursors, measuring less than 1 nm.
3. Natural fullerenes, formed, for example, in the combustion of natural gas or lightning.
4. Complex additives based on nanotubes—in addition to increasing the activity of binder, provide and other specified properties of cement stone or concrete.

2.2. Addition of surface active substances

To improve the efficiency of activation, the effect of reducing the strength of solid materials under the influence of surface-active substances has a great influence by P.A. Rebinder [6]. Addition of surface active substances and others chemical modifiers causes the formation of additional crystallization centers and stimulates the growth of neoplasms of secondary generation. Surfactant molecules, adsorbed on the surface of particles, reduce surface energy, with partial saturation of free chemical bonds on the surface of the solid phase, which prevents blocking. The stability of dispersed powders usually depends on their charge, acquired as a result of adsorption of ions. If the particles have like charges, they repel, respectively, preventing sticking. Hydrated cement and especially CSH are in the form of particles of extremely small sizes, hence a common colloid-chemical approach is applicable to them. So, if two phases are in contact with one another, their electrical charges must be taken into account—in this case the use of plasticizing additives leads to the formation of more dispersed structures from the hydrate phases [13,27–30].

2.3. Binder grinding in the mill

Another known method for optimizing the characteristics of concrete is thinner grinding of cement or activation of cementitious fillers, in which not only the area of the contact surface of the solid constituents increases, but also the number of active centers of crystal formation capable of providing an increased degree of hydration of the activated cement.

Some part of the mechanical energy supplied to the solid body during activation is assimilated to it in the form of a new surface, linear and point defects. It is a well-known fact that the chemical properties of crystals are determined by the presence of defects in them, including their nature and concentration. The mechanical activation of a dry building mix is numerically equal to the total change in the free energy of the system under the action of mechanical forces.

The leading position of mechanoactivation is that there can be mechanoactivation without grinding, but there can be no grinding without activation. From this it follows that, firstly, it is impossible to separate the grinding from activation: Any grinding is activation, because as a result of the influence of external forces, the energy reserve of the ground substance increases, at least by increasing the surface energy; secondly, any grinding unit acts as a mechanical activator.

Proceeding from this, grinding in any aggregate gives the activation of the processed material to some extent [5,31–34]. On the other hand, a study of grinding in various types of mills, carried out by the authors [4,6,35–38], showed the following. The efficiency of the method of grinding the composite binder was evaluated in ball, vibratory and vario-planetary mills.

Dispersing of the material in the ball mill is by free blow, which causes the material to be destroyed into weakest bonds, structural defects at the junctions of crystals, grains, layers, etc. In the industry of crushed stone or artificial sand of various fractions—this is an unequivocal advantage, because the product of impact crushing is represented by isometric grains without internal defects with a small content of ground product. For materials with a large specific surface area, increasing the strength of the particles is made during the increase in the fineness of the grinding, and this produces additional difficulties. At some point in time, when the structural strength of each individual particle reaches its maximum limit, and its mass becomes negligible, the free kick is almost completely replaced by abrasion. The rotor of the centrifugal mill stops fulfilling the function of the accelerator and works already as a swirler of "material-air" flows. Large particles moving to the walls of the grinding chamber displace the smaller ones, which, moving from the edges to the central part, are crushed solely as a result of mutual abrasion in turbulent flows. If we estimate the energy consumption for the formation of a unit of a new surface of solid materials, this is one of the least effective methods of dispersion.

The action of the vibrating mill is based on the intense moving of the grinding bodies, when inertia and centrifugal forces are used instead of the gravitational forces causing the balls to fall, and rotation of the vibrator shaft, and then of the mill itself, causes the grinding bodies to move in accordance with the magnitude of the eccentricity or the radius of the carrier. The transfer of the energy of the grinding charge is carried out through the mill housing. As a result of inertia, centrifugal forces and alternating loads the shock elements inside the body move along a complex trajectory, press against the walls of the drum, strike each other, as well as particles of dispersible material, breaking, crushing and rubbing them. For the production of finely ground materials, vibrating mills are more efficient than ball mills. The shock impact to the dispersible material for this version of grinding is insignificant, but abrasive impact is intensively, which allows to obtain the optimum specific surface area of a binder.

In a vario-planetary mill, the rotational speeds of the grinding jars and the support disc can be independently set. By varying the gear ratio, it is possible to influence the motion and trajectories of the grinding balls in such a way 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 forces). All intermediate stages and combinations between friction and impact pressure can easily change. Accordingly, the dispersion of building powders by vario-planetary grinding units is more energy-efficient than by ball and vibration grinders. In addition, as a result of the synergistic impact of shock, centrifugal shock and abrasive forces, it becomes possible to achieve finer-grained powders.

The effect of mechanoactivation of components of a concrete mixture consists in the transition of the passive (inactive) surface of both astringent and inert materials to a reactive state, which is expressed in increasing the ability to react in subsequent technological operations. An increase in the specific surface area of cement grains, their reactivity (activity) play an important role in the formation of the structure of concrete, the rate of hardening and its strength parameters. The use of activated cement makes it possible to create a more dense and uniform structure of concrete. This allows us to achieve a sharp increase in compressive strength in the first day and its growth at the age of 28 days. The mechanoactivation of components in the foam concrete and polystyrene concrete industry is extremely important, when the quality and retention of the parameters of the components of the building mix plays a significant role. The increase in activity of building binder materials is achieved during grinding in special energy-intensive grinding machines (mills). The most important parameter affecting the degree of structural modification of minerals is the destruction mode determined by the type of grinding machine.

Accordingly, with the foregoing, we outline several basic methods for dispersing astringent systems in energy-stressed fine grinding mills: grinding by crushing, abrasion and splitting (the free-blow method), and a combination of these methods.

Activation of binder and inert components of the concrete (mortar) mixture by the free-impact method and subsequent vibroactivation in the turbo mixer-vibroactivator makes it possible to save expensive binder without reducing the physical-mechanical and exploitational properties of the finished building structures and increasing their cost price, improve frost resistance, improve wear resistance. Researchers for several decades studied and improved the theory and practice of mechanochemical activation of building powders. This area of science and technology concerns the conduct of solid-phase reactions in grinding aggregates and contains a huge innovative potential. Solid-phase synthesis is good because it simplifies the process, makes it possible to carry out reactions in the absence of solvents, and this is important from the point of view of environmental safety. It should be noted that, despite the destruction in the crystal structure and defectiveness, the chemical composition of the material during the activation does not change.

Portland cement is a fine-grained powder with a high specific surface area (1000–6000 cm^2/g). This causes intensive condensation on the cement grains of vaporous moisture and gases from the environment [10,24,39–42]. 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%) has dimensions of more than 50×10^{-6}–60×10^{-6} m. In the process of cement stone strength growth, 3×10^{-6}–30×10^{-6} m [5,21,43–46]. Cement grains 40×10^{-6}–60×10^{-6} m and more remain unhydrated, and only after 6 months the thickness of the cement stone layer reaches 15×10^{-6} m. The incompleteness of the use of cement is aggravated by the difficulties in achieving an even distribution of water between individual particles of the binder, which due to adsorption and molecular bonding forces are aggregated into floccula, preventing uniform wetting. The increase in the specific surface area is considered to be uneconomic, so it is rational to produce activation of the binder during the preparation of the concrete mixture [8,26,47–50].

On the other hand, high rates of hydration of fine fractions of cement grains are associated not only with their high specific surface, but also with the greatest dislocation density and concentration of defects on the surface of small grains of cement. With increasing 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 physicochemical processes, including the hydration activity of clinker minerals. This fact is explained by the fact that in the process of grinding clinker, the particle surface contains a multitude of defects in the form of submicro- and microcracks. Destruction of cement grains at the beginning of hydration occurs and develops on defects, and is accompanied by dislocation movement. The velocity 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 impurities in crystals. In this case, 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 [12,29,51–54].

2.4. Liquid-phase mechanoactivation

The method of solid-phase activation is undoubtedly effective, but at the same time, its application requires considerable expenditure of electrical energy. A more energy-efficient technique is liquid-phase activation, which consists in an external energy action on water containing a chemical modifier. When intensive mechanical action is performed in the rotary pulsation apparatus (RPA), polymer degradation leads to the destruction of polymolecules to form a large number of active groups, which can promote the polymerization of organic molecules with the formation of more complex polymeric structures than the original one. In addition, mechanization is also affected by the water of mixing, whose hydrogen bonds are rearranged, and a certain number of molecules undergo ionization. The resulting cavitation resulting from mechanic processing leads to the development of mass exchange processes, an increase in the liquid temperature, the formation of hydrogen radicals, and radicals of organic molecules. As a result, the structure of the liquid solution changes. Such changes are accompanied not only by temperature increase, but also by changes in the hydrogen index, specific electrical conductivity. The subsequent magnetization of the mechanically activated aqueous solution leads to an even deeper reorganization of the network of hydrogen bonds and some spatial reorientation of the mechanically degraded charged particles of the dissolved substance. Treatment of mixing water with a magnetic field increases the adsorption of water by the surface of cement grains, and, consequently, increases the disjoining pressure, the hydration process is more complete, and the mobility of the concrete mix increases [30,55–57].

2.5. Magnetic activation of mixing water

It was shown in [25] that cyclic magnetic treatment of mixing water has a significant effect on the physico-mechanical and exploitational properties of cement stone. It is established that at a constant magnetic field strength equal to 0.04 Tesla, after 15 processing cycles, the maximum strength of the hardening structures is reached. It was shown that the sequence of the appearance of phases, the nature of the interaction of clinker minerals with water, the kinetics of growth of neoplasms and, in some cases, the symmetry of crystals, is changing. This effect is explained by the fact that when using ordinary water, a long period of crystallization of Portland cement is observed, but when using magnetized water, the plastic strength of Portland cement begins to grow almost immediately after mixing. Positive effects from the use of magnetized water are accelerated hydration of cement, an increase in the amount of calcium sulphoaluminate crystals and calcium hydroxide, with a general tendency to reduce the crystal size. The strength of concrete with the use of this mixing water is increased by 10–25%. With the development of technological methods, methods of action on the structure and properties of mixing water are improved, there is the possibility of purposeful control of the process of structure formation and the properties of cement composites, which represent a complex hierarchical system including the nanoscale [23]. At the present stage of technical progress, studies are being conducted on the modification of the water of immobilization by carbon fulleroid nanoparticles. The proposed method of modifying (activating) mixing water allows, by reducing the cost of expensive components (Portland cement and chemical additives), to reduce the prime cost of concrete, while the physical and mechanical characteristics of the final building product do not fall.

The technology of magnetic activation of mixing water has been developed for a long time, but wide application in construction practice still does not find. 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 processing consists in passing a stream of water through a magnetic field. Strength of building products and structures made with the use of magnetically activated water, statistically significantly increases. The magnetic treatment of mixing water affects the hardening kinetics: The setting speed and the plastic strength of the cement paste vary, the dimensionality of the cement granules decreases, the hydration process is activated. The mixing of concrete mixtures with magneto-activated water intensifies the processes of dissolution and hydration of Portland cement in the early periods of hardening and accelerates the isolation of smaller neoplasms, and this leads to a decrease in porosity, an increase in the density and frost resistance of ready-mixed concrete.

As a result of electromonimpulse activation of mixing water, the cement solution becomes chemically active, acquiring the state of an ionic solution, and can be used as an accelerator for hardening concrete. The chosen method of action, close to critical, promotes an increase in the concentration aqueous solution.

2.6. Hydrodynamic activation

Hydrodynamic activation of water is a method in which the physico-chemical processes occurring in the flowing water are synergistically used: aeration, cavitation (cold boiling), collapsing, coagulation. In the course of these processes, the substances dissolved in water are transferred into insoluble substances and removal. The effects of transforming the kinetic energy of motion into other forms of energy in swirling flows of liquid and gas have been known since the mid-1930s and have found wide application in aviation, energy, and chemical technologies. As a result of the tests revealed under the influence of hydrodynamic generation, de-ironing, demanganization, degassing (removal of oxygen, hydrogen sulphide from water) occurs in the water. When water is processed in a hydrodynamic generator, molecules, atoms, ions are activated and the ions redistributed in the arisen magnetic field. As a result, water acquires recovery properties and stores potential energy. The activation of binders begins from the moment of their production and continues during the entire period of hardening of materials, i.e. the effect of activation treatment is felt in composite materials for a long time of their service due to the phenomena of structural heredity and the preservation of a certain orientation of the hydration process specified at the initial stages of the binder transformation in ductile cement dispersion. The presence in the liquid phase of the cement paste of various ions and molecules entering the system as a result of magnetic and electric fields affects in a certain way not only the structure of the mixing water, but also the processes of adsorption, dissolution and surface hydration, cement composite. Thus, due to the use of activated mixing water, structural indexes, physical and mechanical properties and durability of concretes and other cement materials improve. During hardening, a number of physicochemical processes of dissolution and hydration take place in the cement test, forming a supersaturated solution of crystalline structures, the initial skeleton of which eventually hardens and collects the basic strength for 28 days. Since during the hardening of cement, the determining physical and chemical processes are dissolution and crystallization in the aqueous medium, namely these processes can be significantly activated in water treated in the apparatus, naturally, as a result, the intensification of the process of hardening and maturing of the concrete stone is obtained. Moreover, a set of strength on activated water occurs for 7 days, compared with the usual conditions of 28 days. As chemical processes affecting the processes of hydration, an increase in the content of calcium hydrosilicates is noted, which in turn create centers of crystallization during the transition of cement solutions to the phase of formation of gel structures and a solid phase with a finer crystalline structure. In cement, which was activated by electric current and magnetic field by water, a greater dissolution of clinker minerals is observed with respect to the control composition (on ordinary mixing water) by 10 days of hardening: C_3S by 18.5–35.0%, C_2S by 7%, C_3A by 23.5%, C_4AF by 11–14.5%, and also by almost 25% more than the control composition, the content of portlandite. Also, after 10 days hardening of the cements, formation of CSH gel is observed to be 30% by weight (compared to a control composition of 25%), and after 28 days the amount of CSH gel reaches up to 50% by weight (in the control composition, its content is significantly less and is 40% by weight). By 56 days these indicators reach 57.3% and 45%, respectively. It should also be noted that for formulations on activated water by an electric current and a magnetic field, no ettringite is present by 28 days.

2.7. High-voltage electrical discharge treatment

Among non-reactive methods of activation of dry astringent components, one of the promising ones is the treatment with high-voltage electric discharges. It should be noted the priority of electroactivation in comparison with magnetic activation, because the mechanism of influence of the first, at least at the phenomenological level, lends itself to logical interpretation [34]. The study of the mechanism of the effect of the basic factors of a high-voltage electric discharge on cement-water systems and the effect of discharge parameters on the physical characteristics of activated concrete with a view to reducing energy costs have shown that for the presence of an activation effect, it is necessary to observe the initial conditions:

$$E_{sp} \geq E_i \tag{1}$$

$$E_{sp} \geq E_c \tag{2}$$

here E_{sp} is the specific electric energy introduced into the volume; E_i is the 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 sum of several components, the total value of which is sufficient for dissociative-associative phenomena to occur in the medium being processed. The imposition on a water-cement system of a constant field of high intensity E_{const} leads to phenomena of electrolysis of water and electrophoresis, that is, the motion of charged particles in an electric field, which is considered possible at $E > 100$ V/mm. This facilitates the involvement of water layers located outside the electrical discharge channel in various oxidation reactions. Accordingly, the initial impulse leads to a significant change in the ionic composition of the suspension and the appearance of polarized groups in the water.

When the cement slurry is treated with electric discharges, the specific energy increases and with each subsequent impulse the action of the shock wave, the vapor-gas bubble, the cavitation flows become more significant, and the effect of the electromagnetic field decreases. The mechanical grinding of Portland cement leads to an increase in its specific surface area, morphological homogeneity, increased density and strength characteristics of the finished concrete. On this basis, the alternate execution of the first or second condition forms two stages of the activation process. At the first stage of the treatment, water-cement systems are activated by ionization, and in the second stage, grinding of the cement slurry is observed.

2.8. Electrophysical activation

Research is being developed on electrophysical (electromagnetic) activation methods aimed at intensifying the hydration of individual clinker minerals, regulating the basicity of CSH by using a variable or discrete constant electric field of a certain frequency. Electromagnetic activation of binder systems is less energy-intensive than mechanochemical activation, which is associated with the activation of components of binder compositions. However, all the same, electrophysical (electromagnetic) activation, as well as heat treatment, is quite energy-consuming. In addition, depending on the technological scheme of a specific type of electromagnetic activation, expensive equipment is needed—a magnetic chamber, a steam chamber, etc. [23]. Significant results were obtained with the activation of the cement test by high energy sources, aerohydrodynamic radiators, and also with magnetomechanical, electrohydraulic and thermoelectric effects on solutions and concretes [32]. As a result of electrophysical processing, the rheological properties of the mixtures change significantly and the physical and mechanical properties of the 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 porosity decreases. Cement stone has a more uniform morphological composition, in which smaller particles predominate [11].

2.9. Microwave (dielectric) heating

Recently, along with other areas, there is an interest in the possibility of carrying out technological processes that require thermal activation under microwave (dielectric) heating conditions. The effect of dielectric heating basically consists in the absorption of the material by the energy of the electromagnetic fields of the microwave range and the conversion of this energy into thermal energy. The thermal power emitted by the material depends on its dielectric characteristics and field parameters and provides a number of advantages in comparison with other methods of thermal activation: High speed of the technological process, absence of heat carriers, dynamic regulation of the temperature regime, selective activation of individual components in composite systems, etc. [19].

2.10.Thermal activation

The effectiveness of the application of thermal activation of binders is confirmed by many researchers. The rate of most homogeneous reactions increases by a factor of 2–4 with a temperature increase of 10 °C. However, these same researchers note the need for an individual selection, both the temperature and the method of thermal treatment for each type of binders. It should be noted that thermal activation methods are quite energy-intensive, and also require certain material costs to ensure the safety of technical personnel [2,17,32]. In [11] it describes a method for increasing the activity of binders by heating in furnaces to 400–800 °C for 20 minutes, followed by cooling under normal conditions. The previous method was improved in [18]—the heating is carried out to 1200–1350 °C in 3–5 minutes, then it is kept at the indicated temperatures for 5–10 minutes, and then it is cooled to 800–1000 °C in 1–2 minutes.

2.11.Ultrasonic treatment

Activating effects on the cement paste are ultrasonic treatment, causing the effect of cavitation, grinding of solid particles, microcracks in crystals, and this leads to the dissolution of Portland cement grains and their more complete hydration. Unlike high-frequency vibration with ultrasonic action, the relative increase in strength characteristics increases with increasing water-cement ratio. Under the influence of wave pressure arising in an acoustic field, a dense and strong crystal hydrate structure of cement stone is created.

2.12.Thermoacoustic activation

Intensification of the process of hardening of concrete is achieved by synergistic action of an acoustic field with a frequency of 10–16 kHz and an elevated temperature. The cement paste can be pretreated in an aerohydrodynamic activator, followed by mixing with aggregates and heating before laying at 60–65 °C. Thermoacoustic 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 approximately 1.5 times to increase the strength of concrete at the age of 28 days [32].

3. Conclusion

It should be noted that not all of the above methods are currently implemented on an industrial scale. This happens for various reasons. In particular, methods such as microwave heating, ultrasonic treatment and thermoacoustic activation have not been sufficiently studied, and, accordingly, industrial machine activators have not yet been manufactured. Such methods as electrophysical activation and heat treatment are energy-intensive, so the producers are slow to introduce them. It can be concluded that the main activation method used on an industrial scale is mechanochemical activation by mills of various types.

In addition, from the ecological point of view (optimization of the "man-material-habitat" system), mechanochemical activation makes it possible to obtain the most stable material without producing carbon dioxide emissions into the atmosphere. The stability of the properties of the activated material is achieved through the release of free internal energy, which is determined by the defectiveness of the crystal lattice.

Accordingly, a whole stratum of activation methods has been identified, which, however, should be treated with caution. In particular, we must not forget that the main "elements of durability" are large non-hydrated grains of cement (the so-called "micro-concrete"). During operation, the concrete structure begins to lose its strength (for various reasons—non-normative loading, long-term planned loading—creep of concrete impacts, concrete corrosion, temperature and humidity factors, etc.). As a result of loss of strength in the concrete structure, microcracks begin to form—the initial homogeneity of structure. It is at this moment that "unreacted cement grains" begin to work. The disrupted homogeneity of the cement stone provides the conditions for the beginning of hydration of these grains, and the products of this hydration "heal" the microdefects of the cement stone and do not allow them to develop into macrodefects, which are the beginning of the destruction. Thus, the thoughtless grinding of the binder is unacceptable.

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, the processing of technical normative documents and technological regulations, etc.

Conflict of interest

All authors declare no conflicts of interest in this paper.

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