



Fine-grained self-compacting concrete with polyfunctional additive and enhanced performance properties

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Abstract. The results of experimental studies aimed at improving the strength characteristics of cement stone and fine-grained self-compacting concrete through the use of polyfunctional modifying additives based on nano-silicon dioxide (nano-SiO₂) and micro-dispersed mineral components are presented. It was established that the introduction of 0.03% nano-SiO₂ by weight of cement increases the compressive strength of cement stone by up to 32%, which is associated with the intensification of clinker mineral hydration processes, the formation of an additional amount of low-base calcium hydrosilicates, and an increase in the number of crystallization centers in the early stages of hardening. The effectiveness of the combined use of nano-SiO₂ with microsilica and micro-calcite, which are similar in composition to cement but differ in structure and functional activity, has been experimentally confirmed. The use of two-component systems made it possible to increase the flexural strength of cement stone by up to 29% compared to the reference samples. The greatest effect was achieved by adding a polyfunctional three-component additive, including nano-SiO₂, microsilica, and micro-calcite, to the composition of fine-grained self-compacting concrete. The use of this system increased the compressive strength of concrete by 44% (to class B60) and the flexural strength by up to 12.5 MPa (an increase of 53.7% relative to the reference composition). It was additionally established that the complex of additives contributes to the acceleration of self-organization processes in the early stages of hardening by increasing the density of crystallization centers and a more uniform distribution of hydration products in the cement matrix volume.

Keywords: fine-grained self-compacting concrete, strength, calcium hydrosilicates, cement hydration, additives.

1. Introduction

Fine-grained self-compacting concrete (SCC) is a promising area in the field of building materials, focused on creating compositions with improved processability and performance characteristics. Such concretes eliminate the need for mechanical compaction during laying, ensure high fluidity of the mixture, uniformity of structure, and surface quality without additional labor costs. However, in the production of fine-grained SCC, a number of key issues remain unresolved, including insufficient flexural strength, a tendency to delamination, increased water demand, and cement consumption, leading to increased shrinkage and reduced durability of the material. One potential solution for that is the use of fibers of various compositions and structures [1]. Experience with fiber-reinforced concrete [2] shows that the rational areas of application for such concrete are a specific range of monolithic and precast concrete products, as well as the manufacture of impact-resistant and bendable structures using fiber to eliminate the use of additional reinforcement.

Compliance with requirements for achieving high operational quality indicators for concrete and reducing material and energy costs in the production of concrete mixtures and products based on them makes research in the field of obtaining modern types of concrete, such as high-performance concrete according to [3], relevant. The use of such concretes makes it possible to simultaneously reduce the costs of production and operation of load-bearing structures and ensure high reliability of buildings or structures regardless of external environmental conditions. The main quality indicators

of such concrete should be increased strength (over 55 MPa), durability, and mobility (P5-P6) at a water-cement ratio (W/C) not exceeding 0.4 [4].

Problems of structural instability and porosity, characteristic of fine-grained self-compacting concrete systems, are particularly relevant when using fine aggregates and a low water-cement ratio. Sedimentation pores and capillary structure have a significant impact on water permeability, frost resistance, and resistance to external aggressive influences. In addition, the uneven distribution of mixture components and high water mobility in fresh concrete lead to the formation of a surface layer with an increased water-cement ratio, which impairs the mechanical and operational properties of the hardened material [5].

Current research in the field of self-compacting concrete focuses on finding effective solutions aimed at optimizing the structure of cement stone and reducing the volume of free water. One such solution is the use of polyfunctional modifying additives, including active mineral and nanodispersed components, as well as the latest generation of superplasticizers. These additives not only improve the rheological properties of the concrete mix but also contribute to the intensification of hydration processes, the formation of a denser structure, and a reduction in permeability. Particular attention is paid to triple systems combining microsilica, nanosilica, and chemical additives capable of initiating the formation of low-base calcium hydrosilicates and minimizing the content of free calcium hydroxide [6].

The emergence of special cements on the market, such as low water demand (LWD) binders and other types of cements, played an important role in the creation of high-strength concretes, initiating the possibility of obtaining concretes with high strength and other new qualitative operational characteristics [7].

In [8], the term “Reactive Powder Concrete” (RPC) was used for the first time, the main principle of which is to ensure a uniform concrete structure by replacing coarse aggregate in mixtures with fine-grained aggregate, compacting the mixture by optimizing the granulometric composition of the aggregate, using finely dispersed fillers and complexes of modifying additives, as well as using intensive methods of hardening the concrete mixture, which allows obtaining concrete with high performance characteristics (strength of 60-120 MPa, high durability of hardened concrete, frost resistance of at least F 400 and above, water resistance of at least W12). The component composition of such concrete is: Portland cement, microsilica (15-20% of the cement mass), fine-grained sand with a fraction of 0.3 mm (40-50% of the cement mass), and superplasticizer (2-3%) at $W/(C+Microsilica)$ 0.12-0.15. The disadvantage of such concrete is that its strength largely depends on the hardening conditions and the high consumption of superplasticizer.

Despite significant progress in this area, the complex effect of nano- and micro-dispersed additives on the structure and properties of fine-grained cement-based mixtures, as well as the mechanisms of strength characteristic formation in the early stages of hardening, remains insufficiently studied. Special attention should be paid to evaluating the effectiveness of such modifying systems under conditions of minimal cement and water consumption, which is important for improving the energy efficiency of construction production.

This study is aimed at developing and substantiating the composition of fine-grained self-compacting concrete using polyfunctional additives based on microsilica, nano-SiO₂, and other active components that provide a comprehensive improvement in physical, mechanical, and technological properties.

2. Methods

The research methodology is based on the systematic application of scientific approaches focused on the development and optimization of concrete compositions for various functional purposes. At the initial stage, a working hypothesis was formulated, and a review and critical analysis of literary sources was carried out, which made it possible to justify the choice of micro- and nanoscale modifying components that are chemically compatible with cement hydration products, as

well as to form a detailed plan for experimental work. Nano-silicon dioxide (nano-SiO₂) was selected as the basic nano-sized modifier. Studies were conducted on its effect on the processes of structure formation and the physical and mechanical characteristics of cement stone. Based on the data obtained, the choice of micro-dispersed mineral additives (microsilica, micro-calcite) for the formation of complex (two-component) modifying systems was justified. The compositions of polyfunctional additives, including nano-SiO₂ in combination with micro-dispersed fillers, providing a complex effect on the structure and properties of the cement matrix, have been developed and scientifically substantiated. Taking into account the results of physical-mechanical and physical-chemical tests, a multi-level modifying system for fine-grained self-compacting concrete has been proposed. An algorithm for selecting the composition of the modifying system has been developed, taking into account the influence of components on key performance indicators, and tests have been carried out to determine strength, density, and other characteristics, confirming the effectiveness of the proposed system. To study the effect of complex additives on the structure and properties of cement stone, concrete mixtures, and concrete, Portland cement CEM I 42.5 N produced by Alacem LLP (Almaty, Kazakhstan) was used [9]. The characteristics, properties, chemical, and mineralogical composition of the cement used, as provided by the manufacturer's data, are presented in Tables 1-4.

Table 1 – Chemical composition of clinker, %

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Alkalis	Other impurities
20.9	4.7	3.3	61.9	3.8	2.7	up to 0.8	1.9

Table 2 – Mineralogical composition of clinker, %

C ₃ S	C ₂ S	C ₃ A	C ₄ AF	CaO
68.9	12.9	6.2	11.3	0.7

Table 3 – Physical properties of cement

Residue on sieve 0.08, %	Normal consistency, %	Specific surface area, cm ² /g	Particle size, μm	Setting time, min		Losses during ignition, %
				Start	End	
9.7	27.5	3100	10-25	140	270	3.0

Table 4 – Mechanical properties of cement

Strength at normal hardening				
Bending		Compression		
3 days	28 days	3 days	28 days	
6.8	7.9	36.4	53.6	

Gravel with a particle size of 5-10 mm from the Kentas deposit (Almaty, Kazakhstan), which meets the requirements of [10], [11], was used as the coarse aggregate. The main physical and mechanical characteristics of the gravel aggregate are given in Tables 5-6.

Table 5 – Particle size distribution of gravel aggregate

Passing through a sieve	Sieve mesh size, mm			
	15	10	5	2.5
Total residue, %	100	88.78	11.22	-

Table 6 – Physical and mechanical properties of gravel aggregate

Brand by crushability	Content of plate-shaped and needle-shaped grains, %	Content of dust and clay particles, %	Clay content in lumps, %	Density, kg/m ³	
				Natural	Bulk
1000	12.5 (I group)	0.5	0	2660	1470

Natural quartz sand from the Arna deposit in the Almaty region, which meets the requirements [12], was used as a fine aggregate. The characteristics of the sand are presented in Table 7.

Table 7 – Properties of sand

Gravel content, %	Total residue, % on sieves, mm					Dust and clay particle content, %	Modulus of coarseness	Density, kg/m ³	
	2.5	1.25	0.63	0.32	0.16			Natural	Bulk
-	0.8	1.6	33.0	61.0	96.3	2.1	2.44	1395	2610

Nano-silicon dioxide (nano-SiO₂) synthesized using the plasma arc method was used as a nano-modifier in concrete mixtures. The technological scheme of the experimental setup for obtaining silicon dioxide nano-powder is based on the sublimation process of solid-phase raw materials under the influence of low-temperature arc discharge plasma, followed by the condensation of the vapor phase and the formation of nanoparticles of the target product. The extremely high temperatures of the plasma discharge (up to 5000 K) enable the use of a wide range of materials as raw materials, including natural mineral components [13]. In this work, diatomite from the Utesai deposit in the Aktobe region was used as raw material for obtaining nano-powder.

As can be seen in Figure 1, silicon dioxide nanoparticles with a polydisperse size distribution have a distinctive spherical shape and are represented in the form of agglomerates. The properties of the nano-modifiers used in the work are presented in Table 8.

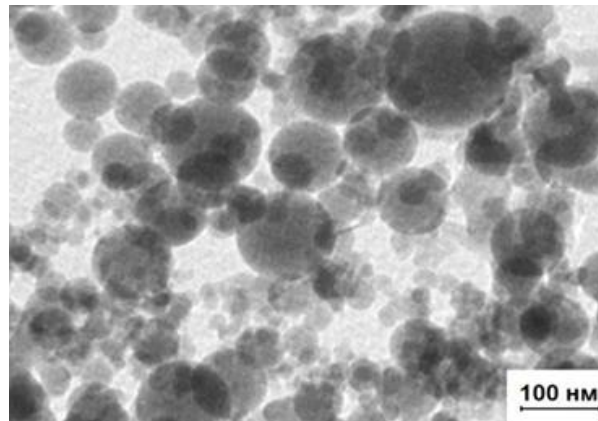
Figure 1 – Micrograph of SiO₂ nano-powder

Table 8 – Properties of nano-modifiers

Label	Specific surface area, m ² /g	Average particle size, nm
H74	282	73.7
H62	392	62.6
H44	511	44.5
H23	740	22.6

Condensed microsilica MCU-95, obtained from the Ferroalloy Plant (Tau-Ken Temir) in Karaganda, was used as the active, finely dispersed component of the modifying additive. According to [14], the annual output of this plant reaches 20,000 tons. The chemical composition and physical and technical properties of microsilica are presented in Tables 9 and 10.

Table 9 – Chemical composition of microsilica

Oxide content, %							
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O+K ₂ O	SiC	SO ₂
95.5	1.4	0.8	1	0.2	0.3	up to 3	up to 0.09

Table 10 – Physical and technical properties of microsilica

Bulk density, kg/m ³	Natural density, kg/m ³	Particle size, μm	Specific surface area, m ² /g	Humidity, %
270	2200	0.1-1.0	2.5	2

Figure 2 presents the electron microscope image of microsilica.

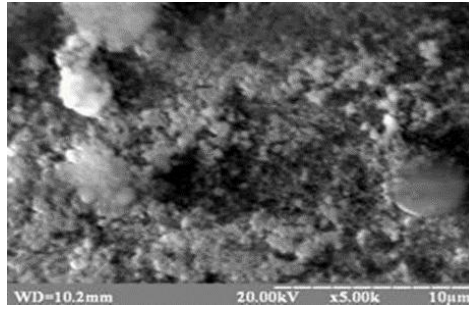


Figure 2 – Electron microscope image of microsilica

Figure 2 shows that the composition of microsilica is predominantly a homogeneous fraction. Microsilica interacts with cement hydration products, forming additional hydrate phases and acting as a gel binder. Microsilica particles, which are 0.5-0.05 μm in size, are capable of filling the voids between cement and aggregate particles, thereby increasing the strength and reducing the delamination of the concrete mixture.

The work used micro-dispersed mineral powder, a waste product formed during the crushing of MK-5 marble, complying with [15], at a quarry of Tekeli-Mramor LLP (Tekeli, Almaty, Kazakhstan). Finely ground marble is a white powder with a crystalline structure. It is characterized by a high calcium carbonate content of at least 95-98%. The physical and chemical properties of micro-calcite are presented in Table 11.

Table 11 – Physical and chemical properties of microcalcite

Chemical composition and properties		
CaCO ₃ , %		96–97
MgO, %		not more than 0.5
SiO ₂ , %		not more than 0.4
Fe ₂ O ₃ , %		not more than 0.2
Mass fraction of fugitive substances, %		not more than 0.15
Mass fraction of water-soluble substances, %		not more than 0.2
Mass fraction of substances soluble in 15% hydrochloric acid solution, %		not more than 97
pH of the aqueous suspension		10.1
Physical properties		
Specific surface area, m ² /g		1.6
Density, kg/m ³		2725
Refractive index		1.6
Hardness on the Mohs scale		3
Humidity, %		not more than 1

The composition of microcalcite is mainly CaCO₃ (96-97%), and it also contains impurities of iron oxide, sulfur, magnesium, graphite, and aluminum in an amount of 1-3%.

A polycarboxylate plasticizer for construction materials based on cement binders AR124 manufactured by Arirang Group in Astana (Kazakhstan), was selected as a plasticizer for self-compacting concrete mix. The additive effectively disperses the cement paste in the concrete mixture, plasticizes the concrete mixture, reduces its water demand, and improves the mobility and homogeneity of concrete mixtures. The AR124 additive complies with [16].

The effect of nano-modifiers was studied on samples – 20×20×20 mm cubes made of normal-density cement paste with different additive ratios. The nano-SiO₂ additive content ranged from 0.01 to 0.05% of the cement mass. Silicon dioxide nano-modifiers with different specific surface areas ranging from 280 to 740 m²/g were used for the studies. Two options were investigated to determine the most efficient method of adding additives: 1) The additive was pre-mixed with the mixing water; 2) The additive was mixed with cement until homogeneous, after which it was mixed with water.

The samples were cured under normal conditions ($T = 18\text{--}20^{\circ}\text{C}$, $\text{RH} = 90\text{--}100\%$) after molding. The compressive strength of the samples was evaluated after 28 days of curing. At least 5 samples were prepared for each composition. The strength value was determined as the arithmetic mean of the 5 samples, with a coefficient of variation of no more than 5%.

To study the deformation characteristics of hardened concrete, samples measuring $70\times 70\times 70$ mm were tested for compressive strength in a hydraulic testing machine.

The frost resistance of concrete samples was determined according to [13]. The water resistance of concrete was determined using an accelerated method following [17]. The average density of samples was determined following [18]. The compressive strength of reference and modified samples was determined according to [19].

X-ray phase analysis (XPA) was used to study the phase composition of cement stone and determine its degree of hydration. Samples of finely dispersed cement stone powder were prepared after 28 days of hardening. XPA is used to identify the minerals that make up each sample. Each mineral has a specific set of peaks with its own intensity, and a multicomponent cement stone sample includes the sum of the X-ray diffraction patterns of individual minerals. The phase composition of the samples was studied using a D2PHASER diffractometer (Bruker, USA). The phase composition analysis was performed using DIFFRAC.EVA and DIFFRAC.TOPAS software.

Electron microscopic analysis and analysis of the elemental composition of additives were performed using a JEOL JSM 520 scanning electron microscope in backscattered electron and elemental analysis modes.

The specific surface area and average particle size of the powders were measured using a PSH-12 instrument.

3. Results and Discussion

To evaluate the influence of the structural characteristics of nano-SiO₂, methods of obtaining nanoscale particles, the rational ratio in the “cement-nanoadditive” system, conditions for uniform distribution of nanoparticles in the cement paste volume, and the stability of the obtained characteristics, experimental studies were conducted, the results of which are presented in Table 12.

Table 12 – Characteristics of cement stone with nano-SiO₂

Sample No.	Sample label	Additive content, % of cement mass	W/C	28 days compressive strength, MPa	
				Saturated	Dry
1	Reference	0.00	0.270	68.1	68.1
2	Cement+H74	0.01	0.275	76.0	77.0
3	Cement+H74	0.02	0.280	75.0	81.0
4	Cement+H74	0.03	0.280	64.9	83.0
5	Cement+H74	0.04	0.285	77.0	83.9
6	Cement+H74	0.05	0.290	78.0	84.0
7	Cement+H62	0.01	0.280	64.6	77.0
8	Cement+H62	0.02	0.285	72.3	77.2
9	Cement+H62	0.03	0.285	75.2	77.3
10	Cement+H62	0.04	0.285	75.0	79.0
11	Cement+H62	0.05	0.290	76.0	81.0
12	Cement+H44	0.01	0.265	66.0	68.0
13	Cement+H44	0.02	0.265	70.0	72.0
14	Cement+H44	0.03	0.265	68.0	73.0
15	Cement+H44	0.04	0.275	65.0	69.0
16	Cement+H44	0.05	0.275	64.9	67.0
17	Cement+H23	0.01	0.270	68.0	71.0
18	Cement+H23	0.02	0.270	69.0	73.0
19	Cement+H23	0.03	0.270	69.9	73.3
20	Cement+H23	0.04	0.280	71.1	74.5
21	Cement+H23	0.05	0.285	73.0	74.9

Analysis of the data presented in Table 12 shows that all types of silicon nano-dioxide (nano-SiO₂) studied in this work contribute to an increase in the strength of cement stone on the 28th day of hardening in the range from 3 to 37% compared to the reference sample. The magnitude of the effect is determined by a combination of variable factors. It has been established that increasing the nano-SiO₂ content from 0.01% to 0.05% of the cement mass provides a strength increase of up to 32% relative to the reference composition. However, a further increase in concentration does not lead to a significant improvement in performance, which is due to an increase in the water demand of the system and corresponds to the results obtained in previous studies [6]. In this regard, subsequent experiments were conducted using the specified percentage range of the nano-modifier.

It has also been established that the effectiveness of modification largely depends on the method of additive introduction. The most pronounced increase in strength (up to 38% compared to the reference composition) was recorded when nano-SiO₂ was pre-mixed with cement. With the alternative method of introduction, agglomeration of nanoparticles is observed, which prevents their uniform distribution in the volume of the binder matrix and significantly reduces the strengthening effect.

Thus, analysis of the results obtained from studying the influence of the characteristics of silicon nanodioxid (nano-SiO₂), methods of its synthesis and introduction into cement paste, as well as the dosage of additives on the properties of the binder system, made it possible to determine the rational content of nanoscale particles in the cement matrix, which is 0.01-0.05% of the cement mass. Within this range, the increase in the strength of cement stone reaches 32%, which determined the choice of this dosage for further research. The data obtained are consistent with the results of [20], where it is noted that excessive introduction of silica nanoparticles can cause “oversaturation” of the system, slowing down the processes of hydration and hardening, which is also confirmed in several works [21].

This effect is explained by the high chemical activity and reactivity of nano-silicon dioxide, which promotes the binding of a significant portion of the mixing water into poorly soluble crystalhydrate compounds. This leads to a deficiency of free moisture necessary for the hydration of clinker minerals and, as a result, a slowdown in structure formation. To identify the mechanisms and patterns of formation of the composition, structure, and properties of cement stone, a series of physical and chemical studies of reference and modified samples was performed.

Comparative X-ray phase analysis of the hydration products of reference cement and cement with H74 (Figure 3) confirms the formation of new crystalline phases in modified cement stone.

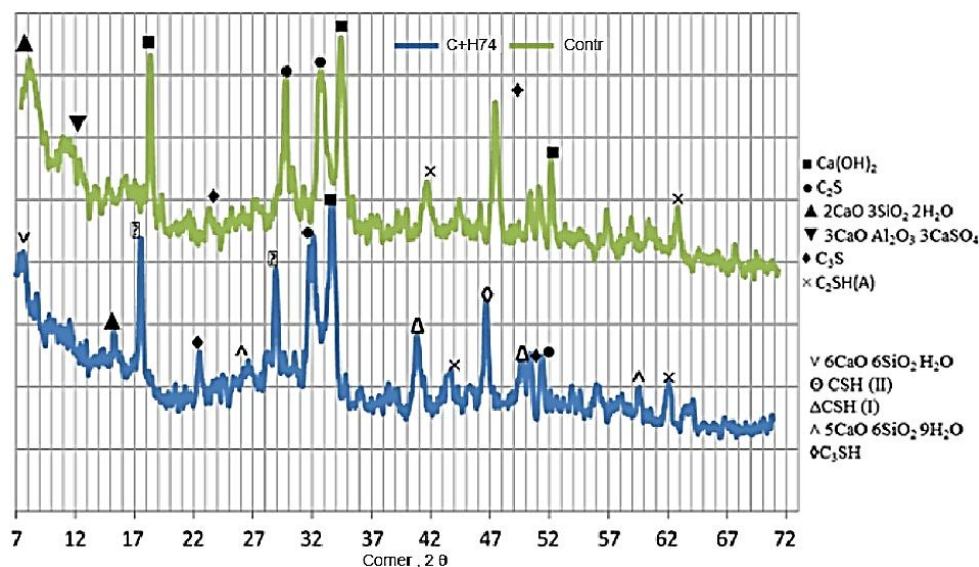


Figure 3 – X-ray images of the reference sample of SCC and SCC with nanomodifier H74

According to X-ray phase analysis data, the introduction of the modifying additive H74 contributes to the intensification of calcium hydroxide binding, which is accompanied by an increase in the content of low-base calcium hydrosilicates C–S–H ($d/n = 4.93; 2.91; 2.19; 2.07; 1.99; 1.81 \times 10^{-10}$ m), the formation of which probably determines the increase in the strength of the cement stone. A significant decrease in the amount of free calcium hydroxide is confirmed by diffractograms showing an increased background in the small-angle region and a decrease in the intensity of the diffraction peaks of the crystalline phases $\text{Ca}(\text{OH})_2$ ($d/n = 4.9; 2.64; 1.8; 1.49 \times 10^{-10}$ m), which correlates with the hydration reactions of cement clinker minerals.

The results of studies on the effect of silicon nano-dioxide with different specific surface areas and concentrations on the behavior of cement systems suggest that the chemical interaction mechanism is only realized if the composition of the nanoparticles corresponds to the hydration products of cement minerals, which ensures their inclusion in the reaction of secondary hydrate phase formation. These conclusions are consistent with the results presented in [22]. Thus, the experimental results confirm the effectiveness of modifying the structure of cement stone by introducing silicon dioxide nanoparticles.

The polyfunctional additive (PA) was made by mixing the components in a high-speed mixer at a working speed of 60 rpm. The components were loaded in stages, starting with the largest fraction (micro-calcite), followed by the introduction of microsilica and nano-modifier H74. The total mixing time was 20 minutes. During mixing, additional grinding of the coarse fraction particles took place, accompanied by their joint mechanical activation with micro-dispersed and nano-dispersed components, which ensured uniform distribution of the modifying components in the system and intensified interaction with the cement matrix. Table 13 shows the elemental composition of the additive components.

Table 13 – Additive component composition

Name	Microsilica	Microcalcite	H74
SiO_2	+	+	+
CaO	-	+	-
Al	+	-	-
C	+	+	-
MgO	+	+	-

The data presented in Table 13 show that the elemental composition of all components of the complex additive (i.e., PA) is qualitatively the same.

Comparative data from electron microscopic analysis of the structure of the reference cement stone and the modified complex additive PD and nano- SiO_2 are presented in Figures 4 and 5.

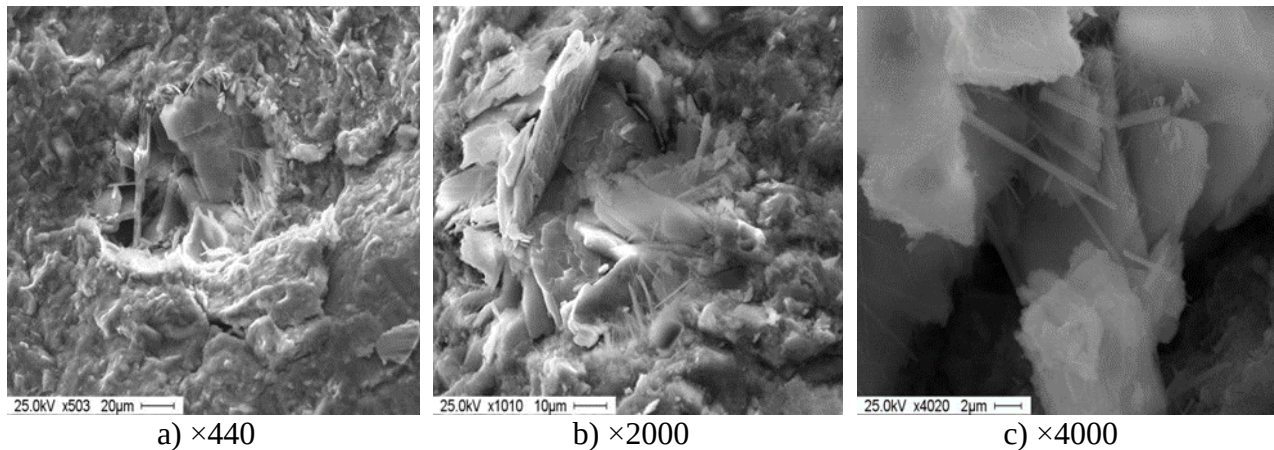


Figure 4 – Electron microscope image of a reference cement stone

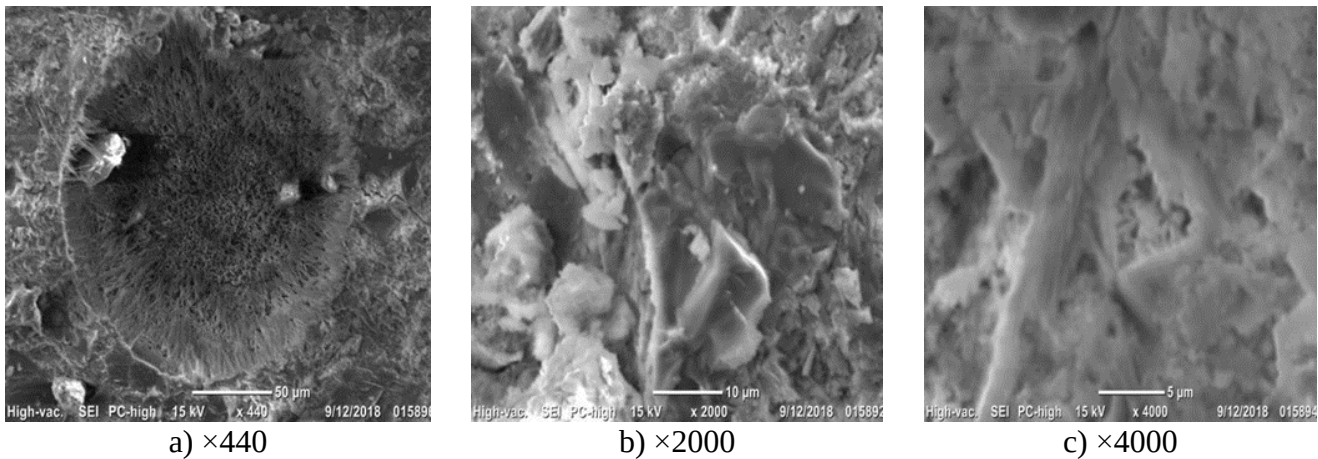


Figure 5 – Electron microscope image of cement stone modified with a complex additive of PA and nano-SiO₂

Analysis of microstructural data (Figures 4 and 5) shows that cement stone samples modified with a complex additive (polyfunctional system and nano-SiO₂) are characterized by a denser and more homogeneous structure compared to the reference samples. The structure of the reference sample (Figure 4) shows pronounced heterogeneity, a significant volume of open pores, and the presence of needle-like crystalline formations characteristic of ettringite. Only insignificant amounts of portlandite are fixed on the surface of the modified sample, while the formation of a layered structure of low-base calcium hydrosilicates (herringbone morphology) is observed.

The pore space of the modified cement stone is almost completely filled with growing hydrosilicate crystals, which ensures the compaction of the structure and the formation of additional substrates for crystallization centers. Such “clogging” of pores contributes to increased water resistance and frost resistance of concrete, which is confirmed by [23].

Given that the specific surface area of the N74 nanomodifier significantly exceeds that of the polyfunctional additive (PA) and cement, the mechanism of their combined effect on the system is determined by the sequence of adsorption on the surface of cement particles and the nature of the physicochemical interaction of the components. During the preparation of construction mixtures, adsorption shells are formed when N74 particles evenly cover the surfaces of cement and PA. The resulting adsorption contacts between the sorbent and the adsorbate act as crystallization centers, which significantly accelerates the processes of hydration and structure formation of cement stone, especially in the initial stages of hardening [24].

Table 14 shows quantitative (oxide) analysis of electron microscopic studies.

Table 14 – Quantitative (oxide) analysis of electron microscopic studies (mass fraction, %)

No.	MgO	Al ₂ O ₃	SiO ₂	SO ₃	Fe ₂ O ₃	CaO
001	1.27	5.54	15.11	4.9	4.72	67.66
002	-	7.55	51.2	10.83	-	30.45
003	-	6.6	51.3	5.7	-	36.4

To verify the results obtained by electron microscopic analysis, Table 14 shows the quantitative oxide composition of the cement stone sample modified by the PD + H74 system at three points under investigation (001, 002, and 003; see Figure 5). Analysis of the data presented allows us to conclude that low-base calcium hydrosilicates belonging to tobermorite-like phases are predominantly formed in the pore space of cement stone (Figure 5). Points 002 and 003 are characterized by a CaO/SiO₂ ratio < 1.5, which confirms the predominance of low-base calcium hydrosilicates in the composition of the formed phases.

Additionally, Figure 6 shows the results of bending tests on modified cement stone, performed in comparison with the reference composition, which allows us to evaluate the contribution of the complex additive to the improvement of strength characteristics.

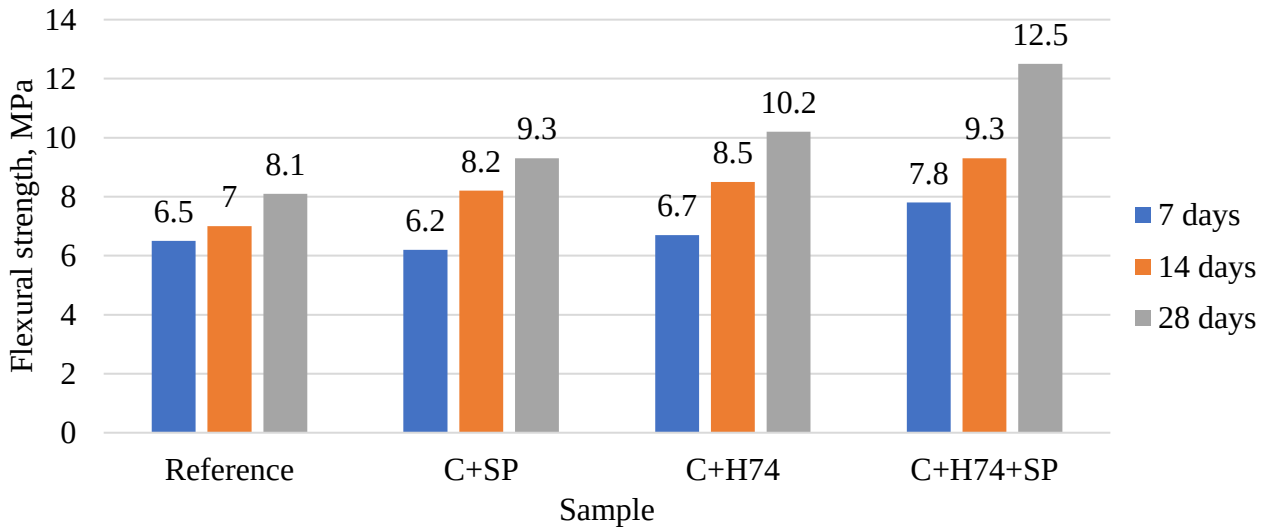


Figure 6 – Flexural strength of modified cement stone

Thus, the use of a complex additive comprising a polyfunctional system (PA) and nanomodifier N74 increased the flexural and compressive strength of cement stone by 29% and 45%, respectively, as well as a reduction in the water demand of the mixture, which is associated with the hydrophobic-hydrophilic properties of the PA components. The achieved effect may be due not only to the modification of rheological characteristics, but also to the participation of the additive in the processes of cement stone structure formation. The pore space of the matrix is filled with growing calcium hydrosilicates, which form a compact structure and additional crystallization centers, which is consistent with the results presented in [25].

The structure of a concrete mix can be represented as a homogeneous mixture of aggregate grains of various fractions and cement paste used to fill the voids between the aggregate grains and coat them. The thickness of the cement paste coating on the aggregate grains h is an input parameter. The value of the thickness of the cement paste coating of aggregate grains h can be determined as the amount of cement paste V_c minus the volume of intergranular voids V_v , relative to the surface area of the aggregate grains, S :

$$h = \frac{V_c - V_v}{S} \quad (1)$$

Taking into account expression (1) and based on the equation of absolute volumes used in calculating the composition of concrete mix, the following system of equations is formed, allowing the consumption of components per 1 m³ of concrete mix to be determined:

$$1 = V_g^{hard} + V_c^{void} + V_c^{paste} \quad (2)$$

$$V_g^{hard} = \frac{m_1}{\rho_1^n} + \frac{m_2}{\rho_2^n} + \dots + \frac{m_n}{\rho_n^n} \quad (3)$$

$$V_c^{paste} = h \cdot S_{sa} \cdot M \quad (4)$$

$$M = m_1 + m_2 + m_n \quad (5)$$

$$V_c = V_c^{void} + V_c^{paste} = C \cdot (W/C), \quad (6)$$

where: V_g^{hard} – объем зерен заполнителей, м³; V_c^{void} – volume of cement paste filling the voids in the aggregate, м³; V_c^{paste} – volume of cement paste enveloping aggregate grains, м³; m_i – consumption of the i -th filler per 1 м³ of concrete mix, kg; ρ^n – natural density of grains of the i -th aggregate, kg/м³; V_p – volume of voids, м³; V_f – total volume occupied by the aggregate mixture, м³; h – effective thickness of the cement paste film enveloping the aggregate grains, μm; S_{sa} – specific surface area of the aggregate mixture, kg/м²; ρ_c – natural density of cement, kg/м³; m_i – mass fraction of the i -th filler; W/C – water-cement ratio.

Depending on the task at hand, the proposed system of equations can be used to determine various parameters of the concrete mix. By setting target indicators for the properties of the concrete

mix and concrete, such as mobility and strength, and using mathematical calculation methods, it is possible to obtain more accurate and reliable predictive values for the strength of the material [26].

In particular, with fixed values of the water-cement ratio, mass fractions of each aggregate, and thickness of the cement shell on the surface of the aggregate grains, the system allows determining the consumption of all components included in the mixture to obtain concrete with specified physical and mechanical characteristics [26].

Two types of cement paste were used in the concrete composition: 1) reference; 2) developed (cement + polyfunctional additive (PA) in the amount of 5% of the cement mass). The initial value of the thickness of the cement paste coating on the grains is conventionally taken as 10 μm .

To verify the convergence of the calculated and experimental data on the compositions of fine-grained self-compacting concrete, a series of tests was carried out on laboratory samples to determine their main physical and mechanical characteristics. The initial compositions of the concrete mixtures used in the studies are presented in Table 15.

Table 15 – Compositions of concrete mixtures per 1 m^3

Composition No.	Crushed stone of 5-10 mm, kg	Sand, kg	Cement, kg	W/C	PA, kg	Superplasticizer, l	Slump flow, cm	Design strength of concrete, 28 days, MPa
1 (reference)	1000	670	545	0.36	-	-	60	46
2	1100	560	555	0.33	-	2.23	63	49
3	950	690	550	0.35	26.85	2.41	64	65
4	1150	590	525	0.32	26.05	2.56	66	67

10×10×10 cm cubic samples were prepared for testing. At least 20 samples were prepared for each composition. Strength was determined as the arithmetic mean of the test results for five samples for each control hardening period, with a coefficient of variation not exceeding 5%.

In concrete production, not only are the proportions of the modifying additives important, but also the algorithm for their introduction into the mixture. The polyfunctional additive (PA) should be introduced into the cement matrix at the mixing stage before the addition of fine and coarse aggregates, which ensures uniform distribution of the modifier in the volume of the cement stone. Violation of the sequence and addition of MA after the cement has been combined with the aggregates leads to uneven distribution of the components, which reduces the effectiveness of the modification. The superplasticizer was added to the finished mixture together with the mixing water.

The strength characteristics of the concrete samples were determined at 3, 7, 28, and 120 days of hardening. Figure 7 shows the comparative results of strength gain over time for the tested compositions.

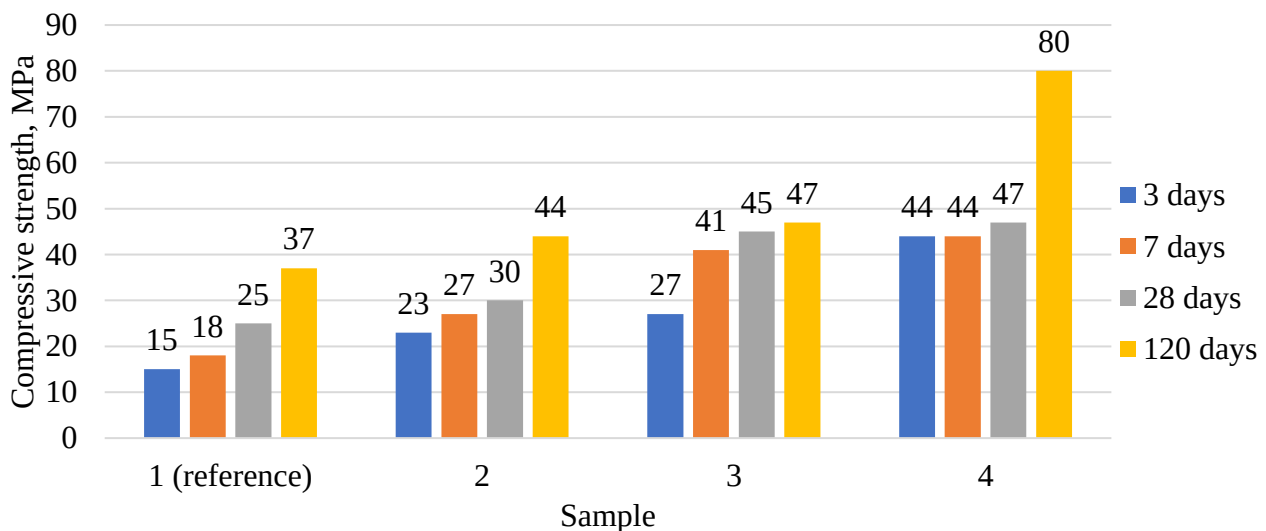


Figure 7 – Strength development kinetics of fine-grained self-compacting concrete

Analysis of the experimental data in Figure 7 shows that the introduction of a polyfunctional additive and the determination of the optimal ratio of dispersed components in the concrete mixture (composition 3) provide an increase in the compressive strength of fine-grained self-compacting concrete at different hardening times compared to the reference samples (composition 1). At 3 days – by 92%, at 7 days – by 64%, at 28 days – by 41%, at 120 days – by 38%. The addition of a plasticizer, together with PD (compositions 3 and 4), contributes to an increase in strength indicators: in 3 days – by 81%, in 7 days – by 54%, in 28 days – by 44%, in 120 days – by 48% compared to the reference (composition 1).

Compositions 3 and 4 were selected based on strength and mobility indicators, and further research was conducted on them. Thus, the water resistance of the reference and modified concrete samples was determined using the AGAMA-2 device. It has been established that modified concrete samples are characterized by a significant increase in water impermeability (grade W16) compared to reference compositions (grade W8). The increase in water resistance is explained by the formation of a denser material structure due to the rational selection of the mixture composition and a reduction in the open porosity of the cement stone.

When exposed to low temperatures accompanied by alternating freeze-thaw cycles, the greatest danger to concrete is the presence of “free water” in the pore space. When it freezes in the pores, internal pressure is formed, and repeated cycles of phase transitions associated with an increase in water volume by approximately 9% lead to progressive destruction of the pore structure. Water penetrating into the resulting microcracks contributes to the expansion of damage and the development of internal destruction in the concrete structure.

The amount of “free water” in the pore space can be reduced by using modifying additives that decrease the open porosity of the cement stone and form a denser concrete structure with increased water resistance and resistance to cyclic exposure to frost and heat.

The frost resistance of the reference and modified concrete samples was determined using the third accelerated method with multiple freeze-thaw cycles in accordance with the methodology [27]. The tests were carried out in accordance with the requirements of [27], with the reference and modified samples being pre-saturated with a 5% sodium chloride solution before testing and subsequent strength determination.

During the experiment, samples were selected for evaluation at several cycles corresponding to the intermediate frost resistance grade (with fixed mass changes of no more than 2%, which meets the requirements of [27]), as well as after the maximum number of cycles at which a decrease in the strength characteristics of the concrete was observed. The processing of the test results for determining the frost resistance grade of concrete was carried out in full compliance with the requirements of [27]. As a result, the reference concrete samples withstood 5 cycles of frost resistance testing using the third accelerated method, which corresponds to the F1200 grade, while the modified concrete with a polyfunctional additive (PA) demonstrated resistance to 27 cycles, corresponding to the F1700 grade. The results obtained confirm that the improvement in the performance properties of fine-grained self-compacting concretes is achieved by the formation of a homogeneous and compacted structure of cement stone and concrete matrix at various scale levels. This effect is due to the rational selection of the component composition of the concrete mix – from the grain composition of aggregates to microparticles of modified binder – and the application of a developed algorithm for designing the composition of self-compacting fine-grained concrete, taking into account the structural and technological characteristics of micro-dispersed components.

Table 16 – Comparative data on the physical and mechanical characteristics of fine-grained SCC

Composition	Slump flow, cm	Design strength of concrete, 28 days, MPa	Experimental concrete strength, 28 days, MPa	Water resistance, (MPa) grade	Frost resistance	Density, kg/m ³
Reference	60	49	53 (B40)	(0,8) W8	F1200	2373
Modified	67	67	77.1 (B60)	(1,6) W16	F1700	2384

Thus, the complex of physical and mechanical studies confirmed the effectiveness of the proposed method for designing the composition of fine-grained self-compacting concrete using the developed polyfunctional additive. Analysis of the experimental data obtained (Table 16) demonstrates that the use of this additive and the proposed approach to designing the composition of fine-grained self-compacting concrete ensures the production of concrete with increased strength, water resistance, and frost resistance.

4. Conclusions

1. It has been established that the introduction of nano-silicon dioxide (nano-SiO₂) with a particle size of up to 40 nm in an amount of 0.03% of the cement mass provides an increase in the compressive strength of cement stone by up to 32% (90 MPa) relative to the reference samples. This effect is due to the formation of an additional amount of high-strength low-base calcium hydrosilicates, an increase in the number of crystallization centers in the early stages of cement hydration, and the initiation of structure formation processes in the “nano-SiO₂ – micro-dispersed component – cement” system.

2. Complex (two-component) modifying additives based on nano-silicon dioxide, microsilica, and micro-calcite have been developed. Their influence on the processes of regulating the structure and physical and mechanical characteristics of cement stone and fine-grained self-compacting concrete has been experimentally investigated.

3. An algorithm for designing the composition of fine-grained concrete has been developed, taking into account the structural and technological parameters of micro-dispersed components and the thickness of the cement shell on the surface of the aggregate grains. The application of this algorithm ensures the formation of a homogeneous and compacted structure of fine-grained concrete with high-performance properties. The calculated values of the mixture composition showed satisfactory convergence with the experimental data.

4. The developed fine-grained concrete compositions with a multi-level polyfunctional additive (PA) in the amount of 5% of the cement mass ensure high performance characteristics: strength class B60, flexural strength 12.5 MPa, frost resistance up to F1700, and water resistance up to W16.

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