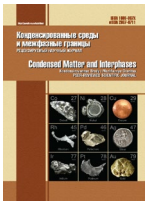

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Investigation of the effect of a multicomponent additive on the structure formation and hardening of cement composites

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Abstract

The development and application of multicomponent multifunctional additives for cement composites is an important research area since the use of such additives allows controlling both the rheological properties of the freshly prepared mixture and the physical and mechanical characteristics of the finished composite.

This work proposes to use a multicomponent multifunctional additive with the composition of "SiO_2 nanoparticle - superplasticiser - polypropylene fibre" for the modification of cement composite materials based on sand and chalky flour. We studied the peculiarities of the influence of this additive on the technological characteristics of mixtures (plasticity and form stability) and the processes of setting-up, hydration, structure formation, and strength gain of the composite materials.

It was shown that the introduction of this additive allows increasing the plasticity limit and structural strength and reducing relative plastic deformations of the cement mixture at the manufacturing stage. At the same time, this additive accelerates the processes of setting-up, hydration, and strength gain of cement composites. It was proved that the increase in strength is due to the formation of a dense structure of hydrated new growths of the cement substance formed by phases of low and highly basic calcium silicate hydrates of various compositions and morphologies, as well as the absence of a portlandite phase.

The optimal ratio of indicators of plasticity and form stability of cement mixtures and the strength of composites based on them obtained by using the studied additive allows us to recommend to use this additive in the innovative construction 3D printing technology.

Keywords: Cement hardening systems, Modification, Structure formation, Multifunctional additives, Rheological characteristics, Compressive strength

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1. Introduction

The emergence and development of new construction technologies, such as the construction of unique high-rise buildings and structures and construction 3D printing, requires improving existing and creating new cement-based composite materials with a set of specific properties. Therefore, during the initial stage, the freshly prepared mixture should have specified fabricability indicators. In particular, for the innovative 3D printing process, of fundamental importance are such fabricability indicators as plasticity, form stability, and accelerated setting-up times which are required to create a structure using off-form additive manufacturing. What is more, resulting composite material must have high physical and mechanical properties (density, compressive strength, bending strength, frost resistance, etc.) to ensure the standard service life of the constructed building or structure.

To create such composite materials, it is necessary to control the formation of their structure in a targeted manner at each scale (micro, ultramicro, and nano) [1], and, accordingly, at each stage of the evolutionary route of the solid phase formation in the cement hardening system: phase nucleation, growth of particles, their agglomeration and spontaneous structure formation [2]. A variety of existing formulation and technological factors (chemical and mineralogical composition of the initial components, the ratio of the mass of water to the mass of cement, mechanical and chemical activation of the binder, mixing conditions and modes, and the use of chemical additives, in particular, nanoadditives) allows controlling the formation of the structure of the cement hardening system at different scales (from nano to micro) [3].

The simplest and most accessible factor for controlling the structure of a cement composite is the use of chemical additives of various nature (inorganic and organic), morphology, and dispersion. Most often, active mineral additives are used as inorganic additives, for example, microsilica, microalumina, and metakaolin [4], as well as chemically synthesised products, for example, calcium nitrate, nitrite, and chloride, sodium silicate, ammonium chloride [5], etc. Various surface-active substances, in particular super- and hyperplasticisers, are typical representatives of organic additives [5, 6]. In addition, to improve the physical and mechanical properties of cement composites, disperse reinforcing components such as polypropylene, glass, basalt, or steel fibres are being used more often [7–9].

The above mentioned individual additives are involved in the structural formation of cement hardening systems at various scales and therefore have a selective effect on the properties of the cement composite. In this regard, it is relevant to study the use of multicomponent multifunctional additives which include inorganic, organic, and micro-reinforcing components in their composition, which will determine the multifunctionality and additivity of their action when obtaining the resulting composite.

To ensure the maximum efficiency of a multicomponent additive, it is necessary to select an inorganic component in accordance with the conditions of molecular, morphological, and topological selection [10]. This means that the crystal-chemical structure of the component particles should be close to those of the cement clinker minerals, which will allow them to form the optimal crystal structure of the material (denser, with fewer pores and voids). For cement hardening systems, amorphous silicon dioxide-based additives will meet these conditions. This is confirmed both by the literature data [11–15] and the results of our own studies [16, 17]. At the same time, the dispersion of SiO_2 particles, which are a part of multicomponent additives, can be different (micro-, ultra-, and nano-). It should be noted that nanosized SiO_2 particles influence the formation of the structure of cement hardening systems during the nucleation stage of the solid phase particles (nanoscale). It is advisable to use a superplasticiser as an organic component of the additive, which will prevent the growth and agglomeration of SiO_2 particles and will solve the complex technological problem of their uniform distribution in the volume of the cement system [16]. Thus, the action of the superplasticiser will manifest itself at the ultrascale level of the formation of the composite structure. Various types of fibres can be used as a micro-reinforcing component, which will contribute to the additional strengthening of the cement composite at the microscale level by preventing

the propagation of cracks formed in the process of the spontaneous structure formation.

In this paper, we propose to use a multicomponent multifunctional additive of the following composition: "nanosized SiO_2 particles – superplasticiser – polypropylene fibre" for the modification of cement composites. Previously, in our own studies [16], we found that the addition of the composition "nanosized SiO_2 particles – superplasticiser" has a positive effect on the processes of hydration, structure formation, and strength gain of cement systems without fillers and aggregates.

Thus, the purpose of this work was to study the effect of a multicomponent multifunctional additive of the composition "nanosized SiO_2 particles – superplasticiser – polypropylene fibre" on the rheological characteristics and the processes of setting-up, hydration, structure formation, and strength gain of cement composite materials based on quartz sand and chalky flour.

2. Experimental

For experimental studies, modified cement systems were obtained. Their initial components were Portland cement (C), grade CEM I 42.5 (GOST 31108-2016), process water (W) (GOST 23732-2011), superplasticiser (SP) based on polycarboxylate esters, grade Sika® ViscoCreat® T100. Chalky flour (CF) containing at least 95% of $CaCO_3$ (GOST 32761-2014) was used as a filler. The particle size of chalky flour was between 2 and 55 μm. Quartz sand (S) with a fineness modulus $M_f \leqslant 1.25$ (GOST 8736-2014) was used as an aggregate.

As a modifier, we used a complex nanosized additive (CNA) with the composition of SiO_2 particle – SP, Sika® ViscoCreat® T100 ($\omega(SiO_2)$ = 0.01%, ω(SP) = 0.2% of the mass of cement) with an average particle size of SiO_2 between 5 and 10 nm obtained by sol-gel synthesis using the procedure described in detail in [10]. It should be noted that this modifier was a mixing liquid. A 12 mm long polypropylene fibre (PF), brand SikaFiber® PPM-12 (ISO 9001:2008, EN 14889-2:2008), was used as a reinforcing component. Its content was 0.5% of the mass of cement. To obtain a multicomponent multifunctional additive, the required amount of superplasticiser was added to the mixing liquid and thoroughly mixed. Next, a polypropylene fibre was added to the resulting solution and mixed again.

Cement systems with the composition C–W–SP–CNA–S, C–W–SP–CNA–S–PF, C–W–SP–CNA–CF, and C–W–SP–CNA–CF–PF were obtained by mixing dry components (cement, sand or cement and chalky flour) and the resulting multi-component multifunctional additive in a mixer for 3 minutes. When obtaining viscoplastic mixtures, the mass ratios of C:CF and C:S were 1:1 and 1:1.25, respectively. The water-cement ratio (the ratio of the mass of water to the mass of cement – formulation and technological parameter, W/C) in systems with sand was 0.26, and in systems with chalky flour was 0.37. These ratios are optimal and were determined experimentally from preliminary studies. The C–W–SP–CNA system (W/C = 0.24) was recognised as a reference system.

The rheological behaviour of the obtained viscoplastic mixtures was evaluated by the methods of compressive rheometry [18–20]. To conduct compression tests, we used cement-water paste to make cylinder samples with the radius R equal to their height h_0 = 25 mm. The tests were carried out using the INSTRON 5982 universal floor hydraulic testing system.

To assess the plasticity of mixtures, the compression test was performed at a constant strain rate of 5 mm/s [18]. The curves "load N – displacement Δ" obtained as a result of testing were interpreted as dependencies of the reduced load F^* on the relative change in sample height h_i/R:

$$F_i^* = \frac{Ph_i}{\pi R^2},$$

where $h_i = (h_0 - \Delta)$, h_0 is the initial height of the sample, Δ is the displacement at the i-th moment of time, the value R was taken as a constant equal to the sample radius at the beginning of the test.

At the first points of inflexion of the obtained experimental curves, the estimate of the plastic yield value K_i(I) was calculated:

$$K_i(\frac{h}{R}) = \frac{\sqrt{3}}{2} F^*.$$

To assess the form stability, a compression test was performed at a constant load rate of

ν = 0.5 N/s [19, 20]. As a result of experimental studies, we obtained the following curves "relative displacement Δ – time *t*", "load *N* – relative displacement Δ", which were used to calculate the values of the structural strength of cement systems at the moments corresponding to the beginning of deformation and the beginning of cracking of the samples according to the formula:

$$\sigma = \frac{P}{\pi R^2}.$$

As a result, the plasticity and form stability of mixtures under conditions simulating the action of compressive stresses during extrusion and layering were evaluated by the following criteria:

– Estimation of plastic yield value K_i (I).

– Structural strength σ_0 at the beginning of deformation, which is responsible for the ability of the system to resist deformation under load.

– Plastic strength σ_{pl} and the value of relative plastic deformations Δ_{pl} at the beginning of cracking. They characterise the ability of the system to deform without destruction.

It should be noted that the optimal values of the plasticity and form stability criteria for viscoplastic cement mixtures were determined in [20] and were: K_i(I) = 1.0–2.5 kPa, σ_0 = 3–5 kPa, σ_{pl} = 30–40 kPa, Δ ⩽ 0.05 mm/mm.

The kinetics of setting-up of the resulting viscoplastic systems was studied by the penetrometer method [21]. Value P_{pl} was calculated as the reduced value of penetration resistance:

$$P_{pl} = \frac{4N}{\pi d^2},$$

where *N* is penetration resistance of the mixture when a plunger with a standard diameter is immersed to a depth of 5 mm, kN; *d* is the plunger diameter, m^2. The method error was 10%.

The phase composition of the cement brick was determined by powder diffraction (ARL X'TRA diffractometer, CuK_α is radiation, λ = 1.541788 Å). The obtained data were processed using the PDWin 4.0 software package [22]. The value of the degree of hydration of the modified cement hardening systems was calculated by the content of the alite phase 3CaO SiO_2 (C_3S) by comparing their XRD patterns with the XRD pattern of the original cement clinker [23]:

$$D_h(C_3S) = (1 - \frac{I_{mod}}{I_0}) \times 100\%.$$

where I_{mod} is the intensity of the diffraction maximum at *d* = 2.75 Å of the C_3S phase of the samples of different compositions by types of additives and the timing of cement hydration; I_0 is the intensity of the diffraction maximum at *d* = 2.75 Å of the C_3S phase of the original cement.

The microstructure of the cement brick was assessed using scanning electron microscopy (SEM) (JEOL JSM-7001F scanning electron microscope).

The kinetics of the strength gain of the studied cement hardening systems was determined by the destruction of sample cubes with the size of 5×5×5 cm using an INSTRON Sates 1500HDS testing machine. To ensure the statistically reliable results of physical and mechanical tests, the number of samples in the series was 6. The measurement uncertainty was 0.5%.

3. Results and Discussion

3.1. Plasticity and form stability of modified systems

Figure 1 shows the curves of the dependence of the reduced load *F** on the relative change in sample height h_i/R.

The studied cement systems were characterised by two types of curves. The C–W–SP–CNA–P, C–W–SP–CNA–S–PF, and C–W–SP–CNA–CF systems had a horizontal section between two points of inflexion, which is characteristic of viscoplastic fluid before the destruction of the structure. The curves of the C–W–SP–CNA–P and C–W–SP–CNA–CF–PF systems were almost horizontal and did not have a pronounced plasticity region. In this case, the value of the plastic yield value $K_i(I)$ (Table 1) for the system with quartz sand, compared to the reference system, increased by 2.3 times, while in the system with carbonate flour it decreased by 1.6 times. In microreinforced cement systems, the plasticity limit values increased by 2.6 times in the C–W–SP–CNA–S–PF system, and by 1.1 times in the C–W–SP–CNA–CF–PF system.

As a result of the experimental investigation of form stability of the studied systems two types of curves were obtained: "relative displacement Δ – time *t*" (Fig. 2a) and "relative displacement –

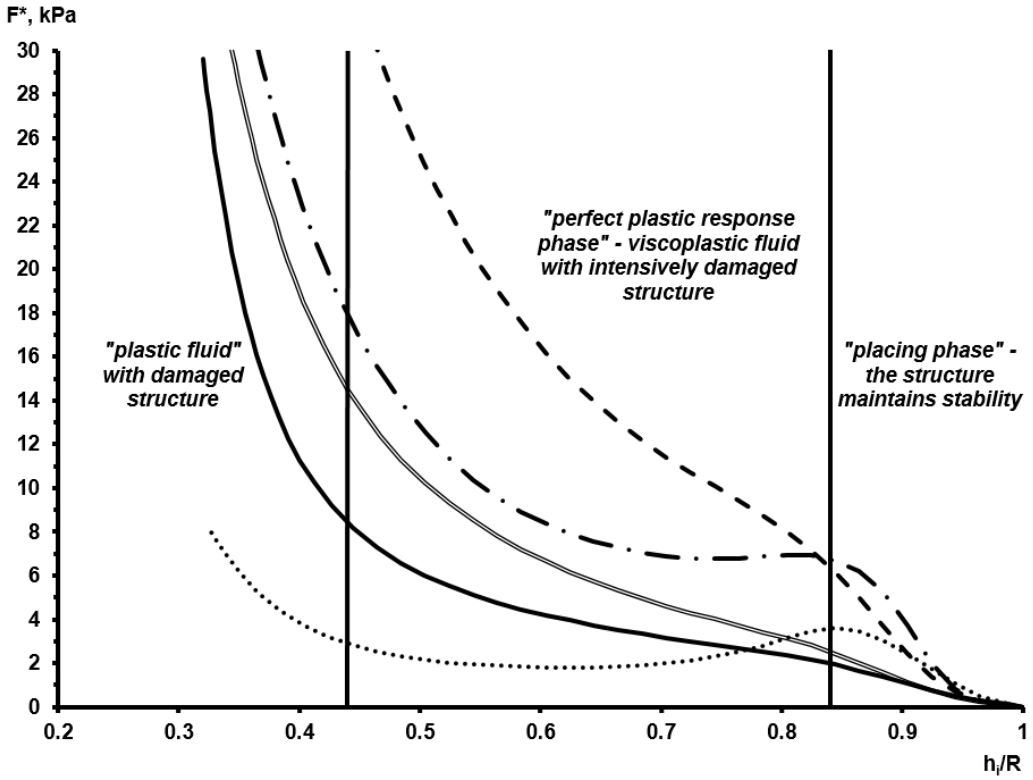


Fig. 1. Curves of the dependence of the reduced load F^* on the relative change in sample height h_i/R. Designated: ━ – C–W–SP–CNA; •••• - C–W–SP–CNA–S; – – – – C–W–SP–CNA–S–PF; –•–•– – C–W–SP–CNA–CF; ═ – C–W–SP–CNA–CF–PF

Table 1. Rheological characteristics of modified cement systems

System	Plastic yield value $K_i(I)$, kPa	Structural strength σ_0, kPa	Plastic strength σ_{pl}, kPa	Relative plastic deformation Δ_{pl}, mm/mm
C–W–SP–CNA	1.42	1.64	41.20	0.13
C–W–SP–CNA–S	3.28	1.17	57.80	0.07
C–W–SP–CNA–S–PF	3.66	5.44	26.75	0.03
C–W–SP–CNA–CF	0.90	1.43	42.48	0.14
C–W–SP–CNA–CF–PF	1.54	3.04	40.75	0.07

load σ" (Fig. 2b). The first type of curves was characterised by three sections: the "phase stability", which characterised the absence of deformations under loads; "plastic phase", which characterised the ability of the system to deform without destruction, and "cracking phase", in which cracking occurred before the complete destruction of the structure. On the "relative displacement – load σ" curves, the moment when microcracks appeared in the systems corresponded to a sharp drop in the load.

The analysis of the obtained results allowed establishing that the studied systems had form stability indicators (σ_0, σ_{pl}, Δ_{pl} Table 1) close to optimal [20].

At the same time, the C–W–SP–CNA–CF–PF and C–W–SP–CNA–S–PF systems had the highest structural strength. In these systems, the values of σ_0 increased by 2.1 and 4.6 times, respectively, compared to the same systems without fibre. It should be noted that the values of maximum structural strength and minimum plastic deformations were achieved in the C–W–SP–CNA–S–PF system and were 5.44 kPa and 0.03 mm/mm, respectively.

The effect of CNA on the rheological behaviour of the studied systems was that nanosized SiO_2

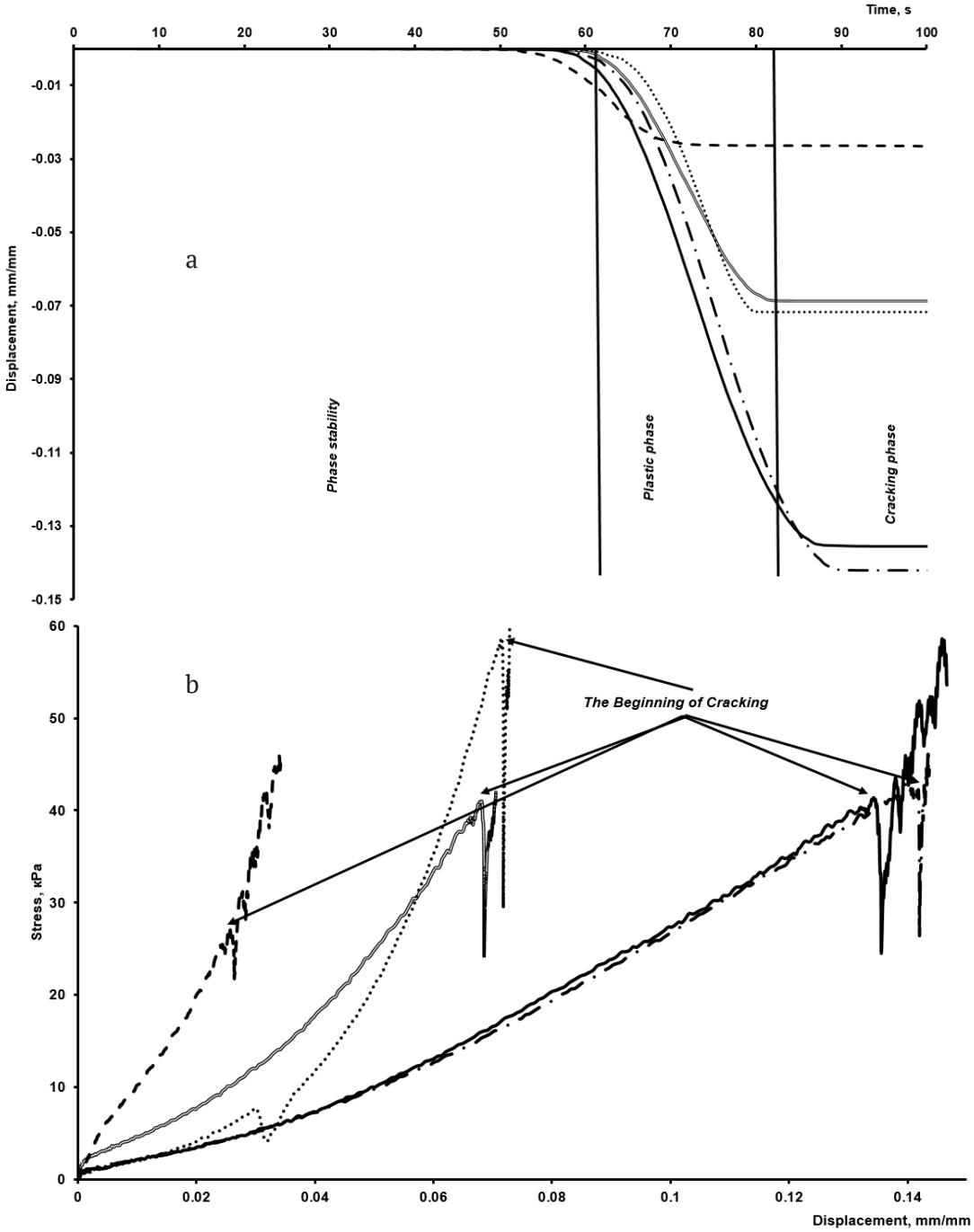


Fig. 2. Dependence curves a) "relative displacement Δ – time *t*"; b) "load σ – relative displacement Δ". Designated: ▬ – C–W–SP–CNA; •••• – C–W–SP–CNA–S; ▬ ▬ – C–W–SP–CNA–S–PF; ▬•▬•▬ – C–W–SP–CNA–CF; ═ – C–W–SP–CNA–CF–PF

particles contributed to the intensification of the processes of dissolution and hydration of clinker minerals, which could result in the increase of the ionic strength of the disperse medium, which would lead to its destruction and a partial decrease in the structural strength of the cement system. At the same time, the superplasticiser which was part of the CNA, due to mono- and polymolecular adsorption on the surface of cement clinker particles reduced their interfacial energy, which resulted in their dispersion. In this case, part of the immobilised water was released, which provided for an increase in the plasticity of the mixture and, accordingly, a slight decrease in

structural strength. Obviously, the polypropylene fibre provided cement systems with additional rigidity, which led to a decrease in their plasticity, an increase in structural strength, and a decrease in relative plastic deformations.

It should be noted that the rheological characteristics of the studied cement systems were affected not only by the used CNA but also by the type and dispersion of the components used as aggregates and fillers. Quartz sand and chalky flour used in the work are substances of a polyfraction composition which differ in their crystal-chemical nature and dispersion. Due to the relatively large size of its particles, quartz sand located between the grains of cement clinker created a denser spatial packing of solid phase particles, which led to an increase in the rigidity of the cement system. Chalky flour helped to reduce the plastic yield value and, accordingly, the aggregative stability of cement systems. This was due to the fact that, firstly, its particles have a smaller size compared to sand. Secondly, these particles have a sufficiently active surface and are capable of forming polymolecular layers of adsorbed water, which leads to an increase in the plasticity of the cement system.

Thus, in terms of plasticity and form stability, the nanomodified cement system with chalky flour was quite plastic and prone to flow, whereas the nanomodified cement system with quartz sand was more rigid. It should be noted that the introduction of a polypropylene fibre allowed increasing the plastic yield value ($K_i(I)$) by 1.1 and 2.6 times and structural strength (σ_0) by 2.1 and 4.6 times and reducing relative plastic deformations (Δ_{pl}) by 2 and 2.3 times in the systems with quartz sand and chalky flour, respectively. The acceptable values of the plasticity and form stability criteria (K_i(I) = 1.54 kPa, σ_0 = 3.04 kPa, and Δ_{pl} = 0.07 mm/mm) were achieved in the C–W–SP–CNA–CF–PF system.

3.2. Kinetics of early structure formation of modified cement hardening systems

According to the obtained results (Fig. 3), the beginning of the setting-up process of the studied cement hardening systems varied between 105 and 210 minutes.

The process of setting-up proceeded most rapidly in the C–W–SP–CNA–CF–PF and C–W–SP–CNA–S–PF systems. Values of plastic strength of 582–585 kPa corresponding to the beginning of setting-up were achieved in these systems

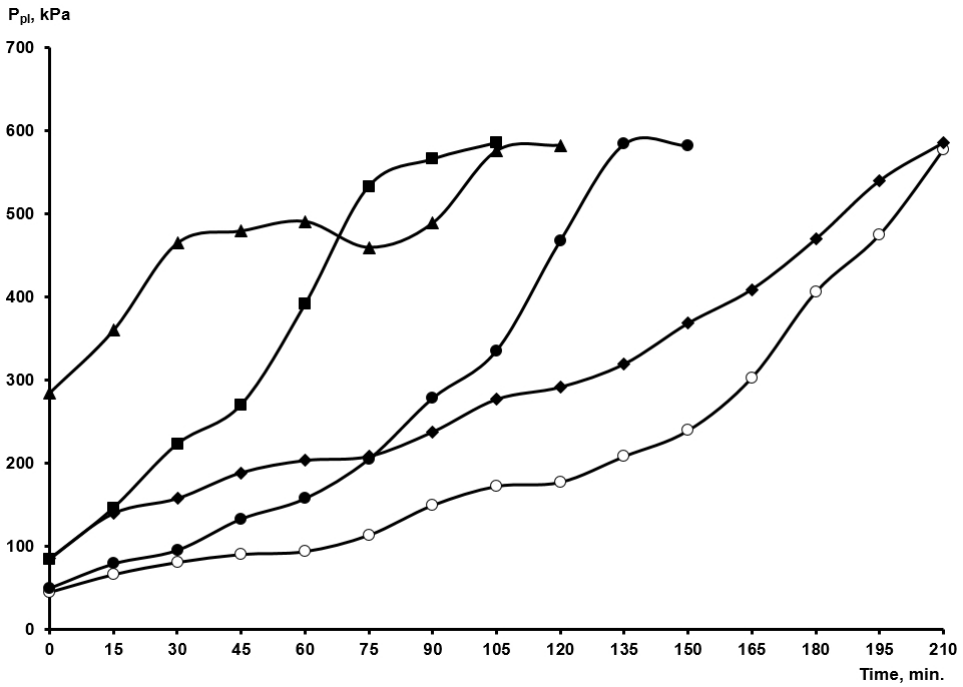


Fig. 3. Curves of the dependence of plastic strength of the studied cement hardening systems on time. Designated: ○ – C–W–SP–CNA; ♦ – C–W–SP–CNA–S; ▲ – C–W–SP–CNA–S–PF; ● – C–W–SP–CNA–CF; ■ – C–W–SP–CNA–CF–PF

within 105 and 120 minutes, respectively. In the C–W–SP–CNA–CF system, similar values of P_{pl} were achieved after 150 minutes, and in the C-W-SP-CNA and C-W-SP-CNA-S systems, they were reached after 210 minutes.

The influence of CNA on the setting-up processes of cement systems was determined by the combined action of its constituent components. For example, the superplasticiser helped to increase the plasticity of cement systems. The mechanism of action was discussed above. At the same time, nanosized SiO_2 particles, due to their high values of surface energy, also acted as ready-made crystallisation centres and chemically could be directly involved in heterogeneous processes of phase formation of hydrated compounds. At the same time, in combination with the effect of the polypropylene fibre, this led to an increase in the values of plastic strength and acceleration of setting-up processes.

It should be noted that the setting-up processes proceeded most rapidly in the nanomodified system with chalky flour, whereas the system based on quartz sand had lower values of plastic strength regardless of the presence of the polypropylene fibre in the system. This was probably due to the fact that the finer grain size of chalky flour allowed obtaining the maximum possible packing density of the particles of the dispersed phase under the given conditions, which, in combination with the CNA effect, contributed to the acceleration of the setting-up process of the cement hardening system.

3.3. Phase composition and microstructure of the studied systems

According to X-ray diffraction analysis (Table 2), after 28 days of hardening, the studied systems were characterised by rather high values of hydration degrees *(D_h),* from 88 to 93%. The highest value of D_h (93%) was achieved in the C-W-SP-CNA reference system.

In cement systems with quartz sand, the dominant phase was quartz (SiO_2), and in systems with chalky flour, it was calcium carbonate ($CaCO_3$) (Fig. 4, Table 2). The main hydrate phases in the reference and quartz sand systems were low and highly basic calcium silicate hydrates

Table 2. Phase composition and degree of hydration of the studied cement systems (duration of hardening 28 days)

System	D_h, %	Phase composition
C–W–SP–CNA	93	$(CaO)_x \cdot SiO_2 \cdot zH_2O$ $xCaO \cdot SiO_2 \cdot zH_2O$ $CaO \cdot SiO_2 \cdot H_2O$ $2CaO \cdot SiO_2 \cdot H_2O$
C–W–SP–CNA–S	89	SiO_2 $CaO \cdot SiO_2 \cdot H_2O$ $2CaO \cdot SiO_2 \cdot H_2O$ $(CaO)_x \cdot SiO_2 \cdot zH_2O$ $xCaO \cdot SiO_2 \cdot zH_2O$
C–W–SP–CNA–S–PF	90	SiO_2 $CaO \cdot SiO_2 \cdot H_2O$ $2CaO \cdot SiO_2 \cdot H_2O$ $(CaO)_x \cdot SiO_2 \cdot zH_2O$ $xCaO \cdot SiO_2 \cdot zH_2O$
C–W–SP–CNA–CF	88	$CaCO_3$ $3CaO \cdot SiO_2 \cdot H_2O$ $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$ $CaO \cdot SiO_2 \cdot H_2O$
C–W–SP–CNA–CF–PF	88	$CaCO_3$ $3CaO \cdot SiO_2 \cdot H_2O$ $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$ $CaO \cdot SiO_2 \cdot H_2O$

$(CaO)_x \cdot SiO_2 \cdot zH_2O$, $xCaO \cdot SiO_2 \cdot zH_2O$, $CaO \cdot SiO_2 \cdot H_2O$, and $2CaO \cdot SiO_2 \cdot H_2O$.

The phase composition of cement systems with chalky flour was represented by low and highly basic calcium silicate hydroxides ($3CaO \cdot SiO_2 \cdot H_2O$ and $CaO \cdot SiO_2 \cdot H_2O$, respectively), as well as a small amount of the calcium hydrocarboaluminate phase $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$.

Therefore, the type of aggregate and filler did not affect the degree of hydration of the studied systems, however, they had a significant effect on the phase composition of hydration products. Due to its inertness, quartz sand did not take part in the reactions of hydration and the formation of new growths of the cement brick, whereas chalky flour, due to the relatively active surface of its particles, was able to partially participate in heterogeneous processes of phase formation resulting in the formation of the $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$ compound. It should be noted that calcium carbonate is able to interact with the aluminate component of Portland cement clinker provided that there is an excess of calcium ions.

It should be noted that the portlandite phase ($Ca(OH)_2$) was absent in all of the studied systems. This was probably due to the fact that nanosized SiO_2 particles are capable of exhibiting a pozzolanic effect: due to their size and high surface energy, they are able to bind free calcium hydroxide into low and highly basic calcium silicate hydrates. In this case, free $Ca(OH)_2$ can be formed in the studied systems in two cases: as a result of the alite hydration reaction (both in systems with quartz sand and in systems with chalky flour) and as a result of the formation of calcium hydrocarboaluminate (in systems with chalky flour). Then, the following chemical transformations take place:

1) dissolution and hydration of alite and tricalcium aluminate:

$$Ca_3SiO_5 + 3H_2O \rightarrow 3Ca^{2+} + 4OH^- + H_2SiO_4^{2-}$$

$$Ca_3Al_2O_6 + 6H_2O \rightarrow 3Ca^{2+} + 2Al^{3+} + 12OH^-$$

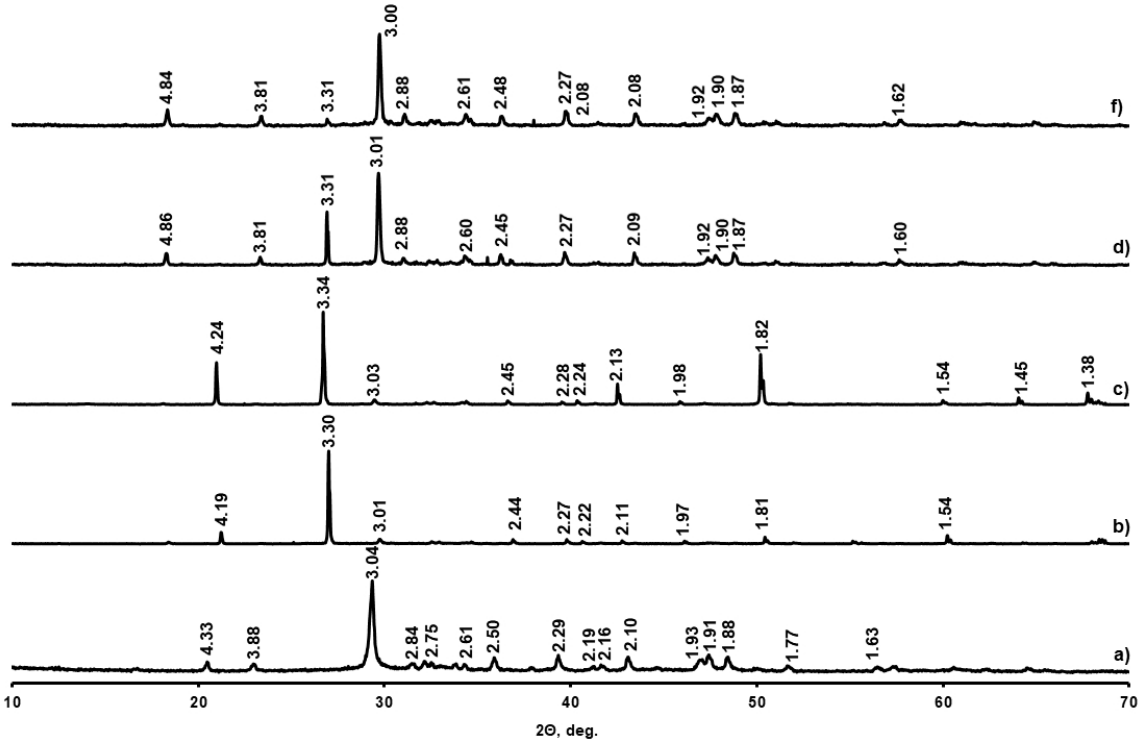


Fig. 4. X-Ray diffraction patterns of the studied cement hardening systems. Designated: a) C–W–SP–CNA; b) C–W–SP–CNA–S; c) C–W–SP–CNA–S–PF; d) C–W–SP–CNA–CF; e) C–W–SP–CNA–CF–PF SiO_2 (d = 4.25, 3.35, 2.45, 1.82, 1.38 Å); $CaCO_3$ (d = 3.34, 3.03, 2.28, 2.07, 1.59 Å); $(CaO)_x \cdot SiO_2 \cdot zH_2O$ (d = 3.05, 2.93, 2.31, 1.67, 1.62 Å); $xCaO \cdot SiO_2 \cdot zH_2O$ (d = 3.06, 2.80, 2.65, 2.14, 2.06 Å); $CaO \cdot SiO_2 \cdot H_2O$ (d = 4.24, 3.01, 2.78, 2.50, 1.89 Å); $2CaO \cdot SiO_2 \cdot H_2O$ (d = 2.92, 2.75, 1.93, 1.86, 1.75 Å); $3CaO \cdot SiO_2 \cdot H_2O$ (d =3.26, 3.01, 2.88, 2.47, 2.08 Å); $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$ (d =3.78, 2.85, 2.52, 2.34, 2.09 Å)

2) formation of calcium hydrocarboaluminate and low and highly basic calcium silicate hydrates:

$$9Ca^{2+} + 2Al^{3+} + 12OH^{-} + CaCO_3 + 11H_2O \rightarrow$$
$$\rightarrow 3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O + 6Ca(OH)_2$$

$$xCa^{2+} + 2(x-1)OH^{-} + H_2SiO_4^{2-} \rightarrow$$
$$\rightarrow (CaO)_x - (SiO_2) - (H_2O)_y$$

The X-ray diffraction data correlated with the SEM data (Fig. 5).

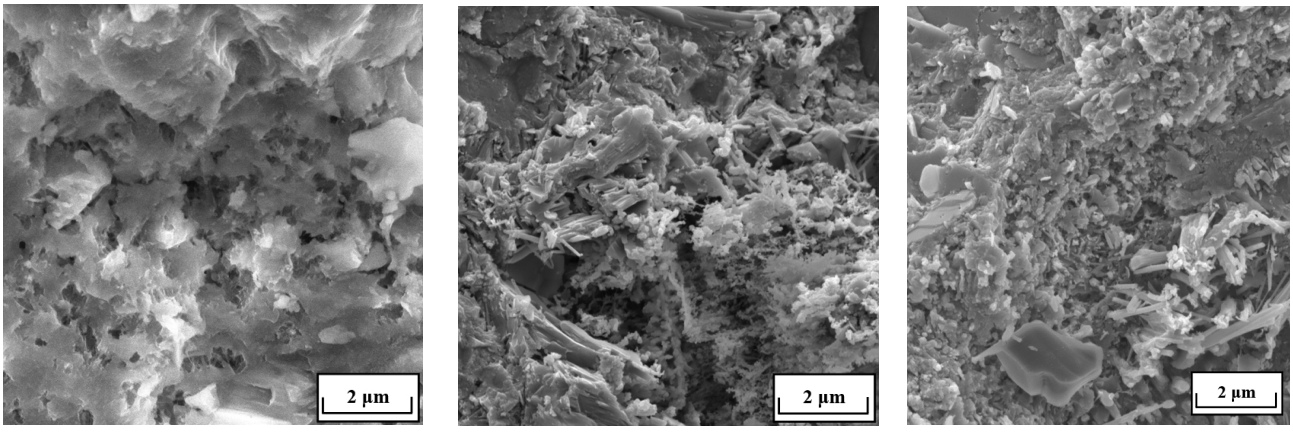
In all studied systems, a sufficiently dense structure was formed with a large number of coalescence and intergrowth contacts between crystallites. What is more, the reference system C–W–SP–NA was characterised by the formation of a predominantly amorphous-crystalline structure from a loose tobermorite-like gel (Fig. 5a). The microstructure of cement systems with sand and chalky flour (Fig. 5b, c) was more crystallised and was represented by crystallites of acicular and fibrous morphology, which probably belonged to low and highly basic calcium silicate hydroxides. In addition, lamellar crystallites adjoining each other were present in the C–W–SP–CNA–CF system (Fig. 5c). Most likely, they were formed by calcium hydrocarboaluminate.

3.4. Kinetics of the strength gain of the studied systems

Physical and mechanical testing of compressive strength showed that after 28 days of hardening, all systems had sufficiently high strength characteristics (Table 3, Fig. 6): R_{com} = 82–93 MPa. What is more, the C–W–SP–CNA reference system had the highest indicator of compressive strength both on the 1st and 28th day of hardening.

With the introduction of an aggregate (quartz sand) and a filler (carbonate flour) into the cement hardening system, its strength, as was to be expected, decreased slightly. The polypropylene fibre, which is part of a multicomponent multifunctional additive, as was to be expectedly, increased their strength. Additionally, at the early stages of hardening (days 1 and 3), regardless of the presence of a polypropylene fibre in the cement system, the system with chalky flour had the lowest values for compressive strength. On day 7 and during the remaining hardening time, regardless of the type of filler, the systems were characterized by close values of R_{com}.

It should be noted that for some systems a drop in strength was observed on the kinetic curves of strength gain (Fig. 6). In the C–W–SP–CNA reference system, it occurred on the 7th day of hardening, and in the C–W–SP–CNA–S and C–W–SP–CNA–CF systems it was observed on the 14th day of hardening. This behaviour of the systems was probably associated with the recrystallisation of primary hydrate formations. However, there was no drop in strength in the C–W–SP–CNA–S–PF and C–W–SP–CNA–CF–PF systems, which was probably due to the presence of the polypropylene fibre in their composition, which contributed to additional strengthening of the systems and compensated the decline in strength that occurred on the 14th day of hardening.



a b c

Fig. 5. Micrographs of the studied cement hardening systems (SEM data). Designated: a) C–W–SP–CNA; b) C–W–SP–CNA–S; c) C-W–SP–CNA–CF

Table 3. Results of physical and mechanical tests of cement hardening systems for compressive strength

No	System	Time, days				
		1	3	7	14	28
		Compressive strength, MPa				
1	C–W–SP–CNA	65	75	70	84	93
2	C–W–SP–CNA–S	53	60	73	67	82
3	C–W–SP–CNA–S–PF	44	62	67	73	85
4	C–W–SP–CNA–CF	38	43	67	59	82
5	C–W–SP–CNA–CF–PF	35	60	69	73	82

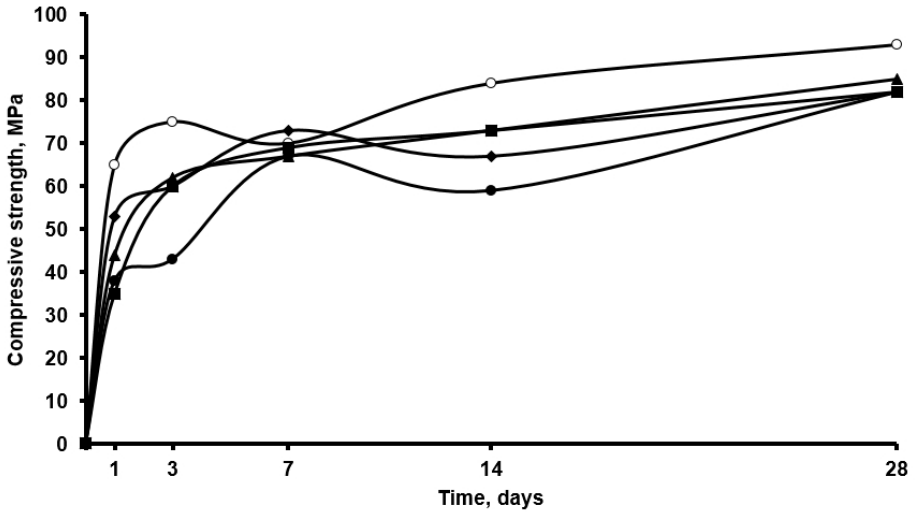


Fig. 6. Kinetic curves of strength gain of the studied cement hardening systems. Designated: ○ – C–W–SP–CNA; ♦ – C–W–SP–CNA–S; ▲ – C–W–SP–CNA–S–PF; ● – C–W–SP–CNA–CF; ■ – C–W–SP–CNA–CF–PF

Therefore, a multicomponent multifunctional additive contributed to the intensification of the process of strength gain in composites based on quartz sand and chalky flour. This effect was probably due to the synergistic effect of all components of the additive but mainly due to nanosized SiO_2 particles which, firstly, performed a catalytic role and acted as ready-made crystallisation centres, they were also directly involved in the formation of hydrated phases of the cement brick. Secondly, they increased the packing density of the system of dispersed particles and changed the porosity structure of the cement composite. This led to a change in the evolutionary route of the structure formation of the cement hardening system at the nanoscale level. What is more, the superplasticiser was able to influence the structure formation of the cement hardening system at the ultramicroscale level, whereas the polypropylene fibre influenced the structure formation at the microscale level due to micro-reinforcement and additional zoning of the composite structure. As a result, the studied cement composites achieved sufficiently high strength characteristics at the early stages of their hardening.

4. Conclusion

We studied the multicomponent multifunctional additive with the composition "nanosized SiO_2 particles – superplasticiser - polypropylene fibre" for the rheological properties of cement composites with quartz sand and chalky flour, as well as the processes of their setting-up, hydration, structure formation, and strength gain. It was established that when this additive is used in cement composites, acceptable values of fabricability indicators (plasticity and form stability) are achieved and the setting-up processes are accelerated. It was shown that a dense structure is formed in modified cement composites mainly from low and highly basic calcium silicate hydrates of various compositions, which provides them with sufficiently high

strength properties throughout the entire hardening time. The obtained results determine the effectiveness of the used additive for modern cement composites and are of high practical importance: high plasticity and form stability of mixtures obtained by using the multifunctional additive determines the possibility of using them in the innovative technology of off-form additive manufacturing. The developed compositions of mixtures have been submitted for patenting and can be offered for commercial sale.

Author contributions

M. A. Shvedova: text writing and editing, conducting experimental studies, systematisation and description of the results. O. V. Artamonova, G. S. Slavcheva: scientific leadership, research concept, methodology development, text writing and editing, final conclusions.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References

1. Artamonova O. V., Chernyshov E .M. Concepts and foundations of nanomodification technologies for structures of building composites. Part 1. General problems of fundamentality, the main directions of research and development. *Stroitel'nye materialy = Building Materials*. 2013;9: 82–90. (In Russ.). Available at: https://elibrary.ru/item.asp?id=20278771

2. Artamonova O. V., Chernyshov E. M. To the problem of conceptual models of management of the evolutionary route of formation of nanomadified solid systems in tht structure of construction composites. *Izvestiya vysshih uchebnyh zavedenij. Stroitel'stvo = News of Higher Educational Institutions. Construction*. 2018;5(713): 44–57. (In Russ., abstract in Eng.). Available at: https://elibrary.ru/item.asp?id=35618470

3. Nizina T. A., Selyaev V. P., Balykov A. S., Volodin V. V., Korovkin D. I. Optimization of compositions of multicomponent fine-grained fiber-reinforced concrete modified at various scale levels. *Nanotekhnologii v stroitel'stve: nauchnyj internet-zhurnal = Nanotechnologies in construction: an online scientific journal*. 2017;9(2): 43–65. (In Russ.). https://doi.org/10.15828/2075-8545-2017-9-2-43-65

4. Kalpana M., Vaidevi C., Vijayan D. S., Benin S. R. Benefits of metakaolin over microsilica in developing high performance concrete. *Materials Today: Proceedings*. 2020;33(1): 977–983. https://doi.org/10.1016/j.matpr.2020.06.566

5. Ratinov V. B., Rozenberg T. I. *Additives in concrete*. Moscow: Stroyizdat Publ.; 1989. 188 p. (In Russ.)

6. Izotov V. S., Sokolova Yu. A. *Chemical additives for concrete modification*. Moscow: Paleotip Publ.; 2006. 244 p. (In Russ.)

7. Kakooei S., Akil H. M., Jamshidi M., Rouhi J. The effects of polypropylene fibers on the properties of reinforced concrete structures. *Construction and Building Materials*. 2012;27(1): 73–77. https://doi.org/10.1016/j.conbuildmat.2011.08.015

8. Shaikh F. U. A., Luhar S., Arel H. S., Luhar I. Performance evaluation of Ultrahigh performance fibre reinforced concrete – A review. *Construction and Building Materials*. 2020;232: 117152. https://doi.org/10.1016/j.conbuildmat.2019.117152

9. Zeyad A. M. Effect of fibers types on fresh properties and flexural toughness of self-compacting concrete. *Journal of Materials Research and Technology*. 2020;9(3): 4147–4158. https://doi.org/10.1016/j.jmrt.2020.02.042

10. Artamonova O. V. *Synthesis of nanomodifying additives for the technology of building composites*. Voronezh: Voronezhskij GASU Publ.; 2016. 100 p. (In Russ.)

11. Plank J., Sakai E., Miao C. W., Yu C., Hong J. X. Chemical admixtures – chemistry, applications and their impact on concrete microstructure and durability. *Cement and Concrete Research*. 2015;78: 81–99. https://doi.org/10.1016/j.cemconres.2015.05.016

12. Kalashnikov V. I., Tarakanov O. V. About the use of complex additives in new generation concrete. *Stroitel'nye materialy = Building materials*. 2017;1-2: 62–67. (In Russ., abstract in Eng). Available at: https://elibrary.ru/item.asp?id=28392793

13. Kaprielov S. S., Shejnfel'd A. V., Dondukov V. G. Cements and additives for the production of high-strength concrete. *Stroitel'nye materialy = Building materials*. 2017;11: 4–10. . (In Russ., abstract in Eng). Available at: https://elibrary.ru/item.asp?id=30744332

14. Tao Y., Rahul A. V., Lesage K., Yuan Y., K. V. Tittelboom, De Schutter G. Effects of colloidal nanosilica/polycarboxylate ether superplasticizer nanocomposite and graphene oxide on properties of fly ash blended cement. *Construction and Building Materials*. 2020;262: 120767. https://doi.org/10.1016/j.conbuildmat.2020.120767

15. Liu J., Yu C., Shu X., Ran Q., Yang Y. Recent advance of chemical admixtures in concrete. *Cement and Concrete Research*. 2019;124: 105834. https://doi.org/10.1016/j.cemconres.2019.105834

16. Artamonova O. V., Slavcheva G. S., Chernyshov E. M. Effectiveness of combined nanoadditives for cement systems. *Inorganic Materials*. 2017:53(10):

1080–1085. https://doi.org/10.1134/S0020168517100028

17. Slavcheva G. S., Artamonova O. V., Shvedova M. A., Britvina E. A. Effect of viscosity modifiers on structure formation in cement systems for construction 3D printing. *Inorganic Materials*. 2021;57: 94–100. https://doi.org/10.1134/S0020168521010143

18. Russel N., Lanos C. Plastic fluid flow parameters identification using a simple squeezing test. *Applied Rheology*. 2003;13(3): 3–5. https://doi.org/10.1515/arh-2003-0009

19. Perrot A., Rangeard D., Pierre A. Structural built-up of cement-based materials used for 3D-printing extrusion techniques. *Materials and Structures*. 2016;49: 1213–1220. https://doi.org/10.1617/s11527-015-0571-0

20. Slavcheva G. S., Babenko D S., Shvedova M. A. Analysis and criteria evaluation of rheological behavior of mixtures for 3D construction printing. *Stroitel'nye materialy = Building materials*. 2018;12: 34–40. (In Russ.). https://doi.org/10.31659/0585-430X-2018-766-12-34-40

21. Lootens D., Joussett O., Matinie L., Roussel N., Flatt R. J. Yield stress during setting of cement pastes from penetration test. *Cement and Concrete Research*. 2009;39: 401–408. https://doi.org/10.1016/j.cemconres.2009.01.012

22. *JCPDS – International Centre for Diffraction Data*. © 1987 – 1995. JCPDS – ICDD. Newtown Square, PA. 19073. USA. Available at: https://www.icdd.com/

23. Bullard J. W., Jennings H. M., Livingston R. A. Mechanisms of cement hydration. *Cement and Concrete Research*. 2011;41: 1208–1223. https://doi.org/10.1016/j.cemconres.2010.09.011

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