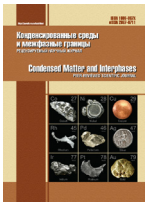

ISSN 1606-867X (Print)
ISSN 2687-0711 (Online)
Condensed Matter and Interphases
Kondensirovannye Sredy i Mezhfaznye Granitsy
https://journals.vsu.ru/kcmf/

Original articles

Research article
https://doi.org/10.17308/kcmf.2023.25/10979

Studying the effect of modifying additives on the hydration and hardening of cement composites for 3D printing

G. S. Slavcheva, O. V. Artamonova, D. S. Babenko, M. A. Shvedova✉

Voronezh State Technical University,
84 20-Letiya Oktyabrya ul., Voronezh 394006, Russian Federation

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 fresh mixtures and the physical and mechanical properties of the hardened composite.

In our study, we used several additives, including metakaolin and xanthan gum together with tetrapotassium pyrophosphate and a SiO_2 based complex additive, to modify cementitious sand-based materials. We studied the peculiarities of the influence of these additives on the technological characteristics of mixtures (plasticity and shape retention) and the processes of setting, hydration, and hardening of the composite materials.

The optimal values of plasticity, for stability, acceleration of hardening were demonstrated by sand-based systems modified with a complex nanosized additive and metakaolin. The hydration products in the such systems are mainly formed from low basic hydroxides. Metakaolin also results in the formation of ettringite. These systems demonstrate the optimal time of the beginning of setting and the maximum strength gain of the modified cementitious sand-based materials at 28 days.

The optimal ratio of indicators of plasticity and shape retention of cement mixtures and the strength of composites based on them obtained by using the studied additives allows us to recommend using these additives in the innovative technologies for 3D-build printing.

Keywords: cement hardening systems, modification, modifying additives, hydration process, rheological properties, compressive strength

Funding: This research was supported by the Russian Science Foundation, No 22-19-00280, https://rscf.ru/en/project/22-19-00280/. The experimental studies have been carried out using the facilities of the Collective Research Center named after Professor Yu.M. Borisov, Voronezh State Technical University, which is partly supported by the Ministry of Science and Education of the Russian Federation, Project No. 075-15-2021-662.

For citation: Slavcheva G. S., Artamonova O. V., Babenko D. S., Shvedova M. A. Studying the effect of modifying additives on the hydratation and hardening of cement composites for 3D printing. *Condensed Matter and Interphases*. 2023;25(1): 112–124. https://doi.org/10.17308/kcmf.2023.25/10979

Для цитирования: Славчева Г. С., Артамонова О. В., Бабенко Д. С., Шведова М. А. Исследование влияния модифицирующих добавок на структурообразование и твердение цементных композитов для 3D-печати. *Конденсированные среды и межфазные границы*. 2023;25(1): 112–124. https://doi.org/10.17308/kcmf.2023.25/10979

✉ Maria A. Shvedova, e-mail: marishwedowa@mail.ru

Designations used in the article:

C – cement
W – water
S – quartz sand
SP - superplasticiser
MKL - metakaolin
XG - xanthan gum
TPPPh - tetrapotassium pyrophosphate
CNA – complex nanosized additive
PF – polypropylene fibre

1. Introduction

The emergence and development of new construction technologies, such as 3D-printing, requires improving the existing and creating new cement-based composite materials with a set of specific properties. Therefore, during the initial stage, the fresh mixtures should have specified fabricability indicators. In particular, for the innovative 3D-printing process, of fundamental importance are such fabricability indicators as plasticity, shape retention , and accelerated setting, which are required to create a structure using off-mould additive manufacturing. What is more, the resulting composite material must have good physical and mechanical properties to ensure the standard service life of the building or structure. To ensure that cement mortar has the characteristics required for 3D printing, it is important to determine the optimal composition and substantiate the use of every component [1, 2].

Cement mortars for 3D printing are highly concentrated heterogeneous disperse systems consisting of a liquid dispersion medium and a solid dispersed phase. The rheological behaviour of fresh mixtures is determined by their structure which changes during the printing process from the coagulation structure (when the mortar is mixed and transferred to the extruder) to the coagulation-crystallization structure (setting and hardening of the mixture in printed layers). We should note that an optimal composition in terms of the type of components, their dosage, chemical and mineralogical composition, dispersion, etc., allows for direct control over the properties of both the dispersed phase and the dispersion medium. This allows for control over the hydration products, and therefore the visco-plastic properties of the cement-water heterogeneous disperse system [3].

The simplest and most accessible factor for controlling the hydration process and the properties of cement composite systems for 3D printing is the use of chemical additives of various nature (inorganic and organic), morphology, and dispersion [4, 5]. An analysis of the studies published by Russian and international researchers [4–12] demonstrated that such additives can be divided into the following groups based on the technological properties acquired by cement mixtures.

– Additives accelerating the setting and hardening process and enhancing the strength properties of printed objects. These additives are usually inorganic salts of alkali metals and calcium (K_2CO_3, Li_2CO_3, Na_2SiO_3, $CaCl_2$, NaAlO) [11], active mineral additives (finely dispersed quartz, metakaolin) [5, 6], and industrial waste (microsilica, fly ash, and waste remaining after the enrichment of mineral resources) [7–10].

– Additives increasing plasticity. These are various types of superplasticizers (SPs), which, depending on the chemical composition and the ability to reduce water, are divided into four groups: lignosulphonates, melamine sulfonates, polyacrylates, and polycarboxylate esters. At the moment, the most commonly used superplasticizers are those based on polycarboxylate esters [4, 5].

– Additives increasing adhesion. They are redispersible polymer powders of polyethylene, polyacrylate, and vinylformamide [4].

– Disperse reinforcing components enhancing the physical-mechanical properties of printed composites. These are various types of fibres - polypropylene, glass, basalt, or steel fibres [13–15].

Each additive works according to a certain mechanism and, when added to cement mortar has a selective effect on the properties of the freshly prepared composite mixture and the final cement composite.

In this regard, it is important to study the use of complex and multicomponent modifiers which include additives of various types. Namely, in our study we considered the use of an additive accelerating the setting and hardening process, a superplasticiser enhancing the plasticity of fresh mixture, and a micro-reinforcing component contributing to the additional strengthening of the cement composite by preventing crack

propagation during the hydration process. When choosing the composition of a polyfunctional additive we should take into account the fact that the particles of the modifying additive should have a similar crystal chemical structure with the particles of the cement clinker. This will allow them to form an optimal crystal structure of the material (a denser one, with fewer pores and voids) [16].

In our study, we analysed the effect the use of various modifying additives on the rheological properties, setting, hydration, and hardening of cementitious sand-based materials.

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), and a superplasticiser (SP) based on polycarboxylate esters, grade Sika® ViscoCrete® T100. Quartz sand (S) with a fineness modulus $M_f \leqslant 1.25$ (GOST 8736-2014) was used as an aggregate.

The modifying additives were: metakaolin (MKL), grade VMK-45 ($Al_2O_3 \cdot SiO_2$; SiO_2 – 53 %, Al_2O_3 – 47 %), a complex additive – xanthan gum, grade FUFENG®80 ($(C_{35}H_{49}O_{29})_n$ ~ 91 %), together with tetrapotassium pyrophosphate ($K_4P_2O_7$ – 98 %) (XG + TPPPh), and a complex nanosized additive based on silicon dioxide (CNA) with a composition "nanosized SiO_2 particles – superplasticiser" obtained by means of the sol-gel synthesis described in [16]. As a result of the synthesis, SiO_2 particles with an average size of 5–10 nm are formed in the system. They retain their aggregate stability for 7 days after the synthesis [16].

To perform the micro-reinforcement of cement composites, we used a polypropylene fibre (PF), grade Sika Fiber PPM-12, in the form of polymerized olefins (l = 12 mm, d = 0.022–0.034 mm; ρ = 910 kg/m^3, tensile strength 300 – 400 MPa). The mass fraction of the PF with regard to the weight of the cement for all the systems was 0.5 %.

Compositions and concentrations of the initial components and the designations of the studied systems are presented in Table 1.

The concentrations of the modifying additives (MKL, XG + TPPPh, CNA) and the aggregate (S) were optimised during the preliminary research and remained constant. The concentration of the superplasticiser for each system was determined empirically in order to obtain the required consistency and bonding properties of the cement mortar.

The cement systems of the described compositions were obtained by mixing of dry components for 3 minutes. When obtaining visco-plastic mixtures, the mass ratios of C : S were 1 : 1.25. These ratios are optimal and were

Table 1. Composition and the main properties of the studied systems

№	System composition	W/C	ω_{SP}, % from the mass of cement	ω_{dmix}, % from the mass of cement	System designation
1	Cement, water, superplasticizer	0.33	0.8	0	C–W–SP
2	Cement, water, superplasticizer, quartz sand, fiber	0.28	0.8	0	C–W–SP–S–PF
3	Cement, water, superplasticizer, metacaolin, quartz sand, fiber	0.29	1	2	C–W–SP–S–MKL–PF
4	Cement, water, superplasticizer, xanthan gum, tetrapotassium pyrophosphate, quartz sand, fiber	0.28	1.2	0.2 0.2	C–W–SP–S–XG–TPPPh–PF
5	Cement, water, superplasticizer, complex nanoadditive based on SiO_2, quartz sand, fiber	0.26	0.7	0.01	C–W–SP–S–CNA–PF

determined experimentally based on preliminary studies [13]. The C - W - SP system and the C–W–SP–S–PF system were recognised as reference systems.

In our experiments, we used systems of the same consistency, which corresponded to the standard density of cement-water paste according to GOST 310.3-76 "Cements. Methods for determination of standard consistency, times of setting and soundness". Based on the consistency, which remained constant, we conducted experiments to determine the water content (W/C ratio) for each of the studied systems.

The rheological behaviour of the cement visco-plastic mixtures was evaluated by the methods of squeeze rheometry [17–20]. For this, we performed squeezing tests of freshly mixed cylinder samples using the INSTRON 5982 universal floor hydraulic testing system. The radius of the samples was equal to their height ($R = h_0 = 25$ mm).

The plasticity of the obtained composite mixtures was determined based on the results of the squeezing test performed at a constant strain rate of 5 mm/s [17]. The curves "load N – displacement Δ" obtained as a result of the testing were transformed into 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, P is the load applied to the sample. The value R was taken as a constant equal to the sample radius at the beginning of the test.

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

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

To assess the shape retention, a compression test was performed at a constant load rate of ν = 0.5 N/s [18, 19]. The results of experimental studies were interpreted as the "relative displacement Δ – time t", "load N – relative displacement Δ" curves, 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:

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

Thus, we determined the criteria for the plasticity and form stability of cement composite mixtures under the modelled 3D printing conditions. These criteria include [19]:

– Plastic yield strength 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.

The setting process in the obtained cement composite systems was studied using the penetrometer method. The plastic strength (P_{pl}) was calculated using the following ratio:

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

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% [20].

The phase composition of the hardened cement paste was determined by powder diffraction (ARL X'TRA diffractometer with CuK_α radiation, λ = 1.541788 Å). The obtained data were processed using the PDWin 4.0 software package [21]. The value of the degree of hydration of the modified cement hardening systems was calculated based on the content of the alite phase $3CaO{\cdot}SiO_2$ (C_3S) by comparing their XRD patterns with the XRD pattern of the original cement clinker [22]:

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

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 composites was assessed using scanning electron microscopy (SEM) (Phenom XL scanning electron microscope).

The kinetics of the strength gain of the studied cement composites 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 shape retention 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. Curves of the first type, including the C – W – SP – S – MKL – PF system, have a prominent horizontal section of plastic deformation between two points of inflexion, which means that the system is rigid. In this case, the value of the plastic yield strength value is $K_i(I)$ = 2.47 kPa.

Reference systems as well as the C – W – SP – S – XG – TPPPh – PF and C – W – SP – S – CNA – PF systems belong to the second type of curves which do not have pronounced transitions between their sections. For these systems, the plastic yield strength value $K_i(I)$ is within the range of 1.06÷5.03 kPa. These systems have a good extrusion ability as a result of their plasticity and viscoelastic flow which does not destruct the structure.

As a result of the experimental investigation of shape retention of the studied systems two types of curves were obtained: "relative displacement Δ – time *t*" (Fig. 2a) and "relative displacement – 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 microcracking 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 results (Fig. 2, Table 2) demonstrated that all the cementitious sand-based materials with modifying additives and fibres are characterised by rational values of plasticity and shape retention , which makes it possible to perform 3D printing without defects

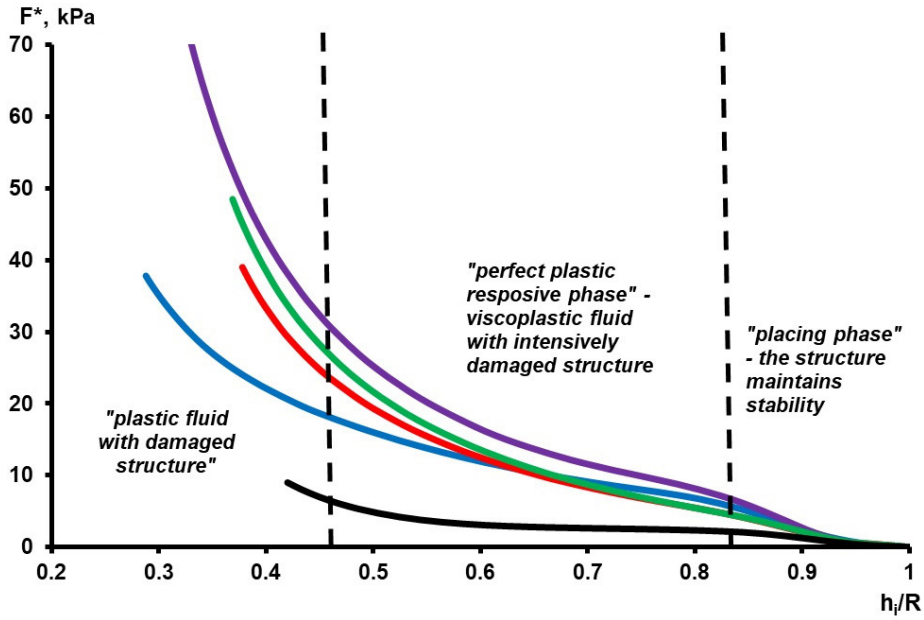

Fig. 1. Curves of the dependence of the reduced load F* on the relative change in sample height h_i/R. Designated: ▬ – C–W–SP; ▬ – C–W–SP–S–PF; ▬ – C–W–SP–S–MKL–PF; ▬ – C–W–SP–S–CNA–PF; ▬ – C–W–SP–S–XG–TPPPh–PF

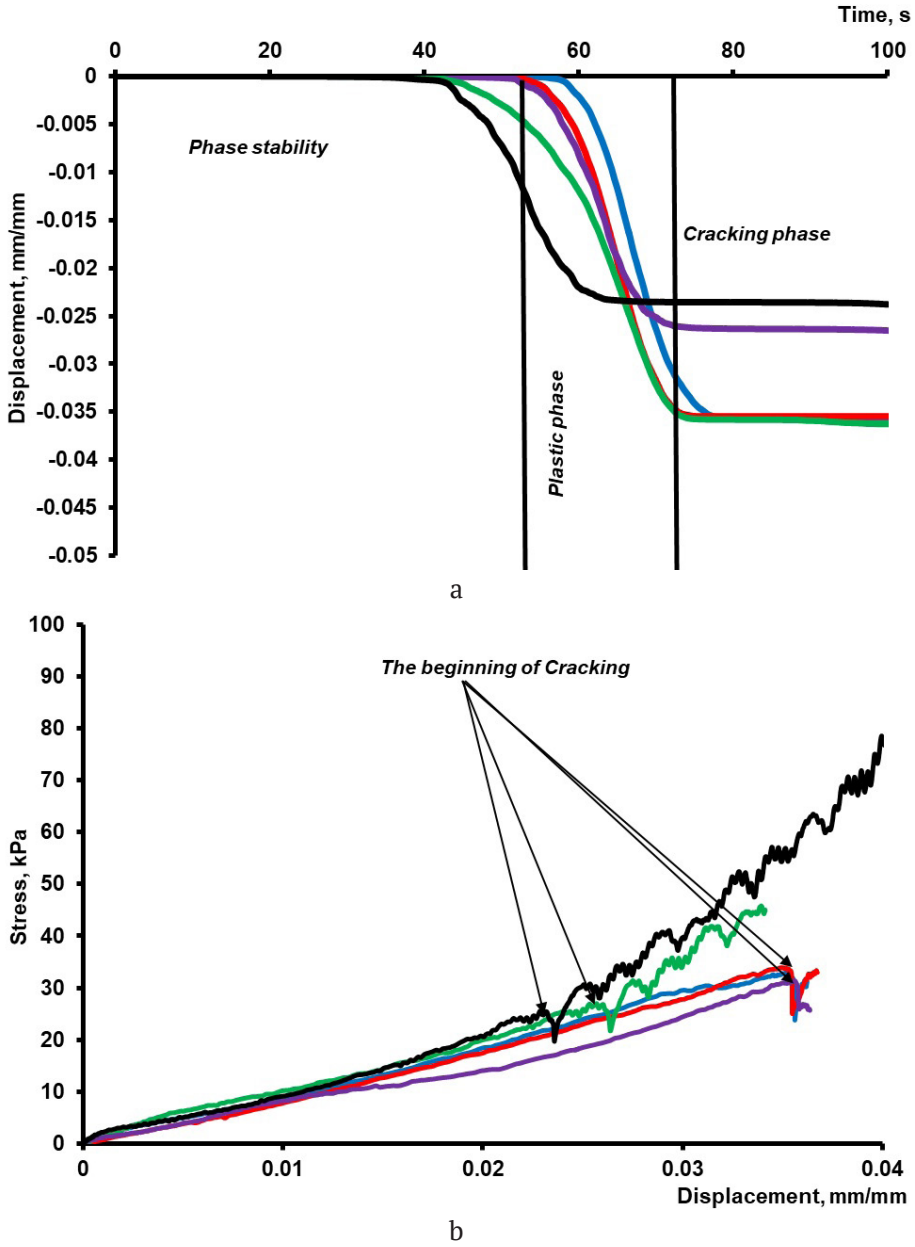

Fig. 2. Dependence curves a) displacement Δ – time *t*; b) load σ – relative displacement Δ. Designated: ▬ – C–W–SP; ▬ – C–W–SP–S–PF; ▬ – C–W–SP–S–MKL–PF; ▬ – C–W–SP–S–CNA–PF; ▬ – C–W–SP–S–XG–TPPPh–PF

and deformed layers. The best shape retention was observed in the C – W – SP – S – CNA – PF system. It demonstrated the highest values σ_0 = 5.44 kPa, and the lowest Δ_{pl} = 0.03 mm/mm.

Thus, the setting, hydration and hardening processes were studied for mixtures whose compositions were optimised based on the plasticity and shape retention criteria (Table 2). They are considered to be basic mixtures for 3D printing.

3.2. Phase composition and microstructure of the studied systems

The X-ray diffraction analysis (Fig. 3, Table 3) of the reference system (C – W – SP), with the hardening process lasting 28 days, demonstrated that hydrated compounds in this system are represented mostly by highly basic calcium silicate hydroxides ($2CaO{\cdot}SiO_2{\cdot}H_2O$), a tobermorite ($xCaO{\cdot}SiO_2{\cdot}zH_2O$), and smaller amounts of the calcium sulphoaluminate phase

Table 2. Rheological characteristics of the modified cement systems

System	Setting start time, τ, min	Plastic yield strength 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	270	1.06	1.10	45.01	0.02
C–W–SP–S–PF	135	5.03	5.03	31.64	0.044
C–W–SP–S–MKL–PF	90	2.47	2.47	36.74	0.035
C–W–SP–S–XG–TPPPh–PF	135	3.50	3.50	33.15	0.035
C–W–SP–S–CNA–PF	120	3.66	5.44	26.75	0.030

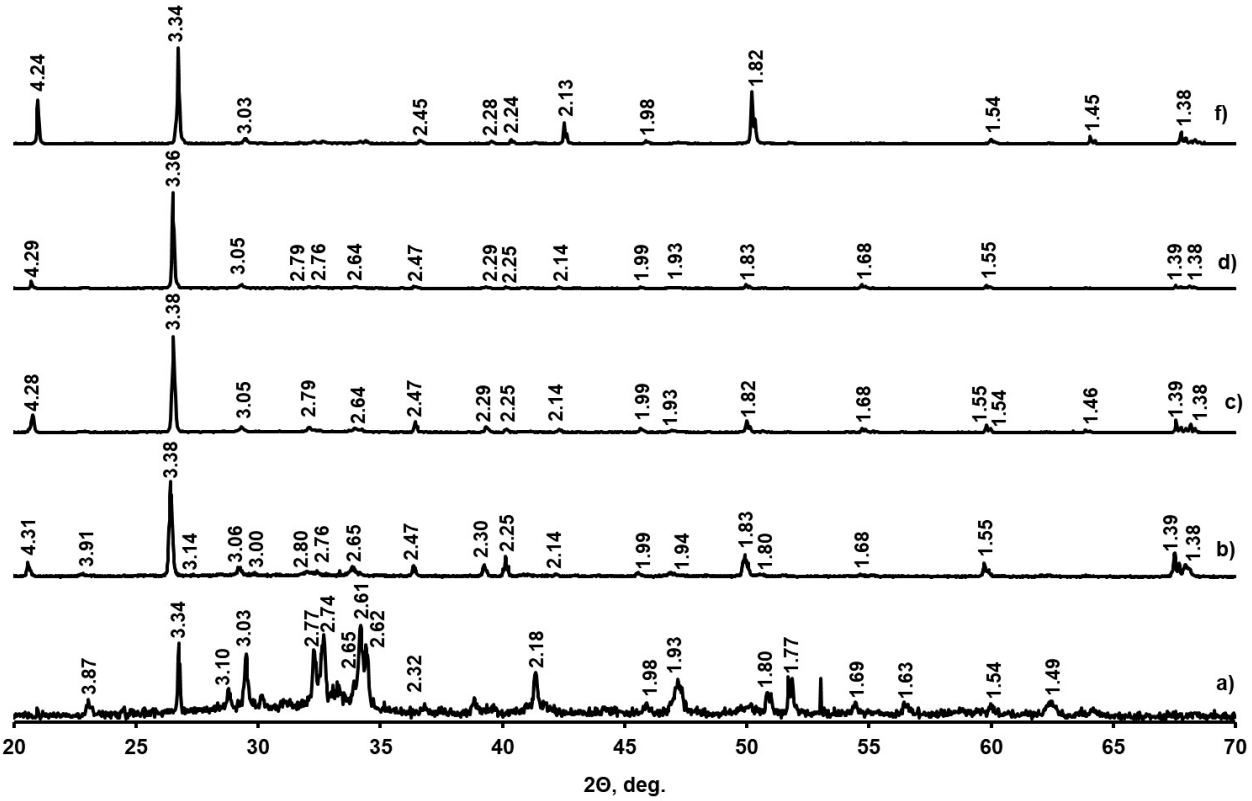

Fig. 3. X-Ray diffraction patterns of the studied cement composites. Designated: a) C–W–SP; b) C–W–SP–S–PF; c) C–W–SP–S–MKL–PF; d) C–W–SP–S–XG–TPPPh–PF; e) C–W–SP–S–CNA–PF

($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}26H_2O$) and the initial non-hydrated phases of alite $3CaO{\cdot}SiO_2$ and belite $2CaO{\cdot}SiO_2$.

The analysis of the X-ray diffraction data regarding the phase composition of the composites for 3D printing which underwent hardening for 28 days (Fig. 3, Table 3), demonstrated that the prevailing phase is the quartz phase, because quartz sand is used as an aggregate in the system. However, the sand, as well as the fibre, has hardly any impact on the chemical composition of the newly formed cement composite. This can be demonstrated by the C – W – SP – S – PF system, where, similar to the reference system 1 (without the aggregate), the dominant phases of the new composites are highly basic calcium silicate hydrates ($2CaO{\cdot}SiO_2{\cdot}H_2O$) and tobermorite ($(CaO)_x{\cdot}SiO_2{\cdot}zH_2O$.

Each additive, on the contrary, results in the formation of additional phases in the system. Thus, the system with metakaolin (C – W – SP –S – MKL – PF) demonstrated the presence of aluminate phases (Fig. 3c) characterised by prismatic, acicular, and fibrous morphology

Table 3. Phase composition and degree of hydration of the studied cement systems (duration of hardening 28 days)

System	W/C	D_h, %	Phase composition
C – W – SP	0.33	73	$2CaO{\cdot}SiO_2{\cdot}H_2O$ $(CaO)_x{\cdot}SiO_2{\cdot}zH_2O$ $Ca(OH)_2$ $3CaO{\cdot}SiO_2$
C – W – SP – S – PF	0.28	95	SiO_2 $2CaO{\cdot}SiO_2{\cdot}H_2O$ $(CaO)_x{\cdot}SiO_2{\cdot}zH_2O$ $Ca(OH)_2$ $3CaO{\cdot}SiO_2$
C – W – SP –S – MKL – PF	0.29	93	SiO_2 $(CaO)_x{\cdot}SiO_2{\cdot}zH_2O$ $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}32H_2O$ $CaO{\cdot}SiO_2{\cdot}H_2O$ $3CaO{\cdot}SiO_2$
C – W – SP –S – XG – TPPPh – PF	0.28	98	SiO_2 $x CaO{\cdot}SiO_2{\cdot}zH_2O$ $2CaO{\cdot}SiO_2{\cdot}H_2O$ $CaHPO_4{\cdot}2H_2O$
C – W – SP – S – CNA – PF	0.26	98	SiO_2 $(CaO)_x{\cdot}SiO_2{\cdot}zH_2O$ $CaO{\cdot}SiO_2{\cdot}H_2O$ $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}32\ H_2O$ $3CaO{\cdot}SiO_2$

(Fig. 4c). The presence of such phases can enhance the shape retention and the strength of this system.

The C – W – SP – S – XG – TPPPh –PF system with xanthan gum and potassium pyrophosphate demonstrated, similar to the reference system, the presence of dyscrystalline highly basic calcium silicate hydrates and tobermorite forming pronounced cluster crystals (Fig. 3d, 4d). There was also a small amount of dicalcium phosphate ($CaHPO_4{\cdot}2H_2O$), which is explained by the partial interaction of the additive with the hydration products.

In the C – W – SP – S – CNA – PF system with SiO_2 based complex nanoadditives, a well-crystallized tobermorite phase and low base calcium silicate hydroxides ($CaO{\cdot}SiO_2{\cdot}H_2O$) (Fig. 3e, 4e) were dominant. There was also a small amount of ettringite ($3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}32H_2O$), which increased the form stability and strength of the system.

All the systems demonstrated high values of hydration degrees, 95–98 % (Table 3), with the maximum hydration degree of 98 % being characteristic for all the systems with the XG + TPPPh complex modifying additive and the CNA additive.

Therefore, we can say that quartz sand does not affect the phase composition of the new hardening system, while the modifying additives have a direct impact on the hydration products of the studied cement systems, since they participate in heterogeneous processes of phase formation. At the same time, the hydration degree of cement increased significantly. The kinetics of hydration and the composition of the new composites are affected the most by the metakaolin additive and the SiO_2 based complex nanosized additive. They increase the formation of low base calcium silicate hydroxides, which is explained by the fact that they have a similar crystal chemical structure with the new the cement composite. Polypropylene fibre is practically inert to the hydration and hardening process.

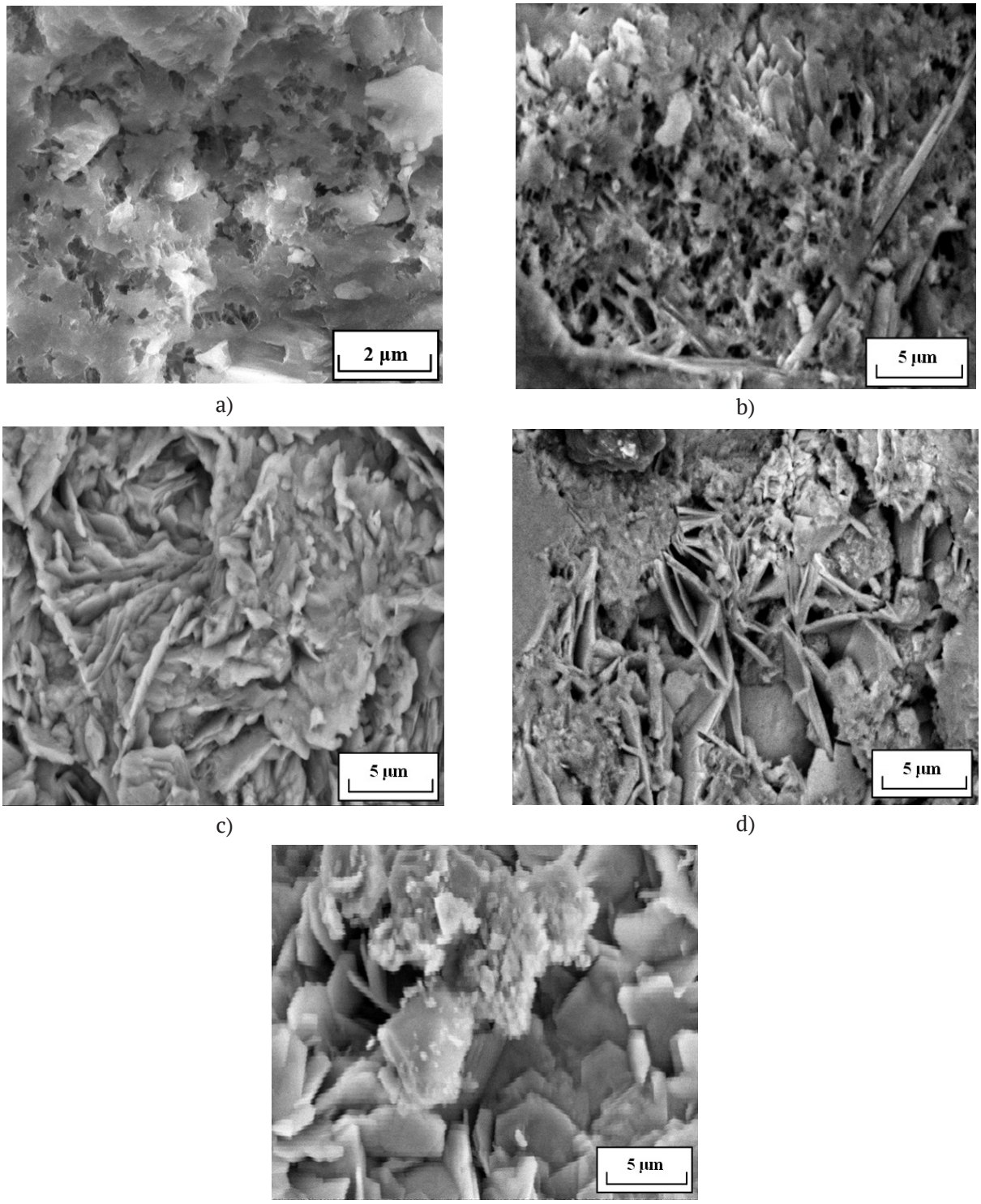

Fig. 4. Micrographs of the studied cement hardening systems. Designated: a) C–W–SP; b) C–W–SP–S–PF; c) C–W–SP–S–MKL–PF; d) C–W–SP–S–XG–TPPPh–PF; e) C–W–SP–S–CNA–PF

3.3. Kinetics of the setting-up and hardening of cementitious sand-based materials

Table 4 presents experimental data for all the studied systems regarding the beginning of the setting process τ, plastic strength P_{pl} at the beginning of setting registered by a standard method, and the compressive strength for standard hardening time. According to the standard method for determination of the speed of setting, the beginning of the process and the value of P_{pl} at the moment of actual setting differ greatly. The beginning of setting is within the range of 45 – 165 minutes, the plastic strength is P_{pl}= 28 – 357 kPa.

The lowest plastic strength (28.35 kPa) and the longest setting time (165 minutes) are characteristic for systems without additives (C – W – SP – S – PF). Quartz sand is chemically inert to the materials of the cement clinker and under standard hardening conditions does not have any noticeable effect on the visco-plastic properties of the systems. Therefore, the plastic strength of the studied systems with sand is affected significantly by the modifying additives used.

Introduction of metakaolin increases the plastic strength significantly and slightly reduces the setting time. Thus, the setting time in this system is 107 minutes with the corresponding P_{pl} = 357 kPa (Table 4).

This can be accounted for by the fact that metakaolin particles, having similar crystal chemical structure with the cement clinker, can occupy space between cement grains in a particular way. This results in a denser spatial packing of solid phase particles leading to a denser structure of the whole system due to a smaller number of pores and voids.

For cement mixtures modified with xanthan gum and potassium pyrophosphate, the setting process started after 136 minutes with the corresponding P_{pl} = 179.19 kPa (Table 4). This can be explained by the fact that xanthan gum can modify the dispersion medium. It affects the density of the dispersion medium and can structure the liquid phase, which reduces the chemical activity of water molecules required for the hydration of cement clinker minerals. These processes result in greater structural strength of the system and faster setting of cement.

Although potassium pyrophosphate accelerates the hydration of cement, this electrolyte additive increases the flow rate of the system and, correspondingly, reduces its plastic strength. As a result, setting of systems with the XG + TPPPh modifier starts practically at the same time is setting of the reference system without any modifiers. At the same time, the plastic strength is 3-6 times higher than that of the reference systems.

Setting of mixtures with CNA starts after 45 minutes with P_{pl} = 293.96 kPa. The faster setting can be explained by the fact that nanosized SiO_2 particles in the CNA, thanks to large surface energy and similar crystal chemical structure with the cement clinker, can accelerate heterogeneous processes of formation of hydrated newgrowths. As a result, the hydration, setting, and strength gaining processes accelerate. At the same time, the superplasticiser which was part of the CNA, due to adsorption on the surface of the hydrated phases of the cement system reduces their interfacial energy, which results in their dispersion. In this case, some of the immobilised water is released, which provides for an increase in the plasticity of the mixture and, accordingly, a slight decrease in plastic strength.

Thus, modifying additives have great effect on the setting speed and the plastic strength of mixtures for 3D printing. Depending on the type of the additive, the difference in the plastic

Table 4. Experimental data regarding the setting and hardening of the cement mixtures for 3D printing

№	System composition	W/C	Setting processes		Compressive strength, MPa				
			P_{pl}, kPa	τ, min	1 day	3 days	7 days	14 days	28 days
1	C–W–SP	0.33	25.92	105	19.41	29.28	35.19	48.17	57.39
2	C–W–SP–S–PF	0.28	28.33	165	20.74	40.90	51.70	58.41	61.01
3	C–W–SP–S–MKL–PF	0.29	356.60	107	25.03	43.12	55.30	60.65	62.70
4	C–W–SP–S–XG–TPPPh–PF	0.28	179.19	136	7.33	39.95	49.92	49.73	58.30
5	C–W–SP–S–CNA–PF	0.26	293.96	45	26.52	45.07	57.36	61.07	65.80

strength can reach 7–12 times, and the difference in the setting speed can reach 1.5–3 times.

An analysis of the study of the strength of cement composites demonstrated that modified cement systems gain strength more intensively, and the values R_{com} are higher than those for the reference system (Table 4).

We should note that the hardening process has the following peculiarities.

The highest values for compressive strength at the initial stages of hardening and after the hardening is complete are demonstrated by cement composites with CNA additives (R_{com} = 27 MPa at1 day, R_{com} = 66 MPa at 28 days) and metakaolin (R_{com} = 25 MPa at 1 day, R_{com} = 63 MPa at 28 days). A marked increase in the strength of these systems is explained by the close resemblance of the crystal chemical structure of the additives to the cement clinker minerals and by the physicochemical activity.

Cement composites modified with xanthan gum and potassium pyrophosphate are characterised by low strength. For the C – W – SP –S – XG – TPPPh – PF system, 1 day after the beginning of hardening R_{com} is7 MPa, which is three times lower than for the reference system after 28 days of hardening (R_{com} = 58 MPa).

Having analysed the effect of the modifying additives on the structure formation process and the properties of mixtures and composites for 3D printing, we can assume the following.

1) Metakaolin particles, due to similar crystal chemical structure with the cement clinker, can behave as nuclei during the structure formation of the cement composite. Located between the cement grains, they result in a denser spatial packing of solid phase particles which affects the porosity of the cement system and makes its structure denser. On the one hand, this increases the plastic strengths of the system in the visco-plastic state. On the other hand, it increases the strength of the cement composite during hardening.

2) Due to its chemical nature, potassium pyrophosphate can change the ion composition and the viscosity of the dispersion medium, accelerating the hydration of the cement clinker and increasing the density and stability of the cement system.

3) Xanthan gum particles are chemically inert to cement clinker minerals. Therefore, they mainly affect the properties of the dispersion medium. When introduced into the cement system, xanthan gum increases the viscosity and density of the liquid phase, as well as the structure formation. This enhances the structural strength of the cement system and slows down the setting and strength gaining processes.

4) A complex nanosized additive based on SiO_2 nanoparticles accelerates the heterogeneous processes of phase formation of hydrated compounds thanks to similar crystal chemical structure and increased surface energy. At the same time, the hydration, setting, and strength gaining processes accelerate.

4. Conclusions

The study determined that the introduction of modifying additives of various nature into cement composite mixtures for 3D printing significantly affects their rheological behaviour, as well as the hydration, and strength gaining processes. The study demonstrated that cementitious sand-based materials modified with CNA and metakaolin are optimal with regard to their plasticity, the shape retention, and the speed of the hydration, setting, and strength gaining processes. The highest values for compressive strength for the said systems were registered after 28 days of hardening. The hydration products of cement composites with CNA and metakaolin additives consists mainly of low base calcium silicate hydroxides. Metakaolin also results in the formation of ettringite.

Therefore, in our study, we determined the optimal compositions for cement composite materials. These compositions make it possible to obtain composites with set properties (faster setting, required degree of plasticity and plasticc yield strength value, physical, mechanical, climate-related indicators). Received patents [23–25] prove that the suggested compositions of cement composites are of great practical value for 3D-build printing .

Author contributions

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

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. Vatin N. I., Chumadova L. I., Goncharov I. S., ... Finashenkov E. A. 3D printing in construction. *Construction of Unique Buildings and Structures*. 2017;1(52): 27–46. (In Russ.). https://doi.org/10.18720/CUBS.52.3

2. Pustovgar A. P., Adamcevich A. O., Volkov A. A. Technology and organization of additive construction. *Industrial and Civil Engineering*. 2018;9: 12–20. (In Russ., abstract in Eng.). Available at: https://www.elibrary.ru/item.asp?id=36296905

3. Puharenko Yu. V., Hrenov G. M. Calculation of the composition when designing concrete mixtures for continuous formless molding. *Zhilishchnoe stroitel'stvo = Housing construction*. 2022;4:40–45. (In Russ., abstract in Eng.). https://doi.org/10.31659/0044-4472-2022-4-40-45

4. Beznogova O. Yu., Potapova E. N. Materials for additive manufacturing construction. *Uspekhi v himii i himicheskoj tekhnologii*. 2022;3(252): 16–18. (In Russ., abstract in Eng.). Available at: https://www.elibrary.ru/item.asp?id=48730949

5. Tramontin Souza M., Maia Ferreira I., Guzi de Moraes E., ... Novaes de Oliveira A. P. Role of chemical admixtures on 3D printed Portland cement: Assessing rheology and buildability. *Construction and Building Materials*. 2022;314: 125666. https://doi.org/10.1016/j.conbuildmat.2021.125666

6. 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

7. Bondarev B. A., Korneeva A. O., Rogotovskij A. N., Meshcheryakov A. A. Development mixtures for additive technologies. *News of Higher Educational Institutions. Construction*. 2021;11(755): 55–63. (In Russ., abstract in Eng.). https://doi.org/10.32683/0536-1052-2021-755-11-55-63

8. Dem'yanenko O. V., Kopanica N. O., Sorokina E. A. Performance characteristics of 3D printing construction mixes depending on thermally-modified peat additive. *Vestnik Tomskogo gosudarstvennogo arkhitekturno-stroitel'nogo universiteta. Journal of Construction and Architecture*. 2018;20(4): 122–134. (In Russ., abstract in Eng.). https://doi.org/10.31675/1607-1859-2018-20-4-122-134

9. Zagorodnuk L. K., Elistratkin M. Yu., Podgornyi D. S., Al Mamuri S. Composite binders for 3d additive technologies. *The Russian Automobile and Highway Industry Journal*. 2021;18(4): 428–439. (In Russ., abstract in Eng.). https://doi.org/10.26518/2071-7296-2021-18-4-428-439

10. Dey D., Srinivas D., Panda B., Suraneni P., Sitharam T. G. Use of industrial waste materials for 3D printing of sustainable concrete: A review. *Journal of Cleaner Production*. 2022;340: 130749. https://doi.org/10.1016/j.jclepro.2022.130749

11. Chen M., Li L., Zheng Y., Zhao P., Lu, L., Cheng X. Rheological and mechanical properties of admixtures modified 3D printing sulphoaluminate cementitious materials. *Construction and Building Materials*. 2018;189: 601–611. https://doi.org/10.1016/j.conbuildmat.2018.09.037

12. 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

13. Kristombu Baduge S., Navaratnam S., Abu-Zidan Y., ... Aye, L. Improving performance of additive manufactured (3D printed) concrete: A review on material mix design, processing, interlayer bonding, and reinforcing methods. *Structures*. 2021;29: 1597–1609. https://doi.org/10.1016/j.istruc.2020.12.061

14. 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

15. 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

16. 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

17. 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

18. Perrot A., Rangeard D., Pierre A. Structural built-up of cement-based materials used for 3D-printing extrusion techniques. *Materials and Structures*. 2016;49(4): 1213–1220. https://doi.org/10.1617/s11527-015-0571-0

19. Slavcheva G. S., Babenko D S., Shvedova M. A. Analysis and criteria assessment of rheological behavior of mixes for construction 3-D printing. *Stroitel'nye Materialy*. 2018;12: 34–40. (In Russ., abstract in Eng.). https://doi.org/10.31659/0585-430X-2018-766-12-34-40

20. 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

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

22. 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

23. Slavcheva G. S., Artamonova O. V., Shvedova M. A., Britvina E. A. *Two-phase cement-based mixture for composites in 3D construction printing technology*. Patent RF No. 2729086, 2020. Publ. 04.08.2020, bull. No. 22. (In Russ).

24. Slavcheva G. S., Artamonova O. V., Shvedova M.A., Britvina E.A. *Two-phase cement-based mixture for composites in 3D construction printing technology*. Patent RF No. 2729220, 2020. Publ. 05.08.2020, bull. No. 22. (In Russ).

25. Artamonova O. V., Slavcheva G. S., Shvedova M. A., Britvina E. A., Babenko D. S. *Nanomodified cement composite for construction 3D printing*. Patent RF, No. 2767643, 2022. Publ. 18.03.2022, bull. No. 8. (In Russ).

Information about authors

Galina S. Slavcheva, Cand. Sci. (Tech.), Associate Professor, Professor at the Department of Technology of Building Materials, Products and Structures, Voronezh State Technical University (Voronezh, Russian Federation).

https://orcid.org/0000-0001-8800-2657

gslavcheva@yandex.ru

Olga V. Artamonova, Dr. Sci. (Tech.), Associate Professor, Professor at the Department of Chemistry and Chemical Technology of Materials, Voronezh State Technical University (Voronezh, Russian Federation).

https://orcid.org/0000-0001-9157-527X

ol_artam@rambler.ru

Dmitry S. Babenko, PhD applicant, Engineer, of Higher School of Building Materials Science, Voronezh State Technical University (Voronezh, Russian Federation).

babenko.dmitrii@bk.ru

Maria A. Shvedova, assistant of the Department of Chemistry and Chemical Technology of Materials, Voronezh State Technical University (Voronezh, Russian Federation).

https://orcid.org/0000-0002-6484-8719

marishwedowa@mail.ru

Received 29.06.2022; approved after reviewing 28.07.2022; accepted for publication 15.09.2022; published online 25.03.2023.