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Original article

https://doi.org/10.15828/2075-8545-2024-16-6-510-524

Modeling of the processes of early structure formation and hardening of cement materials with organomineral additives

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ABSTRACT

Introduction. At present, chemical modifiers are widely used in concrete technology, most of which are complex. The development of the theory and practice of high-strength concrete of the new generation has entailed the development and implementation of complex organomineral additives, which include modern superplasticizers (SP) and finely ground mineral fillers. High-strength concretes are multifunctional concretes that combine, along with high strength, other important properties - high frost resistance, water resistance, elastic-plastic properties, etc. Materials and research methods. Achieving high concrete performance is possible through the use of superplasticizers in combination with finely ground microfillers - stone flour, including nanoparticles and dispersed reinforcement. In this article, the main task is to model the development of the microstructure of cement stone with organomineral additives. For this purpose, a model of the development of the microstructure over time was developed taking into account the possible mechanisms of the influence of components on the composition of hydration products and the nature of early structure formation. Results and discussion. It is shown that the analysis of structural topology and modeling of the processes of formation of the microstructure of filled cement compositions, carried out together with the analysis of hydration products and hardening kinetics, allow us to predict possible mechanisms of action of complex additives and, in a certain sense, to predict possible scenarios for the development of the microstructure of cement stone, which largely determines the main physical and chemical properties of concrete and its durability. Conclusion. Experimental studies have shown that the use of a mixture of microfillers made it possible to achieve a concrete compressive strength of more than 115 MPa on the 28th day of normal hardening, and the insertion of calcium silicate hydrous into the concrete mixture increased the early strength of the hardening composite.

KEYWORDS: structure formation, organomineral additives, microfillers, nanohydrosilicate technologies, crystallization centers, high-strength concretes.

FOR CITATION:

Tarakanov O.V., Erofeeva I.V., Belyakova E.A., Moskvin R.N., Sanyagina Ya.A., Khristoforova I.A. Modeling of the processes of early structure formation and hardening of cement materials with organomineral additives. *Nanotechnology in construction*. 2024; 16 (6): 510–524. https://doi.org/10.15828/2075-8545-2024-16-6-510-524. – EDN: QQDQLS.

INTRODUCTION

Concrete is one of the most durable artificial building materials availble. Its high performance properties are largely determined by its structure [1–5]. It is known [6–8] that as a result of internal stresses, micro- and macrocracks, and corrosion centers, concrete and reinforced concrete products and structures lose their load-bearing capacity and collapse. Therefore, to model the behavior of concrete and reinforced concrete structures throughout a given period of operation, it is necessary to be able to predict the physical and technical properties of the material, which are largely determined by its micro- and macrostructure. It is known that the nature of the change

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in the strength ratio over time indicates a different rate of increase in the former: intensively in the early period of concrete hardening (up to 28 days) and more smoothly and slowly after gaining the design strength [6-9]. However, temperature and humidity conditions that change repeatedly during the calendar year cause internal stresses in the porous structure of concrete structures, which is the reason for strength fluctuations, i.e. the occurrence of the so-called "wave-like" nature of changes in the strength of concrete [11-14]. This effect is characterized by the processes of recrystallization and secondary hydration of the components of the matrix of hardened concrete stone. In this case, a change in the continuity and, as a consequence, the density of the composite structure is possible. To prevent the occurrence of these negative processes in the technological line for the manufacture of concrete products for structures operated in difficult climatic conditions, thermal and thermo-humidity treatment, autoclaving, the introduction of nanohydrosilicate components are provided, which allows accelerating the hardening of the concrete mixture [15-20].

Along with the use of the above methods of influencing the rate of strength gain of concrete mixture, various multicomponent modifiers are currently being actively introduced into the concrete formulation, which requires research into the processes of formation of the microstructure of cement stone and concrete [21-26].

In studies [27] it was noted that the hydration products formed in the presence of certain modifying additives directly depend on the nature of these components and their quantity, which is due to various processes occurring in individual and complex systems with the formation of hydrated phases of different basicity and crystal-chemical structure.

The studies of the mechanisms of influence of chemical additives on the processes of hydration and structure formation of cement systems, conducted by the authors [21-23, 28-31], showed that during the formation of the structure of cement materials, adsorption, electrostatic, chemical and other processes occur in the mixture at different rates and intensities, which are not the same at different stages of the system's hardening. In the initial period, the strengthening of the cement stone is associated with the formation of crystallization centers, the growth of crystalline hydrates and the formation of intergrowths and the formation of a rigid spatial framework occur [28, 32].

In the presence of chemical additives and modifiers, the above interactions are further complicated by the influence of cations and anions of additives, especially complex ones (from the point of view of the conformational structure of superplasticizer molecules, etc.). It is quite difficult to talk about the reproducibility of processes and phenomena occurring in a cement system, the hydration of which occurs even under absolutely identical conditions. In this case, it is possible to talk only about certain tendencies in the hydration development of cement systems and the formation of certain types of structures [25, 33, 34, 35].

The process of formation of the structure of cement stone can be divided into two stages in the first approximation. At the first stage, when the system is in a ductile state, coagulation contacts are formed and adsorptionsolvate layers are formed around the cement particles and filler, the thickness of which depends on the dispersion and charge state of the particles. At the second stage, the system acquires structural strength, and pseudo-crystallization and crystallization contacts are formed between the particles due to the formation and growth of crystals in the diffuse flow.

In the early stages of cement hydration, solid solutions of interstitial hydrosilicate and hydroaluminate phases are formed in the system [36]. In this case, the closeness of the parameters of the crystal lattices and the sizes of the atoms of the components, the parameters of which should not differ by more than 15%, are of great importance. During subsequent hydration, decomposition of solid solutions may occur due to a sufficiently large difference in the sizes of silicon, calcium, oxygen and hydrogen atoms, as well as in the presence of heterogeneities in concentrations and impurity atoms in the solid solutions.

At the early stage of hardening, contacts between the particles of the binder and microfiller are formed due to the formation of hydrates of the AFm- and Aftphases on the surface of the binder particles, as well as in the voids and cavities. At a later stage, a gel-like product of C-S-H and plate-like crystals of lime are formed between the particles and fibers of the hydroaluminates. Impurity ions present in the liquid phase of cement systems distort the structure of the hydrate phases and disrupt the normal order of their formation. For example, most electrolytes and plasticizing additives stabilize metastable calcium hydroaluminates due to the polarization of interlayer water. Subsequently, in the formed structure of the composite, recrystallization of AFm- and AFt-phase hydrates may occur with the release of interlayer water, which may contribute to the occurrence of internal stresses and the occurrence of secondary hydration processes, which leads to the loosening of the structure consisting of C-S-H products reinforced with AFm- and AFt-phase hydrates.

Thus, the density of the most thermodynamically stable phase C_3AH_6 is 2530 kg/m³, and the densities of the metastable phases C_2AH_8 are 1950 kg/m³ and CAH₁₀ are 1730 kg/m³. Recrystallization of hydroaluminate phases occurring in the forming hydrosilicate structures can lead to a decrease in the strength of cement materials during the hardening process. Similar phenomena were noted in our studies of the strength of concrete for a period of up to 18 years [12]. All this indicates that cement systems pass



from one dissipative state to another during the hydration and hardening process.

Nonequilibrium dynamic systems, which are heterogeneous cement systems, exist due to processes associated with energy dissipation: processes of dissolution and crystallization of hydrates from supersaturated solutions, reactions of water dissociation on the surface of solid particles, etc. During the irreversible process of structure formation, a dispersed cement system, which is a large number of interacting phases, extracts and uses energy from the external environment, forming a dissipative structure, i.e. a structure that is formed and preserved due to the exchange of energy and matter with the external environment under nonequilibrium conditions. This is how they differ from equilibrium structures, in which reversible transformations occur with minor deviations from the state of equilibrium.

Setting and hardening are not characterized by a state of thermodynamic equilibrium, since most of the initially formed solid solutions of calcium hydrosilicates and hydroaluminates are unstable and disintegrate with the formation of new metastable phases, resulting in the formation of a hardening structure that proceeds slowly with diffusion control. The closed system is chemically active and any impact on it can change the property of the dissipative structure [36].

In this work, the main objective is to model the development of the microstructure of cement stone with organomineral additives. For this purpose, it is necessary to develop a model of the development of the microstructure over time, taking into account the possible mechanisms of the influence of components on the composition of hydration products and the nature of early structure formation.

METHODS AND MATERIALS

At present, chemical modifiers are widely used in concrete technology, most of which are complex. The development of the theory and practice of high-strength concretes of the new generation entailed the development and implementation of complex organomineral additives, which include modern superplasticizers and finely ground mineral fillers [37, 38, 39]. High-strength concretes are multifunctional concretes that combine, along with high strength (100-150 MPa), other important properties - high frost resistance, water resistance, elastic-plastic properties, etc. [40, 41, 42]. Achieving such indicators is possible due to the use of SP and GP together with finely ground microfillers – stone flour (SF), including nanoparticles and dispersed reinforcement [1, 43, 44, 45].

One of the most important features of high-strength concrete is also the elimination of coarse aggregate and its replacement with quartz sand, which helps to reduce the effect of microhomogeneities in the structure [46, 47].

It is believed that in the matrix (cementing system) the most preferable material is cement with a high content of silicate phases, which perform the main structure-forming role [46].

The cement dosage in high-strength concrete is about 600–800 kg/m³ with a very low water content. Such a cement dosage is important for the formation of a matrix with improved rheological properties, increasing the hydration process. However, an increased amount of cement leads to many disadvantages, such as increased heat of hydration, high shrinkage, etc. An acceptable alternative for replacing cement are mineral additives such as calcite, silicon dioxide, fly ash, blast furnace slag, etc. [48].

Stone flour is used in concrete not instead of cement, but as an additive to cement in an amount of up to 100% of its mass. Being hydration inert in relation to water, stone flour obtained on the basis of strong and dense rocks is more susceptible to the liquefying effect of SP than cements and in cement-mineral mixtures, it helps to create a rheologically active matrix, which increases the efficiency of SP and allows to reduce the water demand of mixtures to a greater extent, in contrast to purely cement mixtures.

The objective of the research was to study and model possible mechanisms for the formation of the structure of cement materials filled with finely dispersed calcium carbonate in the presence of plasticizers, which were considered to be new-generation superplasticizers based on naphthalene sulfonic acid (brand C-3) and polycarboxylate (brand Melflux).

In this work, finely ground calcite $S_{sp} = 13000 \text{ cm}^2/\text{g}$ was used as a microfiller. Superplasticizer C-3 was introduced with mixing water in an amount of 0.5% of the cement mass. The mineral additive was used in an amount of 5 to 50% of the cement mass.

The main objectives in using organomineral additives in building mortars and concretes were the following: increasing the packing density of the system by filling the intergranular space with particles of a smaller fraction; forming a rheologically active finely dispersed matrix that ensures the free movement of larger particles at the appropriate levels, thereby providing the possibility of reducing the water demand of mixtures and increasing the efficiency of superplasticizers; increasing the hydration activity of filled cement systems by using finely ground rocks, the particles of which can provide the possibility of binding free lime into hydrosilicate structures or serve as crystallization centers for hydrated phases of cement stone due to epitaxial build-up (for example, silicon-containing rocks or calcite).

When using finely dispersed microfillers from the point of view of structure compaction, it is obviously necessary to take into account a certain amount of additives that can ensure not only compaction of the system, but also the convergence of particles in order to form intergrowth contacts. The authors of [49] showed that



there is an optimal size and amount of mineral particles that create the possibility of maximum compaction of the structure. The nature of particle packing can be considered using the following three methods: optimization curves of particle packing [48, 50, 51, 52]; analytical models of particle packing [52, 53, 54, 55, 56, 57]; numerical modeling [58].

Modeling of the processes of formation of the structure of the material should be considered from the standpoint of creating an optimal topology and predicting possible scenarios for changes in the microstructure, taking into account the influence of additive components on the composition and properties of hydration products.

Modeling in a heterogeneous cement system is quite complex due to its multicomponent composition, polydispersity and instability, especially at the early stages of hydration, since the constantly developing and changing process of crystallization of hydrated phases contributes to the constant transition of the system from one state to another. At present, the laws of structure formation of disordered systems have not been finally formed, therefore, structural topology with certain assumptions concerning the nature of particle size distribution and their homogeneity, taking into account the influence of additive components on the composition of hydration products, allows us to analyze the nature of changes in the properties of the structure, the possibility of formation and recrystallization of hydrates, which affect, in general, both the early structure formation and changes in the properties of the material over time.

Previous studies [59] have noted an increase in the strength of cement materials filled with finely dispersed carbonate-containing additives, and have analyzed possible mechanisms of calcite action. However, to initiate chemical interaction processes, it is necessary to create "constrained" conditions to ensure the convergence of particles and the formation of strong interparticle contacts in the system.

The possibility of epitaxial growth of hydrates on mineral particles, which contributes to an increase in the number of contacts, can be described by the Verhulst–Pearl equation [60, 61]:

$$N_{k} = \frac{N_{m} \times N_{o}}{N_{o} - (N_{o} - N_{m}) \times \exp(-K_{n} \times \tau)},$$
(1)

where N_0 is the number of contacts at the time $\tau = 0$; N_m is the limiting number of contacts in the solidifying system, corresponding to the complete depletion of contact nuclei at the crystallization centers; K_n is the rate constant of contact formation.

Analysis of the equation shows that an increase in the number of contacts can only be achieved by increasing the number of contact embryos.

Thus, bringing particles closer to distances less than 0.1 R_n (R_n is the particle radius) can promote the for-

mation of crystallization bridges both between cement particles and between cement and microfiller particles, provided that the parameters of the crystal lattices of the hydrated phases of cement and filler are close. In this regard, finely ground calcite is of greatest interest.

The optimal dispersion index of mineral microfiller should be 3–4 times higher than the dispersion of cement. Based on the ratio of the number of microfiller particles to the number of cement particles "C", taking into account the effect of the additive on the strength of cement materials, it is possible to determine the optimal amount of microfiller in the system.

Possible variants of development of microstructure of cement materials with additives of microfiller and superplasticizer are analyzed. In recent years, various nanoparticles (SiO₂, Al₂O₃, Fe₂O₃, boron nitrite, TiO₂) [62, 63, 64, 65], nanoclay [66], as well as crushed granulated slag [67], fly ash [14], finely ground calcium [48], microsilica [43], etc. have been used as fillers. A combination of nanosiliceous technologies with nanohydrosilicate technologies in concrete production is promising. Together, they determine, on the one hand, the reaction of Ca(OH)₂ with SiO₂, and on the other hand, the crystallization of hydrosilicates formed in the solution on the same substrates [17].

RESULTS AND DISCUSSION

When using mineral microfillers, the number of fine particles surrounding the cement particles is important, as it can have a screening effect on the hydration processes of the cement grain, therefore, at the first stage, the countable number of each particle was determined using the methods [68, 69, 70].

$$N_c = \frac{\pi d_c^3}{6} \times \rho_c m_c, \qquad (2)$$

$$N_m = \frac{\pi d_m^3}{6} \times \rho_m m_m, \tag{3}$$

where N_e , N_m are the number of cement particles and microfiller, respectively; m_e and m_m are the mass of cement and microfiller, respectively, in a mixed system, in fractions of a unit; ρ_e and ρ_m are the density of cement and microfiller; d_e , d_m are the diameters of cement and microfiller particles.

The ratio C will be equal to:

$$C = \frac{N_m}{N_c} = \frac{m_m \rho_m^2 S_m^3}{m_c \rho_c^2 S_c^3},$$
 (4)

where S_c , S_m are the values of the specific surface area of cement and microfiller.

Calculations have shown that the number of microfiller particles at dosages of 5, 11, 20, 30, 40 and 50% located around the cement particles in cement-sand mortar



1.2 is, respectively, 3, 6, 13, 19, 26 and 32. Studies of the strength indicators of filled cement-sand mortars with additives of carbonate microfiller have shown that the best strength values of the samples were obtained at dosages in the range of 10-20% of the cement mass (Table 1). The studies were carried out using Portland cement grade PC 400 D20, the water-cement ratio in all cases was taken to be equal to 0.45.

Based on the results of the study, it can be concluded that when the content of microfiller in the mixture is over 20%, the decrease in the strength of the samples is associated with the screening of the active zones of cement particles by calcite particles, which contributes to the slowing down of hydration and hardening.

When binders harden as a result of interaction with water, crystalline and gel-like products are formed, which participate with unhydrated grains in the formation of a three-dimensional framework of cement stone.

Hydration is incomplete when many free cement grains are formed in the structure. They play a vital role. Unhydrated cement grains participate in a higher-level granular packing because their size is between that of silica, quartz powder, or microcalcite in powder-activated concrete.

Such new formations as calcium hydroalumoferrites of variable composition $C_4A_xP_{1-x}H_{13}$ and $C_3(A_xF_{1-x})H_6$, hydrosulfoaluminoferrites of mono- and trisulfate form $C_3A(CS)H_{12}$ and $C_3A(CS)_3H_{12}$, which have a clearly expressed crystalline nature, in the first minutes and hours after mixing the cement with water, form a primary crystalline framework, within which, still very rarefied, all other products of binder hydration crystallize [21, 29, 71].

Crystal hydrates, formed simultaneously or sequentially (depending on the activity of the original mineral), fill the free space in the cement stone and bind to the existing framework by fusion of various conglomerates with each other, and the gel-like hydration products compact it [21, 29].

Hardening structures, depending on the nature of the connection between new formations, can be divided into coagulation, crystallization-condensation, crystallization [21]. Coagulation structures arise in the initial period of interaction of cements with water as a result of adhesion through thin layers of liquid of dispersed particles forming a disordered spatial network. These structures are of low strength, thixotropic. Condensation structures are formed due to a decrease in liquid layers between particles, which is accompanied by their hardening. Crystallization structures are characterized by recrystallization, or the emergence of new phases, the fusion of microcrystals. The formation of a crystallization structure is the basis for creating the strength of the hardening system. Hardening of the structure is explained by the development of crystallization contacts, while a necessary condition is the overgrowth of contacts with a sufficiently thick layer of new formations. The overgrowth of crystals leads to an increase in strength and, at the same time, to the development of internal stresses caused by the growth of crystalline contacts. Therefore, the final strength of the structure will depend on the contribution of each of these factors.

Let us analyze the possible model development of the processes of early structure formation of cement stone with organomineral additives (using the example of superplasticizer (SP) and microfiller (calcite)).

1. Early period (2-5 hours) (Fig. 1)

On the polymineral surface of cement particles a pseudocrystalline layer of AFm-phase hydrates is

Table 1

The influence of mineral and organominer	al additives on the strength of cement stone
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Compound	Amount of additive,	Compressive strength MPa			
Compound	% of cement mass	60 days	1,5 years		
PC400 D20 W/C = 0.45	_	36.0	41.2		
With added calcite	5	38.5	55.8		
With added calcite	10	39.7	49.0		
With the addition of calcite and Superplasticizer C-3	10 0.5	26.9	42.8		
PC400 D20 With added calcite W/C=0.45	20	33.6	40.5		
With the addition of calcite and Superplasticizer C-3	20 0.5	21.5	28.7		
With added calcite	30	24.5	30.5		



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Fig. 1. Early period of structure formation

formed and as a result of the reaction of alluminate phases with $CaSO_4$ fibrous crystals of the AFt-phase are formed. The maximum amount of AFt-phase hydrates is formed in the period up to 24 hours (75% – 3 hours, 84% – 24 hours) [28]. Hydration of silicate phases in the presence of SP is slowed down due to a decrease in the rate of hydration and hydrolysis of silicate phases of cement.

In studies carried out earlier, conducted using several modern SPs, it was shown that, according to X-ray phase analysis, all superplasticizers slow down the hydration of silicate phases of cement [69]. It was found that in the presence of all SPs, the intensity of reflections of lime is lower than in the composition without the additive, and the intensity of reflections of anhydrous silicate phases of cement in samples with all SPs is higher than in the control composition (Figures 2–5, Tables 2, 3).

In previous studies [73, 74], X-ray diffraction patterns of 18-year-old cement stone with the addition of superplasticizer C-3 were analyzed, which showed the formation of a large number and different composition of fine-crystalline hydrosilicate phases with a similar but distorted structure, as indirectly indicated by the shapes of their peaks. The presence of a fine-crystalline multiphase structure of calcium hydrosilicates in cement systems is the reason for the increased strength of stone materials.

It is also necessary to note the process of stabilization of AFm-phase hydrates at the initial stage of formation of the microstructure of cement materials with organic additives, which is characterized by an increase in the plastic and early strength of the system (Fig. 6).

It is characteristic that the formation of crystalline hydrates of the AFm- and AFt-phases occurs in the presence of gel-like C-S-H phases, which helps to reduce internal stresses in the system that arise as a result of the formation of crystalline phases.

The stabilization of ettringite and AFm phases in the presence of SP, noted in our studies [74], can have a negative effect on the structure of cement stone due to the possibility of its recrystallization into the monosulfate form, especially in a period of 28 days or more.



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Fig. 2. X-ray diffraction pattern of cement stone hydrated without additives for 180 days



Fig. 3. X-ray diffraction pattern of cement stone hydrated with Melflux 4930 additive for 180 days









Fig. 5. X-ray diffraction pattern of hydrated cement stone with Melflux 1641 additive for 180 days

Table 2
Intensity of lime reflections on X-ray diffraction patterns of cement stone with superplasticizer additives

Compound	Intensity Imax at d [Å]							
Compound	4.93	3.11	2.63	1.93	1.79	1.69	1.485	1.45
No. 1 (control)	87.3	23.7	110.5	38.6	24.8	23.4	нет	10.8
No. 2 (0.5% Melflux 4930F)	55.2	49.9	85.6	19.0	21.6	11.9	19.2	нет
No. 3 (0.5% Melflux 5581F)	65.4	нет	55.3	25.3	24.0	15.2	13.6	нет
No. 4 (0.5% Melflux 1641F)	58.2	20.4	73.6	15.9	24.4	18.3	12.5	13.6

Table 3

Intensity of C_3S and β - C_2S reflections in X-ray diffraction patterns of cement stone with superplasticizer additives

Compound	Intensity Imax			
	Alit (d = 2.7761Å)	Alit (d = 2.744Å)		
No. 1 (control)	27.7	16.3		
No. 2 (0.5% Melflux 4930F)	40.7	54.7		
No. 3 (0.5% Melflux 5581F)	47.6	51.8		
No. 4 (0.5% Melflux 1641F)	38.8	58.5		

According to [28], during the recrystallization of ettringite into the monosulfate form according to scheme (1):

$$C_3AC\overline{S}_3H_{31} \rightarrow C_3AC\overline{S}H_{12} + 2C\overline{S}H_2 + 15H_2O$$
 (5)

is accompanied by a decrease in the amount of bound water from 45.2 to 24.2%, and the porosity increases to 54.5% with an increase in the total specific volume of the system by 17% compared to the initial specific volume of ettringite. As noted above, recrystallization of AFm-phase hydrates (C_2AH_8 , CAH₁₀, C_4AH_{13-19}) can also lead to a decompaction of the structure associated with the formation

of hydrates containing a smaller amount of chemically bound water and having a higher specific mass (C_3AH_6) compared to the mass of AFm-phase hydrates. Thermodynamic analysis of possible recrystallization schemes was performed in our early studies [26].

2. Average period (5-24 hours)

In the period of up to 24 hours, up to 30% of the cement enters into the reaction. During this period, a gellike layer of C-S-H phases is formed on the cement grains, which absorbs the AFm-phase plates and AFt-phase fi-





Fig. 6. Change in plastic strength of cement-sand mortar with the addition of calcite [26] C/S = 1:2, W/C = 0.5. Ulyanovsk PC 400 D20: 1 – without additive; 2 – with addition of carbonate microfiller 5%; 3 – same, 10%; 4 – same, 20%

bers, the intergranular space is gradually filled with a hydrate mass of complex composition. The formation of AFm- and AFt-phases promotes the reinforcement of the C-S-H layer and the gradual fusion of hydrate shells (Fig. 7).

For coalescence, intergranular contact is necessary, therefore in cement systems filled with hydration-active finely dispersed microfillers, the process will proceed faster. Due to the through-solution mechanism of hydration, the formation of contact bridges can occur when the particles are at a distance of up to 0.1 Rp (Rp is the radius of the particle) (Fig. 8).

As a result of the fusion of hydrate shells of particles, zones of increased density of hydrate phases are formed; the interconnected shells determine the early strength of the structure, which also depends on the distribution of particle sizes (Fig. 9).

The effect of the calcium hydrosilicate additive [17] is noticeable between 6-10 hours after the mixture preparation. After 6 hours, the strength exceeds the control value by 32 times, after 8 hours – by 10.6 times, and after 10 hours – by 4.3 times. After 24 hours of hardening and subsequently, the strength indicators gradually equalize. It is important that after 9–10 hours, it is possible to strip the forms and ensure the hardening of the products at a temperature of about 20 °C without heat-curing treatment. With a content of 3.5% C–S–H additive, the concrete strength of 15 MPa was achieved after 8 hours.

3. Late period

The hydration shells in the accretion zones are compacted and the permeability of the films formed on the cement particles is reduced. Hydration products are formed not only on the cement grains, but also on the microfiller particles. By 7–10 days, the gaps between the particles practically disappear and are filled with hydrate products. AFm-phases can be located both inside and outside the shells. Crystals of the AFt phase (up to 10 μ m) are usually located on the surface of the shells or in the voids of the structure. The subsequent hydration process slows down and proceeds with the formation of dense intertwined hydrosilicate-hydroaluminate phases of complex composition (Fig. 10).

In the period of 60-90 days, large layered crystals of Ca(OH)₂ of irregular shape (Figure 11) and hydrated phases of C–S–H phases in the form of foil and sheet-like structures are observed in the samples with the addition of SP. A dense, well-crystallized structure is formed. According to X-ray diffraction data [26, 75], the following hydrated phases are present in the cement stone with the addition of SP and calcite at the age of 60 days of nor-



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Fig. 7. Average period of structure formation



Fig. 8. Needle-shaped ettringite crystals in the structure of cement stone (\times 3000). SEM

mal hardening: C–S–H, Ca(OH)₂, ettringite (and its iron-containing analogue), calcium monohydrosulfoaluminate, CAH₁₀. A limited amount of C₃AH₆ indicates stabilization of AFm-phase hydrates and a slowdown in their recrystallization into C₃AH₆.



Fig. 9. Particles of hydrated cement stone ($\times 7000$). SEM

The processes of crystallization, stabilization and subsequent recrystallization of hydroaluminate phases are quite complex and depend on many factors. In our studies [74], it was found that stable reflections of the ettringite phase were detected on X-ray diffraction



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Fig. 10. Late period of structure formation



Fig. 11. Ca(OH)₂ crystals in the structure of hydrated cement stone (×1500). SEM

patterns of cement stone hydrated with the addition of superplasticizer C-3 and hardened under normal conditions for 18 years. With regard to hydrosilicate phases, it is noted that the intensities of reflections in samples with the addition of C-3 are somewhat lower than in samples without the additive. The peak shapes of these reflections, which have a stepped, asymmetrical shape, indirectly indicate the possibility of forming a wide range of fine-crystalline hydrosilicate phases in the presence of C-3, which have a similar but distorted structure.

Our studies, carried out using individual carbonatecontaining rocks (ground dolomite and limestone flour) and their mixture, showed that the use of a binary mixture in high-strength concrete, compared to individual ones, allows for a significant increase in the strength of concrete. For example, the strength of a composition with the addition of ground dolomite at the age of 1 day is 40.8 MPa, and that of a composition made from a mixture of dolomite and limestone flour is 74.4 MPa, i.e. almost 2 times. In subsequent periods, the increase in strength is 15–20%. The studies carried out in work [76] also showed that the use of a binary mixture of microfillers was significantly more effective compared to individual ones. At the age of 28 days, the strength of concrete on a mixture of microfillers was 115 MPa.

CONCLUSION

A promising direction of research is the analysis of the possibility of using binary and more complex and multicomponent mixtures of microfillers in cement systems, differing in chemical and mineralogical composition and the state of the surface of the particles. In this case, it is possible to level the different nature of the influence of SP and GP on the liquefaction of mineral powders and the possibility of crystallization of hydrated phases on the substrate of microfiller particles.

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The authors declare no conflicts of interests.

The article was submitted 02.11.2024; approved after reviewing 04.12.2024; accepted for publication 09.12.2024.