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NANOTECHNOLOGICAL TECHNIQUES OF OBTAINING BUILDING COMPOSITES ON A SILICATE MATRIX OF THERMO-MOISTURE HARDENING

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Introduction. The progress in the construction industry is connected with the development and implementation of nanotechnology, reducing the material and energy intensity of production, as well as the cost of the construction. One of the urgent tasks of Materials Science in the framework of nanotechnology development is the description of the mechanisms of the known hydration processes of various types of binders at the nanoscale.

Fundamentals of the production of building composites on silicate matrix of non-autoclaved hardening

The authors have developed nanotechnological techniques for producing building composites on silicate matrix of thermo-moisture hardening. The transition from expensive autoclaving with "hard" activation modes to thermo-moisture hardening under energy-saving modes is ensured by implementing complex activation of the silicate-concrete mixture [1]. The obtained results can be explained by the description of the mechanisms of action of the known hydration processes of lime-silica binder at the nanoscale.

Experimental and theoretical results of studies have shown that for activated lime-silica composites the presence or absence of a particular mineral is not an exceptional prerequisite to obtain the required specific physical and mechanical properties. Perhaps the most significant factor is the size of the neoplasms and the nature of the relationship between them.

In this study, the nanotechnological methods of quartz activation and the structure formation of nanoscale are implemented through the development and implementation of complex activation of the raw mix, which made it possible to go from hydrothermal synthesis of calcium hydrosilicates (*HSC*) in autoclaves to thermo-moisture hardening [2]. To obtain a multicomponent lime-silica binder, quicklime, lime, crushed with quartz sand accordingly to related ratio are used; separately, the rocks of amorphous structure, specifically tripoli, are crushed to related specific surface area. To produce the concretes based on a three-component binder, the raw quartz sand was used as a fine-grained aggregate.

Complex activation includes a sequential cycle of various types and methods of activation: mechanochemical activation of crystalline quartz in aqueous environment of a mixer-activator, chemical one – due to the introduction of amorphous silica, chemoactivation one – due to elevated pH values of the medium, thermoactivation one – due to the exotherm of quicklime.

The activation of quartz consists of converting the crystal surface structure of the quartz grain layer to the amorphous state, however, it can be assumed that the mechanism of the processes under the influence of activation's various types is different. Primarily the differences are dependent to the nature and type of dislocations, taking into account the degree and duration of exposure.

Nanotechnological aspects of complex activation

Mechanochemical activation occurs due to the special properties of newly formed surfaces, particularly due to the change (predominantly local) of chemical and phase composition of solids, as well as their aggregate state under the action of high-intensity mechanical effects [3].

As a nanotechnological method, the mechanochemical activation of crystalline quartz is carried out in an aqueous medium of industrial mixer-activators. It allows to reduce the viscosity of the lime-silica binder by an order [4]. This effect of viscosity reducing is used to compensate the increased water demand of the mixture due to the introduction of a porous mineral additive and the binder activation together with fine-grained aggregate.

For mechanochemical activation, the change of the chemical, physical, and aggregative state is connected with linear, spatial, deep-seated, and especially edge dislocations, depending on the force of action. The type of dislocations will be determined by the trajectory of the quartz grain movement at the moment of impact with the blades of the mixer-activator: direct, tangential or tangential ones.

As a result of mechanical action, the stress field is created in the local areas of solid particles. Relaxation of the local stress fields can occur through the formation of new edge dislocations and point defects in the crystals and the formation of new surfaces, which contributes to the initiation of solid-phase chemical reactions.

Unlike the mechanical dispersion, the main purpose of mechanochemical activation is the initiation of chemical reactions in the solid phase, moreover, both on the surface of ground quartz sand (as a binder component) and the surface of non-ground quartz sand (aggregate).

Chemical activation is carried out by introducing of the mineral additive, containing amorphous (active) silica. Chemical activation increases the soluble silica content in the mixture. Grinding in the process of tripoli dispersing to the size of chalcedony balls determines the possibility of regulating the processes of structure formation at the nanoscale. In addition, the presence of tripoli in the dispersed system contributes to increase the chemical activity of the system due to its amorphous structure and causes the formation of nanoscale *HSC* in the pores of tripoli. A small proportion of nanoparticles are entered to the concrete mixture during fine grinding (dispersion, as a nanotechnological method of activation) of the silica components of the binder: quartz sand and tripoli of amorphous-crystalline structure with a porosity more than 60%. Dispersed highly porous tripoli can serve as a "nano-reactor", its walls limit the growth of tumors in the space.

During the contact with water, the grains of tripoli almost instantly absorb it under the action of capillary forces. As a result, the dissolution and hydration reactions occur on a strongly developed surface under the conditions of high concentrations of ions SiO_2^{4+} inside the tripoli particles. They are the source of nutritive for the crystallization of *HSC*, growing in the direction from the surface to the center of the tripoli particle. The neoplasms formed in the pores, in particular the tobermorite-like gel *SCH(II)*, hillebrandite $C_2SH(B)$ and $C_2SH(C)$ are characterized by nanoscale. The resulting *C-S-H* can be considered as a gel, but not necessarily amorphous. And its crystal structure is evidenced by defractograms, which are observed in the cases when *C-S-H* is obtained from an aqueous suspension in the $CaO\text{-}SiO_2$ system. Approximately all *C-S-H* particles are nanoscale. The presence of a tripoli particle in the binder can regulate the speed and kinetics of hydration reactions.

Thermal and chemical activation (at the stage of preconditioning) are carried out due to exotherm of quicklime and elevated pH values of the medium, whereby the additional sources of dislocations appear on the surface of crystalline quartz.

The use of quicklime and thermo-moisture hardening (*TMH*) provide additional soft and less energy-intensive thermoactivation modes. Under the conditions of *TMH* at T=85°C, the contradiction, associated with an increasing of the quartz solubility, but with decreasing of lime solubility, is annulled, under the conditions of accelerating process of its dissolution [5]. In addition, increasing of *pH* system leads to the creation of favorable conditions for durability and deformation resistance of *HSC* neoplasms at the operation stage ($11.5 \leq pH \leq 12.5$).

Due to the above activation methods, the conditions are provided for creating the necessary physicochemical activity of silica and the formation of calcium hydrosilicates at the required amount at T=85ºC.

Experimental-statistical modeling of experimental results

It is known that with the same water content of expanding and conventional concretes, the relative values of shrinkage are the same. Therefore, in lime-silica mixtures, which are capable of expanding, the destruction processes of shrinkage, which are characteristic of ordinary concrete, also occur, but in the increased volume of the mixture. The optimization of the binder compositions and mixtures was carried out based on the analysis of the possibility of directional control of swelling deformations and shrinkage in the activated lime-silica composites [16]. The minimum shrinkage value ε=0.02 mm/m corresponds to the compositions with the maximum value of volume expansion $z=0.1\%$, in this area the residual deformations (the difference between the values of expansion and shrinkage) $\Delta\varepsilon \rightarrow 0$.

In research it is calculated two comparable complex of sixfactors experimental-statistical models describing the dependency of the "structure – technology – properties" what allowed to study the dependency "characteristics of the structure – property".

Analyzed the influence of composition and conditions of curing more than ten properties, including compressive strength (R_b), tensile bending (R_{btb}), frost- (F), water- (k_r), crack-resistant (k_{Ic}), microhardness (H), heat conductivity (λ), modulus of elasticity (E) and more than ten characteristics of the structure, including the relative average size of capillary pores (d_k), total porosity (P), the ratio of open to the general (k_{sat}), and content in the composites of mineral and phase compositions.

Nanotechnological techniques allow not only significantly to reduce the energy consumption of the production, but also to obtain competitive composite wall materials with significantly higher quality indicators compared with the silicate pressed autoclaved products such as thermal conductivity, density, water and crack resistance, corrosion resistance, and elastic modulus.

Summary. Complex activation, implemented as a sequential cycle of elementary nanotechnological techniques, contributes to the development and reduction to building practice of the resource-saving injection molding nanotechnologies for the production of effective non-autoclaved hardening silicate wall products.

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НАНОТЕХНОЛОГИЧЕСКИЕ ПРИЕМЫ ПОЛУЧЕНИЯ СТРОИТЕЛЬНЫХ КОМПОЗИТОВ НА СИЛИКАТНОЙ МАТРИЦЕ ТЕПЛОВЛАЖНОСТНОГО ТВЕРДЕНИЯ

С использованием нанотехнологических приемов комплексной активации разработаны составы и технология изготовления строительных композитов на силикатной матрице тепловлажностного твердения с пониженной энергоемкостью.