

It is shown that high operational reliability of structural materials, in particular at high temperatures, is achieved through the use of ultra-high strength cement composites. Studies of various types of Portland cements with mineral additives of the CEM II/A type have established that a stone based on Portland cement with superzeolite is the most resistant to high temperatures. It has been proven that due to the "self-autoclaving" effect, the strength of a stone based on CEM II/A-P 42.5 R is 1.2–1.3 times higher than a stone based on other types of CEM II/A. To obtain fast-hardening cement composites, a nanotechnological approach based on the use of sol-gel technology has been implemented. Using the methods of IR spectroscopy, electron microscopy, the fact of obtaining, by the chemical method of synthesis, an alkaline nanomodifier N-C-S-H-PCE, which is a nano-liquid based on nano-core seeds of sodium/calcium hydrosilicates, has been proved. It has been confirmed that the introduction of the alkaline nanomodifier N-C-S-H-PCE provides a significant intensification of the early structure formation processes in the paste based on Portland cement with superzeolite (after 12 hours, 24 hours and 28 days, the strength is 16.9; 30.5 and 104.1 MPa). It has been established that the complex combination of Portland cement with superzeolite, corundum aggregate, basalt fiber and alkaline nanomodifier provides rapid-hardening of ultra-high strength cement composites ($T=400\text{ }^{\circ}\text{C}$) with improved operational properties. Thus, there is reason to assert the feasibility of developing rapid-hardening ultra-high strength cementitious composites. This solves the problems associated with the need to increase their early strength and performance. As a result, it is possible to carry out repair work to protect equipment from abrasive wear at elevated temperatures

Keywords: ultra-high strength cementitious composite, superzeolite, alkaline nanomodifier, high temperatures, operational properties

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DEVELOPMENT OF RAPID-HARDENING ULTRA-HIGH STRENGTH CEMENTITIOUS COMPOSITES USING SUPERZEOLITE AND N-C-S-H-PCE ALKALINE NANOMODIFIER

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1. Introduction

One of the most important areas in building materials science is the development of new generation structural materials, in particular, ultra-dense, high strength concretes, characterized by improved construction and technical properties and durability. The need to create such highly functional building composites is due to extreme operational impacts. At the present stage, from the point of view of increasing the durability of concrete, the most promising concept is [1], according to which it is advisable to use a physical approach. According to this concept, it is necessary not to change the chemical composition of Portland cement clinker, but to reduce the water-binding ratio using highly efficient polycarboxylate-type superplasticizers and the introduction of ultrafine fillers. This will increase the packing density of the binder parts in the cement paste and improve

quality indicators. In this case, high strength concretes are obtained, having a compressive strength after 2 days of 30–50 MPa, 28 days – 60–120 MPa, frost resistance – F600, water absorption of no more than 1–2 mass %, abrasion is not more than 0.3–0.4 g/cm². Such high strength concretes are characterized by adjustable deformation indicators, including those with shrinkage compensation after 14–28 days of natural hardening.

Ultra-high performance concretes are characterized by even higher technical indicators. They represent a cementitious composite material with increased strength, durability and impact strength in comparison with high performance concretes [2]. Ultra-high performance concretes are obtained by multilevel reinforcement of the structure with multi-scale elements based on in-depth understanding of the nature of their static and dynamic strengthening during dispersed reinforcement. This provides the necessary technical

indicators, including increased crack resistance, compressive and flexural strength, impact toughness, and abrasion resistance under various operating temperature conditions. In this case, the compressive strength after 28 days should be at least 120 MPa. Ultra-high performance concretes are also used in structures subjected to various types of force effects, including dynamic and shock [3].

According to new technical solutions in the development of structural materials, the nanotechnological approach to the control of the strength synthesis of the cementitious matrix is increasingly taken into account [4]. Dispersed reinforcement with steel fibers, basalt fiber in combination with nanomodifiers allows to increase the flexural strength by 6–8 times, impact strength by 15–20 times in comparison with concretes of classes C25/30–C32/40 [5, 6].

An innovative direction in modern materials science is the development of rapid-hardening ultra-high strength cement composites with high operational properties. Therefore, studies aimed at determining the effect of mineral components, hyperplasticizers and nanomodifiers on technical indicators to achieve durability and reliability of structural materials should be considered relevant. These materials are designed to protect equipment from severe abrasive and erosive wear, in particular at high temperatures, in the cement, mining, metallurgical and energy industries. This approach makes it possible to solve a number of important environmental, economic and social problems, since the process of nanomodification of the cementitious matrix provides significant prospects in the development of technology of structural materials. At the same time, the production of cementitious composites becomes more economical in comparison with organic polymers, and products based on them become fire-resistant. As a result, new opportunities are created to develop intelligent nano-engineered concrete with increased durability.

2. Literature review and problem statement

The work [7] presents the results of studies of the mechanical and thermal properties of ultra-high performance concretes with a strength of more than 120 MPa when exposed to high temperatures up to 500 °C. However, issues related to the delayed kinetics of strength development and thermal stability of such cementitious composites remained unresolved. The reason for this may be the low reactivity of granulated blast furnace slag as one of the components, as well as the phenomenon of spalling at high temperatures. A variant of solving this problem can be the use of ultra-high strength concretes based on Portland cement CEM I with the addition of silica fume and polycarboxylate superplasticizer [8]. At the same time, microsilica can be unstable in its properties, including activity, water demand. At the same time, as a result of agglomeration processes, the problem arises of the exact distribution of this mineral additive in the mass of concrete. In addition, the introduction of an increased amount of polycarboxylate ethers in a complex with silica fume leads to a slowdown in hydration processes.

It should be noted that nanomaterials are increasingly used as modifiers, among which nanosilica is the most widely used [9]. Due to the self-autoclaving effect, nanosilica reduces thermal degradation and the risk of explosive cracking in cement composites when exposed to high temperatures [10].

The use of nanosilica makes it possible to increase the strength, durability, and waterproof of concrete, due to the extremely high chemical activity of this additive [11]. At the same time, a combination of nanoadditives and superplasticizers presents significant prospects for improving the properties of cementitious composites. Thus, complex nanomodification of polycarboxylate superplasticizer and ultradispersed additives, as well as dispersed reinforcement with heat-resistant basalt fibers provides improved properties of concretes based on Portland cement, which were exposed to elevated temperatures of 200, 400 and 600 °C [12]. Such dispersion-reinforced composites based on cement systems are characterized by high early and standard strength due to optimization of particle packing with an increase in the density of the cement paste. As a result, porosity indicators are improved, shrinkage is reduced and resistance to thermal-fire effects increases.

It should also be noted the importance of using natural ultradispersed active mineral additives, which belong to superpuzzolan, providing accelerated binding of calcium hydroxide, a hydrolysis product of the alite phase of Portland cement clinker. These mineral additives include finely ground highly dispersed zeolite tuff – superzeolite, which increases the strength and cohesion of the cementing paste [13]. As shown [14], in cementitious systems, superzeolite by Pozzolanic activity approaches microsilica. At the same time, due to the combination of mineral components with different distribution of particles by volume and specific surface area, it is possible to create microstructure-engineered composite cements with high strength. In addition, zeolite tuff determines the durability of cementitious systems in corrosive environments [15]. It is characteristic that cements containing highly dispersed zeolites are characterized by increased water retention capacity. At the same time, as a result of the microporous framework structure, the water demand of zeolites is higher than that of Portland cement CEM I, which leads to a slowdown in the kinetics of increasing the strength of the cement stone in the early period of hardening [16].

It is shown in [17] that a complex modifier based on polycarboxylate ethers (PCE), nano-SiO₂ and an alkali-sulfate activator provides the necessary quality indicators for low-energy clinker-efficient concretes. On the other hand, the use of complex organic-silica finely dispersed additives leads to the production of high strength cement compositions [18]. Increasing the packing density of cement materials by mixing with ultrafine active mineral additives plays a major role in improving the properties of cementitious composites. At the same time, ultrafine particles of mineral additives, which are characterized by high values of the specific interfacial surface area in combination with polycarboxylates, provide a more complete synergistic effect of the interaction of other components [19].

This indicates that at the present stage, one of the most promising directions for obtaining highly efficient and durable ultra-high strength concretes is the use of composites with the inclusion of nanoparticles in the cementitious matrix. The special molecular configuration of polycarboxylate superplasticizers promotes acceleration of cement hydration, and the rapid adsorption of molecules on nanoparticles in combination with the dispersion effect ensures the growth of the surface of cement compositions for reaction with water. Due to the formation of a highly rheological mixture with a minimum water content, it is ensured by the formation of a

dense microstructure of the cementitious matrix in the ultra-high strength concrete. This opens the way for the transfer of ultra-high performance concretes to a new generation of composite materials. The result is very strong and durable nano-engineered cementitious composites that provide multifunctional/reasonable performance significantly different from conventional building materials [20].

At the same time, there were still unresolved issues related to the insufficiently high kinetics of hardening of ultra-high strength concretes. This is caused by the inhibition of the processes of early structure formation in the cementitious matrix of concrete due to the increased dosage of polycarboxylate ethers [21]. It should also be noted that the main problem in the creation of nano-modified concretes is the need for uniform distribution of nanoadditives in the volume of the cementing matrix. To solve this problem, an additional liquid dispersion medium is required, which makes it possible to achieve phase continuity and control the restructuring of the substance in the nanometric order (≤ 100 nm) [22]. In this direction, the development in the direction of using nano-liquid as accelerators of the processes of early structure formation of cement systems deserves attention [23]. However, such phases do not always allow obtaining an accelerating effect as a result of agglomeration and aging processes.

Sol-gel technology in the direction of the synthesis of nanocomposites is currently of particular importance [24]. Thanks to the modification by PCE molecules with nanosized chains, ultrafine C-S-H particles are formed, which are characterized by a extremely high surface area. This creates a very strong seeding effect during the hydration of C_3S/C_2S and leads to a significant increase in the early strength of Portland cement [25]. The work [26] describes methods for the synthesis of C-S-H inoculation by using a mechanochemical approach and sol-gel synthesis. It is found [27] that C-S-H-PCE nanocomposites can effectively increase the early strength of a mortar, since the barrier to the nucleation of products decreases and the growth of large crystals is inhibited. This indicates the feasibility of developing research in the direction of increasing the efficiency of C-S-H-PCE nano-seeding to accelerate cement hydration, as well as the need to optimize their parameters, which determine significant effects as accelerators of hardening of cementitious systems.

On the other hand, alkaline activation of cementing systems also provides significant opportunities for the intensification of early structure formation processes [28]. In the process of alkaline activation based on sodium silicates, an increase in the crack resistance of concrete and an increase in the coefficient of tensile strength in bending to compressive strength up to 37–49 % is provided [29]. At the same time, sodium silicates, due to interaction with dihydrate gypsum in the composition of Portland cements, cause a sharp reduction in their setting time. Therefore, the use of multicomponent chemical additives of polyfunctional action is promising, experimental studies of the effect of which have shown an increase in the strength and waterproof of concrete due to pore colmatation by the hydration products of Portland cement [30].

Considering the above, the processes of structure regulation at the nanoscale level in cementitious systems using superzeolite, C-S-H-PCE nanocomposites and alkaline activators are of considerable scientific and practical interest. The difference between this works lies in the complex com-

ination of alkaline activators, nanomodifiers of the C-S-H type and polycarboxylate superplasticizers to intensify the processes of early structure formation of Portland cement systems with superzeolite. The study of the effectiveness of such cementitious systems determines the possibility of creating multifunctional rapid-hardening ultra-high strength composites of a new generation, which provide long-term high mechanical characteristics. This is important for the development of lining materials, in particular for cyclones in the cement industry, operated at high temperatures and severe abrasive wear.

The authors have shown some of the work that was done using C-S-H-PCE [25, 26].

3. The aim and objectives of research

The aim of research is to develop ultra-high strength composites using superzeolite and complex modifiers of the cementitious matrix at the nano-, micro- and macroscale levels.

To achieve this goal the following tasks were solved:

- to establish the influence of mineral constituents and high temperatures on the strength of different types cements;
- to synthesize the alkaline nanomodifier N-C-S-H-PCE by the method of sol – gel technology and to establish its structural features using a set of methods of physico-chemical analysis;
- to study the effect of alkaline nanomodifier N-C-S-H-PCE on the processes of structure formation of Portland cement with the additive of superzeolite;
- to determine the performance properties of rapid-hardening ultra-high strength cementitious composites, including at high temperatures.

4. Materials and methods of research

4. 1. Investigated materials and equipment used in the experiment

In the study, cements with the additive of superzeolite CEM II/A-P 42.5 R and CEM IV/A (P) 42.5 R with high strength produced by PJSC Ivano-Frankovsk (Ukraine) were used. Finely ground natural zeolite tuff of the clinoptilolite type was used as a superzeolite, which has a Blaine specific surface area of $1200 \text{ m}^2/\text{kg}$. Superzeolite has a bimodal distribution of particles by volume, while the amount of fine fraction in the range of up to $5.0 \mu\text{m}$ is 38 vol. %. This fraction makes the main contribution to the specific surface area of superzeolite, since the maximum value of the surface activity coefficient K_{isa} corresponds to $1.2 \mu\text{m}$ and is $9.71 \mu\text{m}^{-1}\text{vol.}\%$ [14]. Technologically optimized cements obtained by separate grinding and mixing of superzeolite with Portland cement. For a comparative assessment of the effect of high temperatures ($T=150-800 \text{ }^\circ\text{C}$) on the strength of the cement stone, cements of the types CEM I 42.5 R, CEM II/A-S 42.5 R, CEM II/A-LL 42.5 R PJSC Ivano-Frankivskcement”(Ukraine) were used. The grinding fineness of Portland cements according to the specific surface area is in the range of $350-440 \text{ m}^2/\text{kg}$.

Sodium/calcium hydrosilicates synthesized by the sol-gel method were used as alkaline nanomodifiers to obtain rap-

id-hardening ultra-high strength cementitious composites. Calcium nitrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and sodium metasilicate $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ were used as chemicals. For the adsorptive nanomodification of the artificially obtained C-S-H seeding, a polycarboxylate superplasticizer of the MasterGlenium ACE 430 type (PCE) based on polymers of a comb structure with nano-engineered chains (manufactured by BASF, Germany) was used. Polycarboxylate polymers provide nanomodification of C-S-H seeds with obtaining a colloidal gel, which allows accelerating the processes of cement hydration. Sodium hydroxide (NaOH) solution was used to adjust the pH of the colloidal suspension with PCE. A nanocomposite gel was obtained by mixing solutions based on $\text{Ca}(\text{NO}_3)_2 + \text{Na}_2\text{SiO}_3$ (sample 1) and $\text{Ca}(\text{NO}_3)_2 + \text{Na}_2\text{SiO}_3 + \text{NaOH}$ with the addition of polycarboxylate polymers followed by their dispersion (sample 2).

The study of the chemical composition of nanomodifiers was carried out using an ARL 9800 XP X-ray spectrometer (Thermo Electron SA, Switzerland). The fineness of the cement was determined by the Blaine method of air permeability. When determining the pH of the gel based on the C-S-H seed, a pH meter of the pH-150MI type (Ukraine) was used. C-S-H-PCE IR spectra were acquired using an FT-IR-Nicolet 8700A spectrometer. To determine the particle size distribution, a Master Sizer 3000 laser analyzer (Malvern Panalytical, Great Britain) was used. The shape and size of nanomodifiers particles, the microstructure of cement and ultra-high strength concretes were investigated using a scanning electron microscope REM 106I (SELMI, Ukraine). The microscope is equipped with microanalyzers of chemical composition, allows the use of energy-dispersive X-ray spectroscopy (EDX) for elemental analysis of a solid.

For the development of ultra-high performance composites, basalt fiber RBR-18-T10 with fiber lengths of 5 and 12 mm from TechnobasaltInvest LLC (Ukraine) was used. Corundum aggregate with fractions of 1...4 mm (hardness on the Moss scale – 9, average density – 4.02 g/cm^3) (“KORUND”, Ukraine) was used as a material with increased wear resistance.

To determine the effect of high temperatures on the strength of cement stone and ultra-high strength composites, a muffle furnace of the SNOL 8.2/1100 type (Ukraine) was used; the rate of temperature rise is $150 \text{ }^\circ\text{C/h}$. Determination of abrasion cementitious composites was carried out according to DSTU V.2.7-212: 2009 using an LCI-3 grinding wheel.

4. 2. Methods for determining indicators of properties of samples

Determination of water demand, setting time, grinding fineness and strength of cements was carried out according to DSTU EN 196-3: 2015, DSTU B EN 196-6: 2015 and DSTU B EN 196-1: 2015. Average density, water uptake and porosity of the developed ultra-high strength composites were determined according to DSTU B.2.7-170: 2009.

Particle size distribution of alkaline nanomodifiers C-S-H-PCE was determined by laser diffraction. The calculation of the particle size distribution of this method is carried out according to the Mi theory of light scattering using the model of a sphere of equivalent volume. According to the developed methodology [14], the calculation of the differential coefficient of distribution of particles by the specific surface area K_{isd} was carried out. This differential coefficient is de-

termined by the product S_p (the ratio of the surface area of the particles to their volume A/V characterizes the specific surface area relative to the volume, $\mu\text{m}^2/\mu\text{m}^3 = \mu\text{m}^{-1}$) by the content of each fraction of the material. The width of the variation of the particle distribution was determined by the slope of the uniformity of the particle size distribution (n). The slope was determined from the distribution of the data in the Rosin-Rammler-Sperling-Bennett grid.

The compressive and flexural strength of the ultra-high strength composites was determined after 2 and 28 days, including after exposure to high temperatures. The stage-by-stage heating of the samples followed by holding at temperatures in the range of $150\text{--}800 \text{ }^\circ\text{C}$ was carried out in a SNOL 8.2/1100 muffle furnace. Impact bending tests (impact strength) were carried out on pendulum impact drivers according to the Charpy method. Impact strength was determined as the ratio of the work expended to fracture the sample to the area of the sample section weakened by the notch.

5. Results of research of ultra-high strength cementitious composites with improved operational properties

5. 1. Study of the effect of main constituents and high temperatures on the strength of various types of cements

Experimental studies have established that for cement pastes CEM I 42.5 R, CEM II/A-S 42.5 R, CEM II/A-LL 42.5 R, CEM II/A-P 42.5 R and CEM IV/A (P) 42.5 R-SR cone spreading using a Vicat ring at $W/C=0.43$ is in the range 110–120 mm. As can be seen from Fig. 1, for cement stone specimens $2 \times 2 \times 2 \text{ cm}$ in size after 28 days of hardening at normal conditions, the highest compressive strength ($R_c=53.7 \text{ MPa}$) is characteristic for Portland cement with the additive of superzeolite CEM II/A-P 42.5 R. After heating of such specimens up to a temperature of $300\text{--}500 \text{ }^\circ\text{C}$ and holding them for 2 hours, the strength increases by 11 % in comparison with cement stone based on CEM I 42.5 R. In this case during the holding of the samples at $T=500 \text{ }^\circ\text{C}$ as a result of the partial decomposition of portlandite, the strength of the stone decreases slightly compared with the samples, they were kept at $T=300 \text{ }^\circ\text{C}$. It is characteristic that the largest loss of strength is characteristic of the samples based on Portland cement with limestone CEM II/A-LL 42.5 R. It should also be noted that for Portland cements CEM I 42.5 R, CEM II/A-S 42.5 R and CEM II/A-LL 42.5 R, cracking is observed on the surface of the samples. At the same time, in the temperature range up to $500 \text{ }^\circ\text{C}$ for a stone based on Portland cement with superzeolite CEM II/A-P 42.5, no cracking is observed on the surface of the samples. With a further increase in temperature, due to the decomposition of calcium hydroxide and carbonate compounds, the strength of the cement stone decreases significantly.

Studies show that stone samples based on Portland cement with superzeolite type CEM II/A-P 42.5 R are characterized by high strength indicators after exposure to temperatures in the range of up to $500 \text{ }^\circ\text{C}$. High specific surface area and volume of closed micropores in superzeolite in relation to their total volume contribute to an increased water content in such pores. This leads to the effect of “self-autoclaving” of cementitious composites with the addition of superzeolite, which ensures an increase in their strength during heat treatment.

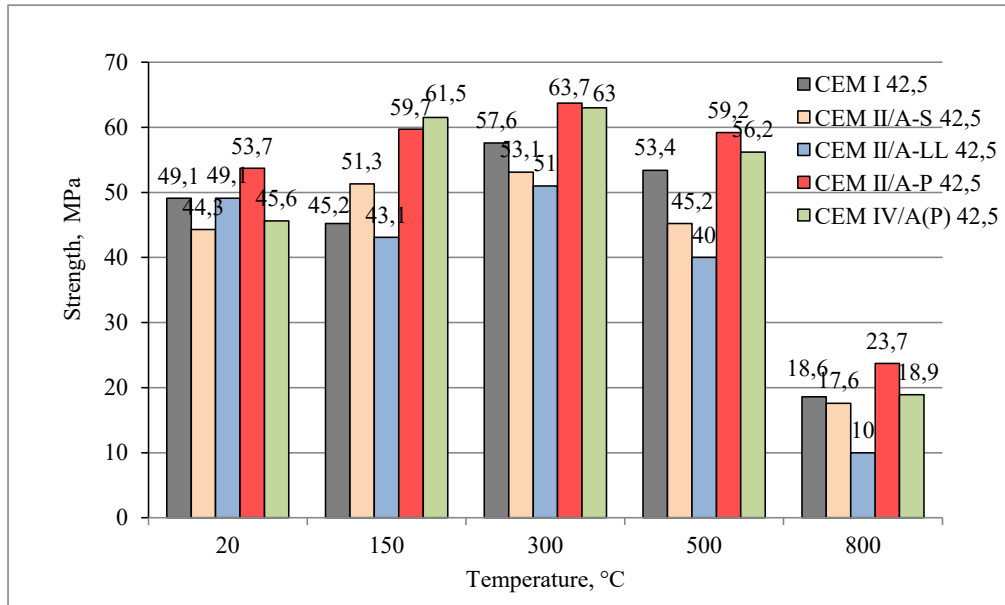


Fig. 1. The strength of a stone based on various types of cements after 28 days of hardening at normal conditions and after exposure to high temperatures (after 28 days the samples were kept at a given temperature for 2 hours)

5.2. Synthesis of alkaline nanomodifiers N-C-S-H-PCE and studies of its structure using methods of physico-chemical analysis

Using the chemical method of synthesis using the sol-gel technology, nanomodifiers were obtained, which are a colloidal mixture of ultrafine mixed sodium/calcium hydrosilicates ($xNa_2O/CaOySiO_2zH_2O$, N-C-S-H) and polymer dispersants (PCE polycarboxylate esters). It was established by IR spectroscopy (Fig. 2) that for a hydrosilicate gel (example 1) there are characteristic absorption bands in the range of $3600...3200\text{ cm}^{-1}$ and 1640 cm^{-1} , characteristic of stretching and bending vibrations of hydroxyl groups of crystallization water. Absorbances in the ranges $1468-1348\text{ cm}^{-1}$ and $840-800\text{ cm}^{-1}$ indicate the presence of nitrate groups NO_3^- . Characteristically intense absorption at $1130-1000\text{ cm}^{-1}$ and $456-400\text{ cm}^{-1}$ can be attributed to stretching and deformation vibrations of Si-O-Si bonds. It should be noted that the IR spectra of sample 2 partially show the bands of polycarboxylates, as evidenced by the absorption of stretching and bending vibrations of C-H ($2880, 1470, \text{ and } 1360\text{ cm}^{-1}$).

The microstructure and surface composition of the synthesized gels after drying at $50\text{ }^\circ\text{C}$ were studied by scanning electron microscopy and X-ray spectral analysis. As can be seen from Fig. 3, and the surface of sample 1 is strongly segmented with the formation of layered clusters based on primary inoculum particles. At the same time, on the surface of sample 2 (Fig. 3, c), more finely dispersed agglomerates appear, which, in turn, consist of submicroscopic hydrosilicate phases.

According to the data of microprobe X-ray spectral analysis (Fig. 3, b), sample 1 represents inoculation embryos with basicity $C/S=1.51$, which can be attributed to highly basic calcium hydrosilicates C-S-H (II). At the same time, for sample 2 (Fig. 3, d) the ratio $C/S=1.16$, which corresponds to low-base hydrosilicates of calcium C-S-H (I).

By the method of X-ray phase analysis it is shown (Fig. 4), for sample 1, characteristic formations of various kinds of crystal hydrates. At the same time, for sam-

ple 2, lines with $d/n=0.303$ appear; $0.279; 0.230\text{ nm}$, which can be attributed to sodium nitrate [31]. This compound crystallizes from the liquid phase of the colloidal mixture during the drying process. It should be noted that the diffraction patterns of alkaline nanomodifiers show a halo-like fragment at $2\theta=20...35^\circ$, which indicates the presence of X-ray amorphous phases. Such phases are at the stage of nucleation at the nanostructural level, since the PCE molecules, due to the phenomenon of adsorption modification, impede the processes of their recrystallization. These gel-like clusters can be classified as N-C-S-H-PCE nanocomposites.

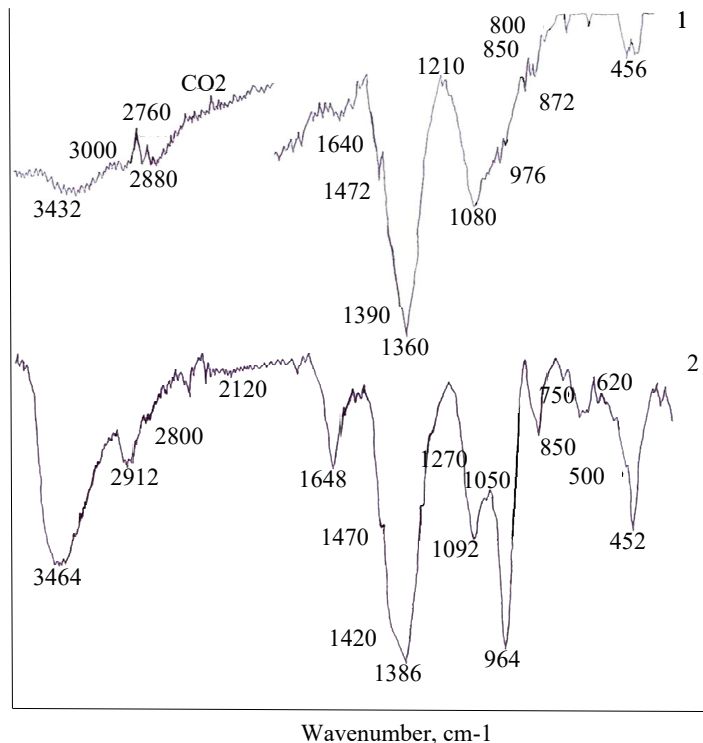


Fig. 2. IR spectra of the synthesized gels C-S-H (sample 1) and N-C-S-H-PCE (sample 2)

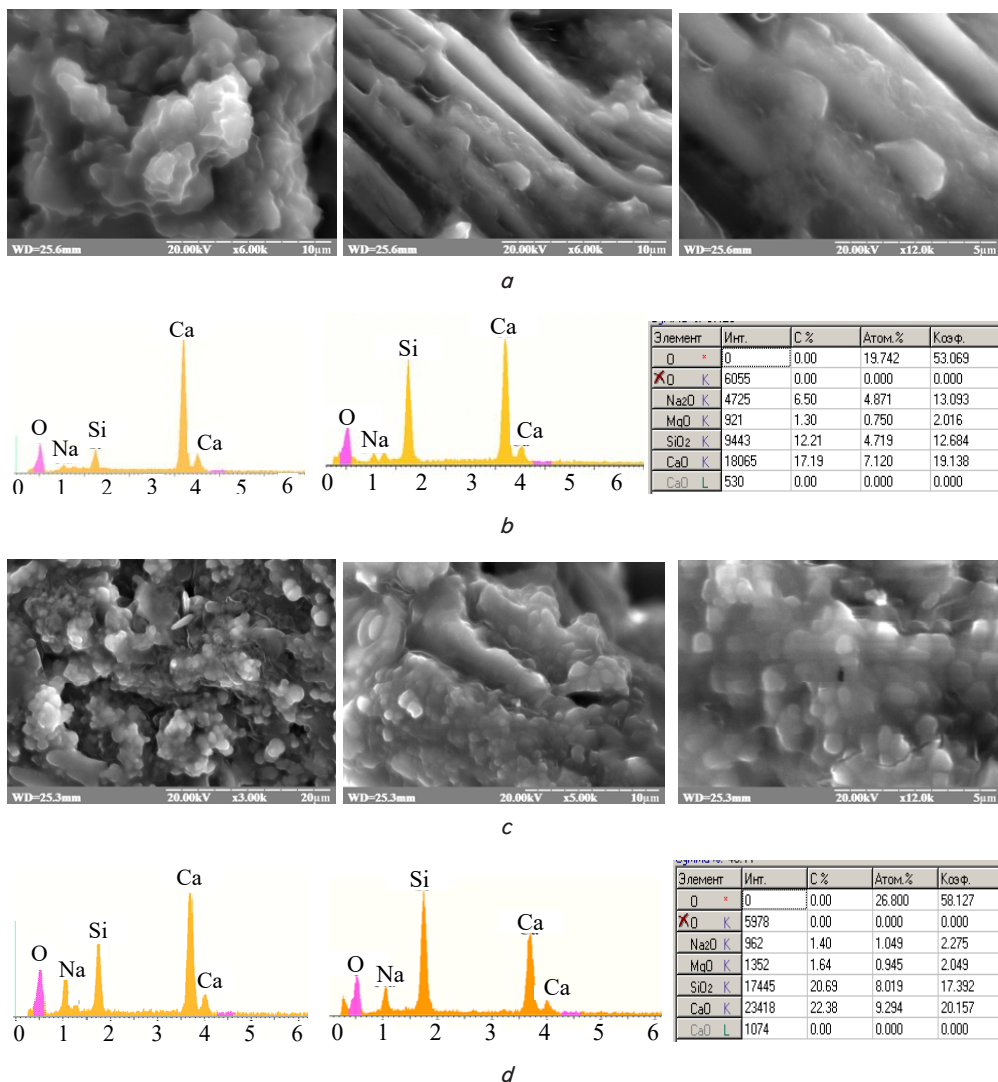


Fig. 3. Synthesized gels: *a* – micrographs of C-S-H; *b* – EDX spectra of the C-S-H surface; *c* – micrographs of N-C-S-H- PCE; *d* – EDX spectra of the N-C-S-H- PCE surface

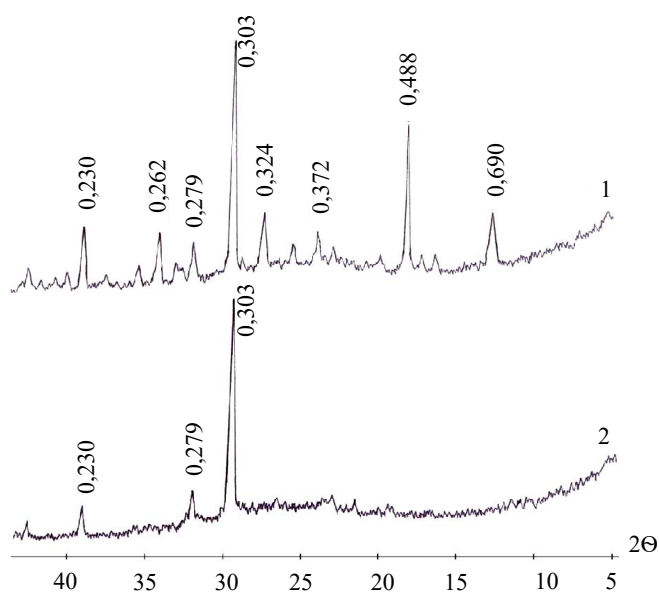


Fig. 4. Diffraction patterns of synthesis products sol-gel technology: 1 – C-S-H; 2 – N-C-S-H-PCE

According to laser diffraction data (Fig. 5, *a*), the synthesized alkaline nanomodifiers N-C-S-H-PCE has a bimodal particle distribution by volume with two maxima at 0.5 and 5.6 μm (for these fractions, the content of particles by mass is 36 and 64 mass. %). At the same time, according to the data on the distribution of particles by specific surface area (Fig. 5, *b*), namely, in the range up to 1.0 μm , almost 90 % of the specific surface area of ultrafine particles of the alkaline modifier is concentrated. At the same time, the maximum value of the differential coefficient by specific surface area ($K_{isa}=45 \mu\text{m}^{-1} \text{vol. \%}$). Is an order of magnitude higher compared to the highly dispersed fraction of Portland cement ($K_{isa}=4.5 \mu\text{m}^{-1} \text{vol. \%}$). The high granulometric uniformity of the N-C-S-H- PCE nanogel is confirmed by the slope n , which reaches $n=0.85$.

Thus, based on the above research results, it is possible to state the fact of obtaining alkaline nanomodifiers based on mixed low-basic sodium/calcium hydrosilicates N-C-S-H-PCE. At the same time, the chemical method for the synthesis of alkaline nanomodifiers of the N-C-S-H-PCE type makes it possible to obtain nanofluids based on nanosized seed nuclei of sodium/calcium hydrosilicates, on the surface of which PCE molecules are adsorbed. A by-prod-

uct of this synthesis in the liquid phase is sodium nitrate, which is often used to accelerate the hardening and increase the strength of concrete.

N-C-S-H-PCE cement stone with a large number of gel-like phases is formed (Fig. 6, c). Microprobe X-ray spectral analysis (Fig. 6, b, d) indicates that when N-C-S-H-PCE nanomodifiers are introduced, mixed calcium/sodium hydrosilicates are also fixed.

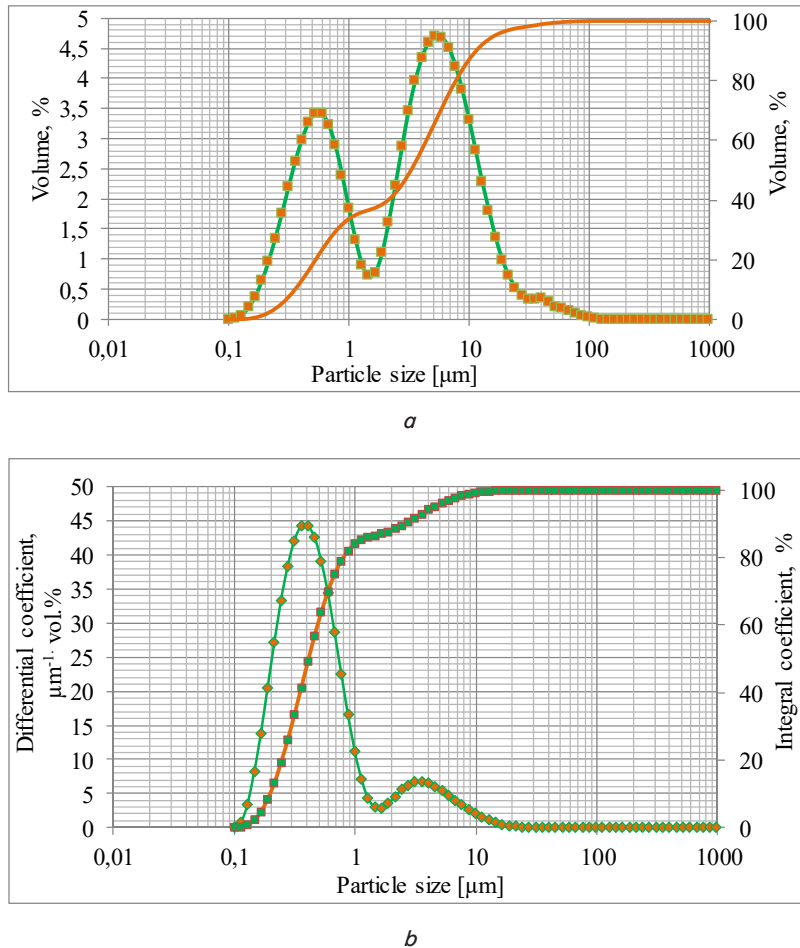
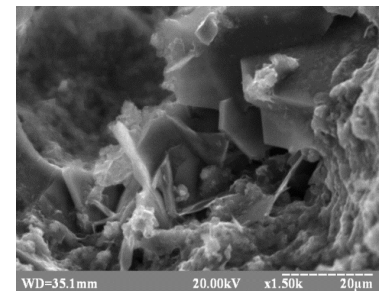


Fig. 5. Granulometric composition of the synthesized alkaline nanomodifiers N-C-S-H-PCE: *a* – by volume, *b* – by specific surface area

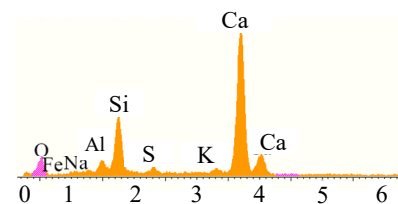
5. 3. Study of the influence of alkaline nanomodifiers N-C-S-H-PCE on the processes of structure formation of Portland cement with the addition of super zeolite

Studies of the physical properties of the cement paste found that the introduction of 1.5 mass. % alkaline nanomodifiers N-C-S-PCE accelerates the setting time of Portland cement CEM II/A-P 42.5 R by 30–40 min. The strength of a stone based on nano-modified Portland cement CEM II/A-P 42.5 R in the early period (after 12 and 24 hours) increases by 4.9 and 2.8 times compared to CEM I and reaches values of 16.9 and 30,5 MPa respectively. After 7 and 28 days, the strength of the nanomodified cement stone increases 1.9–1.5 times and is 72.1 and 104.1 MPa, while its capillary porosity decreases to 1.2 %. The above results indicate that the increased surface activity of the N-C-S-H-PCE nano-seeding provides a significant accelerating effect in the early period of structure formation.

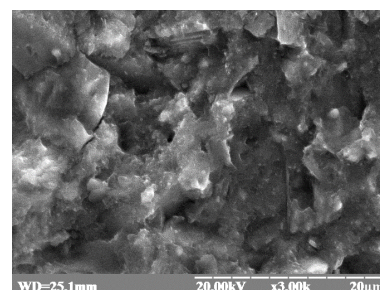
As can be seen from Fig. 6, a, for a stone based on Portland cement with superzeolite CEM II/A-P, modified with C-S-H, a characteristic inhomogeneous porous structure in which hexagonal crystals of portlandite are located. With the addition of 1.5 mass. % alkaline nanocomposite



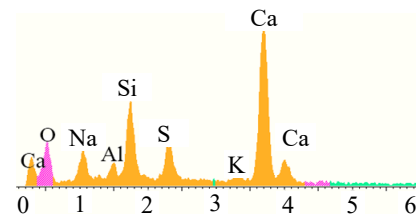
a



b



c



d

Fig. 6. Micrographs and EDX-spectra of cement stone modified with additives: *a* – C-S-H; *b* – C-S-H; *c* – N-C-S-H-PCE; *d* – N-C-S-H-PCE

It should be noted that sodium/calcium hydrosilicates can largely be analogs of pectolite (mixed Ca, Na-hydrosilicate), the structure of which is based on silicon oxygen radicals [Si₃(O,OH)₉], which are analogs of wollastonite chains. At the same time, such phases are characterized by an unstable structure and can decompose with the age of hardening. However, in the presence of aluminate anions, they serve as a matrix for the formation of an N-A-S-H gel, consisting of crystals of a frame structure of a zeolite nature, which ensure the durability of the cement matrix of concrete [29].

5.3. Determination of the performance properties of ultra-high strength cement composites, including at high temperatures

Based on the studies carried out, the composition of the ultra-high strength cementitious composites was designed based on Portland cement with superzeolite CEM II/A-P 42.5 R, corundum aggregate (CA) of fractions 1...4 mm (C:CA=1:2) and alkaline nanomodifiers N-C-S-H-PCE. As can be seen from table 1, nanomodified concrete characterized by increased mechanical properties at an early age – at 2 days compressive strength reaches $f_{cm2}=91.6$ MPa, and tensile strength – $f_{ct2}=10.8$ MPa. It is characteristic that during thermal exposure to a temperature of 400 °C for such composite, compressive and tensile strength increase to $f_{cm2}=157.5$ MPa and $f_{ct2}=15.6$ MPa. A similar strength of composites is achieved during hardening under normal conditions only after 28 days ($f_{cm28}=160.5$ MPa). In this case, the impact strength is 2.7 kJ/m², the abrasion index is 0.02–0.04 g/cm².

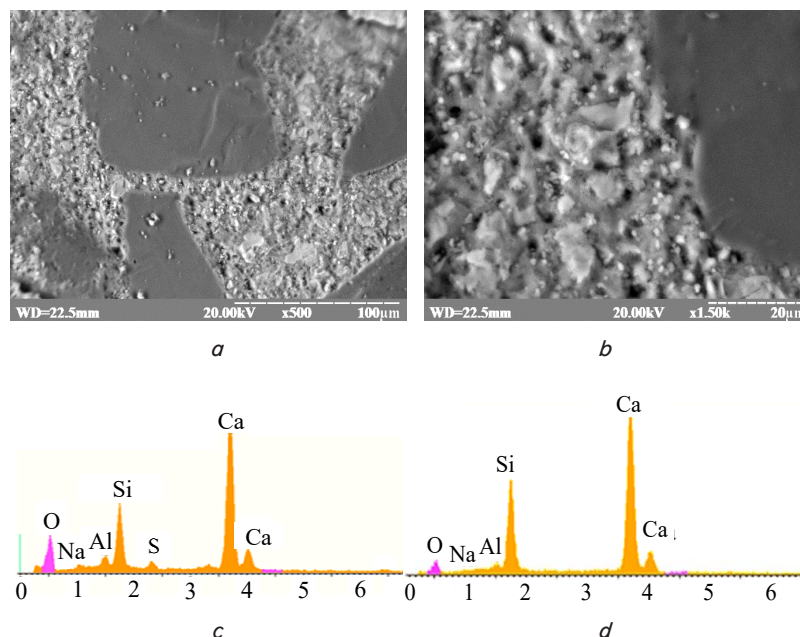


Fig. 7. Rapid-hardening ultra-high strength cementitious composite after heat treatment ($T=400$ °C): *a, b* – electron micrographs; *c, d* – spectra of microprobe X-ray spectral analysis

Table 1

Indicators of ultra-high strength cementitious composite
(Water/Mix=0.10)

Properties	Results
Use temperature, °C	400
Average density, kg/m ³	2900
Flexural/compressive strength, MPa:	
after 2 days (n.c.)	10.5/90.8
after 2 days *	15.6/157.5
after 28 days (n.c.)	15.9/160.5
Impact strength, kJ/m ²	2.7
Abrasion, g/cm ²	0.02

Note: * – the strength of the samples after 2 days in n. c. and after holding ($\tau=4$ h) at $T=400$ °C

According to the data of scanning electron microscopy (Fig. 7, *a, b*), the ultra-high strength composite after heat treatment ($T=400$ °C, $\tau=4$ h) is characterized by a dense microstructure and strong contacts between the corundum aggregate grain and the cementitious matrix. At the same time, the strengthening of the transition zone and the improvement of interfacial interaction in composite is largely ensured by the introduction of alkaline nanomodifiers N-C-S-H-PCE. Microprobe X-ray spectral analysis confirmed the presence of blended calcium/sodium hydro-silicates (Fig. 7, *c, d*).

The data presented indicate the high efficiency of the developed ultra-high strength cementitious composites and the possibility of their use under conditions of abrasive wear and thermal effects. The combination of rapid-hardening Portland cements with superzeolite, alkaline nanomodifiers, corundum aggregate and basalt fiber makes it possible to obtain a high-intensity mixture with increased operational properties, in particular at temperatures up to 400 °C.

Thus, the developed rapid-hardening ultra-high strength cementitious composites provides a significant increase in especially early strength, as well as abrasion resistance during operation at high temperatures. This indicates that such composites can be used for the repair work of cyclone heat exchangers of the upper stages of a cement kiln and other equipment under conditions of high temperatures and extreme abrasive wear.

6. Discussion of the results of the study of ultra-high strength cementitious composites

Ultra-high strength cementitious composites are a new generation of concretes based on high-tech mixtures that provide the necessary properties during hardening under various operating conditions. This creates the possibility of obtaining materials designed to protect equipment from abrasive and erosive wear at high temperatures in various industries. The main condition for efficiency is the use of reliable cement composites for lining and repairs, ensuring long equipment life.

As follows from the results obtained, the addition of superzeolite in the composition of blended Portland cement CEM II/A-P largely determines the operational properties of the cementitious matrix of ultra-high strength composites, especially when exposed to high temperatures. At the same time, the wrong choice of the mineral components of the cement when designing ultra-high strength composites can lead to a decrease in the quality of the material and an obvious deterioration in operational properties. The results show that cement stone based on CEM I 42.5 R, CEM II/A-S 42.5 R and CEM II/A-P 42.5 R (paste 1: 0, W/C=0.42) is characterized by spreading cone within 110–120 mm. It is shown (Fig. 1) that the highest strength ($R_c=53.7$ MPa) after 28 days of hardening under normal conditions is characteristic of

Portland cement with superzeolite CEM II/A-P 42.5 R. After further heating of cement specimens to $T=300\text{--}500\text{ }^{\circ}\text{C}$ high strength at the level of 63.7–59.2 MPa is characterized by a stone based on Portland cement with superzeolite. This is due to the structural features of super zeolite, the main mineral of which is clinoptilolite. Due to the specific structure of the three-dimensional and aluminosilicate lattice of clinoptilolite, a developed system of micropores and channels is formed, filled with water molecules and exchangeable cations (Na, Ca). As a result, after heat treatment of such a cement stone, the effect of “self-autoclaving” is created, which largely provides an increase in strength without cracking. It has been established (Fig. 1) that Portland cement with superzeolite CEM II/A-P 42.5 R is the most resistant to high temperatures and makes it possible to obtain a strong cementitious matrix.

On the other hand, the addition of superzeolite leads to a decrease in the mobility of the cement paste, which leads to an increase in the water demand of cement composites [16]. An effective solution to this problem is the application of the principle of nanomodification with gel-like particles C-S-H using polycarboxylate ethers [17]. The advantage of such accelerators in comparison with traditional ones is that the growth of early strength occurs without a decrease in the final strength. However, it is impossible not to notice the practical data of works [9, 11, 12], the authors of which also describe the significance of the effect of nanosized additives using the nanotechnological bottom-up approach on the acceleration of the processes of early structure formation of concrete. However, as a result of agglomeration processes, the effectiveness of such nanomodifiers as accelerators of hardening of cement systems may decrease. According to studies [25], after dispersing agglomerates using ultrasound, the average particle size of the colloidal gel can reach $d_{50}=50\text{ nm}$, which corresponds to the nanostructural level.

On the basis of these studies, using the chemical method of synthesis according sol-gel technology, alkaline nanomodifiers N-C-S-H-PCE were obtained. A new type of innovative accelerators is a seeding gel containing sodium/calcium hydrosilicates N-C-S-H, stabilized by polycarboxylate polymers with a comb structure. Such nanodispersed compounds act as a catalyst for hydration reactions of clinker minerals. The results indicate that the alkaline modifier is a nano-liquid based on nano-core of blended Na, Ca-hydrosilicates N-C-S-H and PCE polycarboxylate esters. It was established by the methods of physico-chemical analysis (Fig. 2–4) that agglomerates of low-basic hydrosilicates ($\text{Ca/Si}<1.5$) predominate in the composition of nanomodifiers to a greater extent. The method of laser diffraction (Fig. 5) shows an increased surface activity of particles of alkaline nanomodifiers ($K_{isa}=45\text{ }\mu\text{m}^{-1}\text{ vol. \%}$) and their granulometric uniformity ($n=0.85$).

The high effectiveness of the action of alkaline nanomodifiers is confirmed by the results of studies of the processes of structure formation of cement paste based on Portland cement with superzeolite CEM II/A-P 42.5 R. At the same time, alkaline nanomodifiers N-C-S-H-PCE also stimulates the interaction of active mineral additives, in particular superzeolite, and in combination, this provides a significant increase especially early and final strength of cement stone. So, after 12 and 24 hours, the strength increases 4.9 and 2.8 times and is 16.9 and 30.5 MPa, and after 7 and 28 days it increases 1.9–1.5 times and reaches values of 72.1 and 104.1 MPa.

The result of the proposed solutions is the development of rapid-hardening ultra-high strength cementitious composites with improved performance after heat treatment ($T=400\text{ }^{\circ}\text{C}$) – flexural/compressive strength 15.6/157.5 MPa, impact strength – 2.7 kJ/m², abrasion – 0.02 g/cm² (Table 1). The use of Portland cement with the superzeolite, corundum aggregate and alkaline N-C-S-H-PCE nanomodifiers leads to the production of ultra-high strength composites, which represent a new generation of ultra-high performance concretes. In this sense, of particular interest is the interpretation of the results of electron microscopy and microprobe X-ray spectral analysis shown in Fig. 6, *a–c*, confirming the establishment of the described fact. The method of electron microscopic analysis (Fig. 7) shows the formation of a particularly dense fine-grained microstructure of the cementitious matrix of the ultra-high strength composite. At the same time, low-basic hydrosilicates C-S-H (I) improve interfacial interaction with strengthening of the transition zone with corundum aggregate.

Thus, the control of the structure at the nanoscale level provides an opportunity for the development of multifunctional rapid-hardening ultra-high strength binders of a new generation with high mechanical characteristics, wear resistance, etc. reinforcement with basalt fiber and fine-grained corundum aggregate. Such nano-engineering cementitious composites can be classified as chemically bonded ceramic compounds. The relevance of their use is due to the fact that the service life of objects increases by 2–6 times. At the same time, resistance increases under conditions of extreme abrasive wear and heat-fire exposure, determines the efficiency of using the developed cement composites when exposed to high temperatures in a short-term or long-term mode. At the same time, the use of the developed Portland cement composites is limited to a temperature range of up to 400 °C, because at higher temperatures due to the decomposition of portlandite is possible for their explosive cracking. Therefore, in order to increase the efficiency of rapid-hardening ultra-high strength composites at high temperatures, it is advisable to continue research towards the development of alkali-activated zeolite-containing cements with various types of nanomodifiers.

In this case, it is also advisable to study the effect of various types of fibers and aggressive media on the mechanical and operational properties of hybrid engineering cementitious composites. This determines the further direction of the development of this research.

7. Conclusions

1. It has been found that for cement stone based on Portland cements CEM I 42.5 R and CEM II/A-S 42.5 R (W/C=0.43, paste 1:0) after 28 days of hardening followed by exposure to high temperatures ($T=300\text{--}500\text{ }^{\circ}\text{C}$), the strength is about 45.2–57.6 MPa. By visual observations, it was established that hair cracks are present on the surface of the cement stone based on CEM I 42.5 R and CEM II/A-S 42.5 R. It has been shown that the highest strength at the level of 59.2–63.7 MPa is characteristic of Portland cement with superzeolite CEM II/A-P 42.5 R. This indicates its high resistance to high temperatures due to the so-called “self-autoclaving” effect.

2. Using the sol-gel technology, an alkaline gel N-C-S-H-PCE was synthesized, which is a nanomodifier of

cement composites. It has been shown by IR spectroscopy and microprobe X-ray spectral analysis that for alkaline nanomodifiers N-C-S-H-PCE, blended sodium/calcium hydrosilicates N-C-S-H are characteristic. It has been established by laser diffraction that alkaline nanomodifiers are characterized by increased surface activity ($K_{isa}=45 \mu\text{m}^{-1}$ vol. %) and high granulometric uniformity ($n=0.85$).

3. It has been shown that the addition of nanomodifiers N-C-S-H-PCE provides a directed regulation of the processes of structure formation and a significant increase in the early strength of stone based on Portland cement with superzeolite CEM II/A-P 42.5 R. Thus, after 12 and 24 hours, the strength is 16.9 and 30.5 MPa, and after 7 and 28 days it increases 1.9–1.5 times and reaches values of 72.1 and 104.1 MPa. In this case, its capillary porosity decreases to 1.2%. It has been established that the microstructure of nanomodified cement stone is denser due to colmatation by finely dispersed low-base C-S-H phases and hydroaluminosilicates.

4. It has been established that the production of rapid-hardening ultra-high strength cementitious composites, operated at high temperatures, is provided through the use of Portland cement with superzeolite, corundum

aggregate, basalt fiber and alkaline N-C-S-H-PCE nanomodifiers. After holding at high temperatures ($T=400 \text{ }^\circ\text{C}$, $\tau=4 \text{ h}$), such cementitious composites are characterized by even higher flexural/compressive strength ($f_{ct2}/f_{cm2}=15.6/157.5 \text{ MPa}$), increased impact strength – 2.7 kJ/m^2 , low abrasion – $0.02\text{...}0.04 \text{ g/cm}^2$. It has been shown that the high efficiency of the developed nano-engineering composites is provided due to the dense monolithic structure at the nano-, micro- and mesostructural levels by improving the interphase interaction and strengthening the transition zone. This ensures a long service life in extreme abrasive environments and makes them suitable for use in the cement industry as a lining material at temperatures up to $400 \text{ }^\circ\text{C}$.

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