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Study of the Structure and Properties of Concrete Modified with Nanofibrils and Nanospheres

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Abstract: The application of modifying nanoadditives in the technology of cement composites is currently a relevant and widely researched topic in global materials science. The purpose of this study was to investigate new nanoadditives—nanofibrils made from synthesized wollastonite (NF) and nanospheres from corundum (NS)—produced by LLC NPK Nanosystems (Rostov-on-Don, Russia) as a modifying additive. During the experimental investigations, the mechanical properties of cement pastes and concrete were examined. This included an analysis of the density, compressive and bending strength, as well as water absorption of concrete that had been modified with NF and NS additives. X-ray phase and microstructural analyses of concrete were performed. It was established that modification of cement composites with NF and NS additives had a beneficial effect on their properties, and the optimal amount for both types of additives was 0.3% by binder weight. The highest recorded enhancements in compressive and flexural strength of concrete with 0.3% NF were 7.22% and 7.04%, respectively, accompanied by a decrease in water absorption by 4.70%. When modifying concrete with 0.3% NS, the increases in compressive and flexural strength were 2.71% and 2.48%, and water absorption decreased by 1.96%. Modification of concrete with NF and NS additives did not have a significant effect on the change in concrete density, which was no more than 1%. Based on the results of phase analysis, it was established that concrete with NF and NS additives were characterized by the presence of five main phases: quartz, portlandite, calcite, larnite, and olivine-Ca. It was found that compositions with 0.3% NF and NS differed from the control composition by the presence of such a phase as olivine-Ca. Microstructural analysis confirmed the effectiveness of NF and NS additives. The microstructure of the modified concretes was distinguished by the extensive occurrence of clusters composed of calcium silicate hydrate zones. The conducted studies prove the possibility of using NF and NS as modifying nanoadditives in the technology of cement composites. The addition of nanofibrils from synthesized wollastonite is the most effective and promising and is recommended for use in real construction practice.

Keywords: concrete; modification; nanoadditives; nanospheres; nanofibrils

1. Introduction

The topic of enhancing the quality of building materials bears relevance in current construction. This stems from the requirement for optimizing the utilization of existing materials by maximizing their potential through appropriate modification. The enhancement of current materials is a crucial task that enables significant savings in material, economic, and labor resources [1–3]. This requires not only experimental confirmation of the effectiveness of modification of existing building materials but also scientific and fundamental justification at all levels of interactions occurring during the formation of structures of modified materials [4–6].

Concrete is one of the most promising and commonly used building materials, and nanomodification is an innovative method for improving its structure and properties. Nanomodification involves the introduction of additional components called nanoadditives into the composition of existing known concretes [7]. Research on the nanomodification of cement composites is conducted globally, with multiple advanced theories addressing topics like the modification of concrete using nano-SiO_2, carbon nanotubes, cellulose nanotubes, and other nanoadditives [8]. The addition of nano-SiO_2 for the modification of cement composites is considered one of the most widely studied and highly popular topics. With its high content of over 90% silicon dioxide, this additive plays a crucial role in activating hydration processes and enhancing the formation of additional calcium hydrosilicates (CSH), thereby greatly enhancing the properties of the composite. For example, in [9], modification of concrete with silicon dioxide made it possible to maintain higher resistance to destruction after several freeze–thaw cycles in comparison with identical concrete of a control composition. The introduction of 2% nano-SiO_2 into concrete with recycled aggregates can improve its properties and reduce shrinkage strains [10]. The addition of 5% nanosilica together with fly ash increased the strength and crack resistance parameters of concrete by up to 40% and reduced CO_2 emissions [11]. Similarly, in studies [12–14], the introduction of nano-SiO_2 additive provided an improvement in both strength and durability properties. Another relevant and popular nanoadditive is carbon nanotubes. In a study [15], the use of carbon nanotubes up to 0.05% in UHPC led to minor increases in compressive strength and increased resistance to chloride penetration. Adding carbon nanotubes to recycled fine aggregate concrete improves strength properties. SEM analysis proves that carbon nanotubes in these types of concrete fill the pores inside the sample and bridge cracks [16]. The positive effect of modifying cement composites with carbon nanotubes was also confirmed by studies [17–19]. It should be noted that the use of cellulose nanofibrils is being actively studied in the technology of cement binders. In [20], the use of 0.09% cellulose nanofibrils provided an increase in compressive strength of up to 26%. This additive also helps to change the microstructure of the composite, creating tunnels in it for transporting water to unhydrated cement grains. Furthermore, in previous research [21,22], it has been observed that the incorporation of a small amount of cellulose nanofibril additive, specifically up to 0.2%, leads to a substantial enhancement in strength characteristics, with an increase of up to 28%, improved frost resistance, and a denser composite structure. The reason for the beneficial outcome achieved through the integration of cellulose nanofibrils into cement composites can be attributed to the additive's capacity to enhance the microstructural characteristics of the cement matrix. This improvement results in a condensed matrix with reduced capillary pores and micro-cracks. Hence, all the positive effects associated with improved strength properties, increased corrosion resistance, and frost resistance are observed [23–26].

A notable area that attracts attention is the modification of cement composites with additives based on synthetic wollastonite and corundum. CaO and SiO_2 are the two primary constituents that make up wollastonite. In addition to the principal constituents, there may be trace amounts of Al_2O_3, Fe_2O_3, MgO, and Na_2O [27,28]. For example, in [29], replacing part of the binder with the addition of finely ground wollastonite accelerated the hydration of C_3S and the reaction of the aluminate phases. The substitution of some of the cement with a blend of wollastonite and fly ash, up to 45–55%, leads to an improvement in mechanical properties [30]. Similarly, in studies [31–33], modification of cement composites with wollastonite improved their physical and mechanical properties and increased durability. Corundum is a crystalline α-aluminum oxide (Al_2O_3). In [34], the use of Al_2O_3 micropowder up to 10% improved strength properties and reduced shrinkage. The use of nano-Al_2O_3 in an amount from 1% to 4% increased the density of the composite and its mechanical properties [35]. The positive effect of nano-Al_2O_3 on the properties of cement composites is confirmed by research [36,37]. Note that in most cases, the additives of wollastonite and corundum, introduced instead of part of the cement, are crushed powder with a particle size comparable to the size of cement particles [27–34]. In general, in comparison with other additives such as ash, microsilica, slag, graphene), wollastonite is somewhat inferior in terms of the final physical and mechanical properties of composites [38,39]. However, in some aspects, wollastonite shows a better result, for example, in comparison with talc and fly ash, in terms of the setting time of the repair mortar [40]. In addition, wollastonite, a natural material with easy access and low cost, can be added in a higher proportion to the mixture of magnesium–potassium phosphate cement, and therefore is especially attractive in comparison with metakaolin, fly ash, and pumice, while all additives provided high compressive strength of the composite [41]. Corundum, in comparison with other additives, is also somewhat inferior in terms of the characteristics of composites, but the mechanism of its action in cement composites has not yet been studied much [34–37,42]. In this study, the use of a new type of additive of nanofibrils from synthesized wollastonite and nanospheres from corundum produced by NPK Nanosystem LLC (Rostov-on-Don, Russia) was studied.

The scientific novelty of the research lies in the investigation for the first time of the effect of nanoadditives in the form of nanofibrils and nanospheres. The relationships between the initial parameters and properties of nanofibrils and nanospheres and the output values of the properties of cement pastes and concrete, such as compressive and bending strength, density, water absorption, phase composition, and microstructure, were obtained. The purpose of the research was to analyze the possibility of using nanofibrils from synthesized wollastonite and hollow nanospheres from corundum produced by LLC NPK Nanosystems (Rostov-on-Don, Russia) as nanomodifying additives in the technology of cement composites. The primary goals of the study were as follows.

- Development of experimental compositions of concrete mixtures, taking into account the actual properties of the raw materials.
- Production of experimental samples of cement pastes and concretes of control composition and compositions modified with nanofibrils from synthesized wollastonite and hollow nanospheres from corundum in various dosages.
- Conducting experimental studies of cement pastes and concretes, including an assessment of compressive and flexural strength for cement pastes and assessment of density, compressive and flexural strength, water absorption, phase composition, and microstructure for concrete.
- Comparison of nanofibrils and nanospheres according to the criterion of the effectiveness of their influence on the properties of cement composites.
- Analysis of the experimental results obtained and determination of the most effective type of additive and optimal ranges of its dosages, as well as comparison of the results obtained according to the criterion of efficiency of nanofibrils and nanospheres with other types of nanoadditives used in the technology of cement composites.
- Development of real recommendations for the concrete industry.

Achieving the research objective will contribute to the development of construction. The reason for this is primarily the advantage of raw materials, such as the use of inexpensive nanoparticles derived from by-product waste, which can potentially replace costly components. In terms of prescription advantages, existing concrete compositions have been corrected with the rationalization of their cost and resource intensity. From a technological point of view, new organizational and technological solutions have been provided on the production base of construction. Finally, from the point of view of achieving the goals of sustainable development in construction, a reduction in construction costs and an increase in the environmental friendliness and cost-effectiveness of construction have been achieved. All this will favorably affect the achievement of the goals of sustainable development in construction.

Taken together, all the knowledge gained will form the basis of new theoretical principles regarding the nanomodification of concrete.

2. Materials and Methods

2.1. Materials

For the manufacture of experimental samples of cement pastes and concrete, the following raw materials were utilized as the primary components:

- Portland cement CEM I 42.5N (PC) produced by CEMROS (Moscow, Russia);
- Crushed sandstone (CrS) produced by Solntsedar-Don (Rostov-on-Don, Russia);
- Quartz sand (QS) and polyfractional sand (PS) produced by Don-Resource (Kagalnik, Russia);
- Nanofibrils from synthesized wollastonite (NF) and nanospheres from corundum (NS) produced by LLC NPK Nanosystems (Rostov-on-Don, Russia).

Table 1 provides an overview of the characteristics of the raw materials.

Table 1. Characteristics of raw materials.

Raw Materials	Indicator	Actual Value
PC	Specific surface area (m^2/kg)	340
	Setting times (min) - start - end	 140 220
	Standard consistency of cement paste (%)	28.3
	Compressive strength at 28 days (MPa)	48.1
	Bending strength at 28 days (MPa)	5.9
	C_3S (%)	72.3
	C_2S (%)	8.1
	C_3A (%)	5.2
	C_4AF (%)	12.9
	CaOfr. (%)	1.5
CrS	Particle size (mm)	5–20
	Bulk density (kg/m^3)	1458
	Apparent density (kg/m^3)	2571
	Resistance to fragmentation (wt %)	12.0
	The content of lamellar and acicular grains (wt %)	9.5
QS	Fineness modulus	1.81
	Bulk density (kg/m^3)	1387
	The content of dust and clay particles (%)	0.03
	Content of clay in lumps (%)	0.11
	Organic and contaminant content (%)	No
PS	Silicon oxide content SiO_2 (%)	99.0
	Humidity (%)	0

Figure 1 exhibits the granulometric curves of Portland cement, crushed stone, quartz sand, and polyfractional sand.

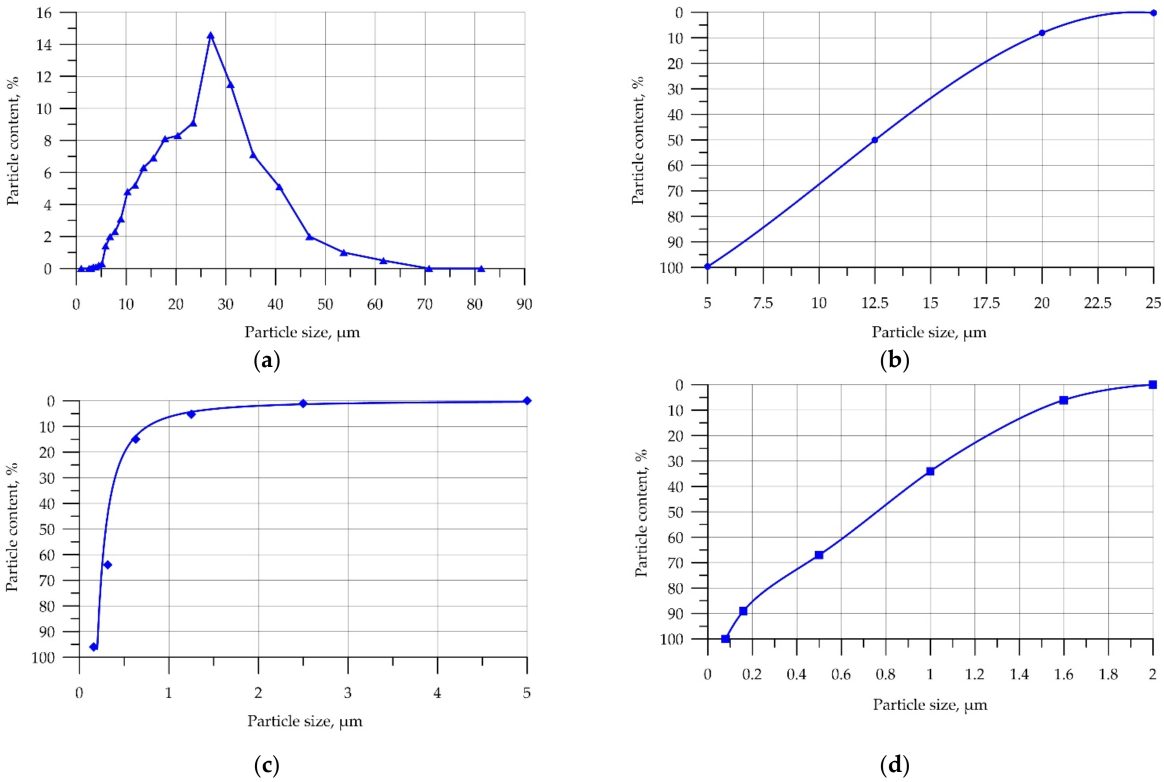


Figure 1. Particle size distribution: (**a**) Portland cement; (**b**) crushed sandstone; (**c**) quartz sand; (**d**) polyfractional sand.

According to Figure 1a, 85.0% of the cement particles are in the size range from 8 μm to 40 μm. The distribution peak of 14.6% falls on cement particles with a size of 27 μm. Crushed stone has a fraction from 5 to 20 mm (Figure 1b), and the fineness modulus of quartz sand is 1.81 (Figure 1c). Polyfractional sand in terms of grain composition (Figure 1d) meets the requirements [43]. Characteristics of PC, CrS, QS and PS are provided by the manufacturers.

Nanofibrils from synthesized wollastonite with a high characteristic ratio of 1:250–1:400, needle-shaped, and hollow nanospheres from corundum (Al_2O_3), the size of which varies from 30 nm to 500 nm (data provided by the manufacturer), were used as modifying nanoadditives. The appearance of these additives is shown in Figure 2.

Figure 2. General view of nanoadditives in an agglomerated state: (**a**) NF; (**b**) NS.

2.2. Methods

Tables 2–4 present the experimental compositions of cement pastes and concretes that were modified with NF and NS.

Table 2. Compositions of cement pastes with NF.

Composition	PC (g)	PS (g)	W * (mL)	NF (g)
CP0	450	1350	225	0
CPNF0.1	450	1350	225	0.45
CPNF0.2	450	1350	225	0.90
CPNF0.3	450	1350	225	1.35
CPNF0.4	450	1350	225	1.80
CPNF0.5	450	1350	225	2.25

* Water.

Table 3. Compositions of cement pastes with NS.

Composition	PC (g)	PS (g)	W * (mL)	NS (g)
CP0	450	1350	225	0
CPNS0.1	450	1350	225	0.45
CPNS0.2	450	1350	225	0.90
CPNS0.3	450	1350	225	1.35
CPNS0.4	450	1350	225	1.80
CPNS0.5	450	1350	225	2.25

* Water.

Table 4. Compositions of concrete mixtures.

Composition	Concrete Mixture Proportion per 1 m^3					
	PC (kg/m^3)	W (L/m^3)	CrS (kg/m^3)	QS (kg/m^3)	NF (kg/m^3)	NS (kg/m^3)
C	358	780	1090	190	-	-
CNF0.2	358	780	1090	190	0.72	-
CNF0.25	358	780	1090	190	0.90	-
CNF0.30	358	780	1090	190	1.07	-
CNF0.35	358	780	1090	190	1.25	-
CNF0.4	358	780	1090	190	1.43	-
CNS0.2	358	780	1090	190	-	0.72
CNS0.25	358	780	1090	190	-	0.90
CNS0.30	358	780	1090	190	-	1.07
CNS0.35	358	780	1090	190	-	1.25
CNS0.4	358	780	1090	190	-	1.43

Modification of cement pastes with NF and NS additives was carried out in the range from 0.1% to 0.5% by weight of PC. The standard recipe was selected in accordance with the specified requirements [44].

The preparation of cement paste samples was carried out as follows. First, all raw materials were dosed according to the compositions presented in Tables 2 and 3. Then, a standard cement mortar was prepared. Water was poured into the bowl of a laboratory mixer Matest E093N (Matest, Treviolo, Italy) previously wiped with a damp cloth, and

Portland cement was added, followed by mixing for 30 s. Then, sand was introduced and the solution was mixed for another 30 s. Next, the mixer stopped, the entire solution was scraped from the walls of the bowl into the middle, and a modifying nanoadditive was introduced. Since the NF and NS additives were presented in powder form, it was important to prepare them correctly and introduce them into the fresh cement paste with maximum distribution throughout its entire volume. To achieve this, the NF and NS additives were poured out on a sheet of paper in advance, then introduced into fresh cement paste by pouring them from the sheet into several places. After introducing the modifying additive, the mixture was stirred for 60 s. Then, 40 × 40 × 160 mm beam forms were filled with the prepared solution and compacted on a vibrating platform SMZh-739M (IMash, Armavir, Russia) for 60 s. Freshly prepared samples of cement pastes were kept for 1 day in a normal hardening chamber (KNT-1). After 1 day of hardening, they were carefully dismantled and placed in a container with water, where they were stored for another 27 days.

Table 4 presents the compositions of concrete mixtures obtained in this study.

The production of concrete samples modified with NF and NS additives was carried out as follows. At the beginning, all components were dosed in accordance with the recipe presented in Table 4. Then, the concrete mixture was prepared in a BL laboratory concrete mixer (ZZBO, Zlatoust, Russia). The introduction of NF and NS additives into the concrete mixture, as in the case of cement pastes, was carried out last. Since the NF and NS additives were presented in powder form, it was important to prepare them correctly and introduce them into fresh concrete with maximum distribution throughout its volume. For this purpose, the NF and NS additives were poured onto a sheet of paper in advance and introduced into fresh concrete by pouring from the sheet into several different places. After preparing the concrete mixture, it was poured into metal cube molds and prisms, followed by compaction on a laboratory vibrating platform for 60 s. The surface of the finished samples was smoothed and leveled. After 1 day of hardening, the experimental concrete samples were dismantled and placed in a normal hardening chamber for the remaining 27 days of hardening.

Tests of modified cement pastes were carried out in accordance with the requirements of [44]. After 28 days of hardening, the samples were removed from the water, wiped with a damp cloth, and tested for compression and bending on a Press P-50 unit (PKC ZIM, Armavir, Russia). First, the samples were installed in a special device to determine bending strength and loaded at a load rate of 50 ± 10 N/s. The determination of flexural strength was conducted using the following formula:

$$R_{bt} = \frac{1.5\,F\,l}{b^3} \quad (1)$$

where F is the breaking load (N); b is the size of the side of the square section of the prism sample (mm); and l is the distance between the axes of the supports (mm).

After the bending test, all six halves of the prisms obtained after the bending test were subjected to compression. During the testing, the force was applied at a rate of load increase of 0.6 ± 0.4 MPa/s. The determination of compressive strength was made using the formula:

$$R_m = \frac{F}{S} \quad (2)$$

where S is the area of the working surface of the plate (mm^2).

The process of testing samples of cement pastes for bending and compression and special devices for this are presented in Figure 3.

(a)

(b)

Figure 3. Testing of cement paste samples: (**a**) flexural strength (**b**) compressive strength.

The determination of the density of hardened modified concrete was carried out in accordance with specified requirements [45], and the calculation was performed using the following formula:

$$\rho = \frac{m}{V}1000 \quad (3)$$

where m is the mass of the sample (g) and V is the sample volume (cm^3).

The evaluation of the compressive and flexural strength of the modified concrete was carried out following the guidelines specified in references [46–50].

The cube samples were installed in a Press P-50 laboratory setup and loaded at a constant load rate of 0.6 ± 0.2 MPa/s. The calculation of concrete's compressive strength was performed using the following formula:

$$R_c = \alpha\frac{F}{A} \quad (4)$$

where A is the sample working section area (mm^2) and α is a coefficient considering the dimensions of the samples (for samples with a side of 100 mm α = 0.95).

For bending testing, prism specimens were placed in a bending test fixture (Figure 4). Next, the sample together with the device was installed in a laboratory Press P-50 and loaded until complete destruction at a constant rate of load increase of 0.05 ± 0.01 MPa/s. The flexural strength of concrete was calculated using the formula:

$$R_{tb} = \delta\frac{F\,l}{a\,b^2} \quad (5)$$

where a, b, and l are the cross-section dimensions of the prism and the distance between the supports (mm) and δ is the coefficient that considers the dimensions of the samples (for samples with a side of 100 mm, δ = 0.92).

The determination of water absorption of modified concrete was carried out in accordance with the requirements of [51,52]. The water absorption value was calculated using the formula:

$$W = \frac{m_w - m_d}{m_d} \times 100 \quad (6)$$

where m_{w} is the mass of the sample saturated with water (g) and m_{d} is the mass of the dry sample (g).

Figure 4. Concrete bending test.

X-ray phase analysis of concrete with NF and NS additives was carried out on a DRON-7 diffractometer (NPP Burevestnik, St. Petersburg, Russia) using radiation from a copper anode (wavelengths $CuK\alpha_1$ 1.5406 Å, $CuK\alpha_2$ 1.5444 Å).

The microstructure of concrete samples was analyzed using a VEGA II LMU electron microscope (Tescan, Brno, Czech Republic) at an accelerating voltage of 20 kV. All images were obtained in reflected electrons (BE): phases with a higher average atomic weight are colored in lighter shades. The chipping of hardened concrete samples after compression and bending tests was studied. The surface was sprayed with carbon.

The general program of experimental research is presented in Figure 5.

As a result, as part of this study, 36 prism samples of cement pastes were created (6 of the control composition, 15 with NF and 15 with NS); 66 cube samples of concrete (33 for testing for density and compressive strength and 33 for testing for water absorption); and 33 concrete prism samples for testing flexural strength.

It should be noted that the test results presented in Section 3, as well as the graphs and processing of the experimental data using statistical methods, were produced based on a large representative sample of experimental results due to the massive volume of data obtained in the experiments, as well as a large number of similar results, and taking into account the heterogeneity of concrete and the probability of errors and outliers of individual results from the general line. It was decided to present the most verified results that showed good repeatability and convergence from the point of view of the previously conducted mathematical planning of the experiment. The influence of individual factors on the output parameters of concrete, their significance, and all statistical criteria were determined by us in accordance with the existing methods of mathematical planning of the experiment approved in the scientific field. In view of the large volume of methodological and experimental data, a detailed description of the existing statistical methods is defined by us as optional in order to highlight the most interesting and new information in the text of the manuscript for the readers of the journal and interested scientists. It was the extensive statistical work carried out using methods of mathematical experimental planning and selection of experimental data with the exclusion of erroneous and outlier results that made it possible to ensure the reliability of the results, such as the significance of differences in strength properties between concrete modified with NF and NS.

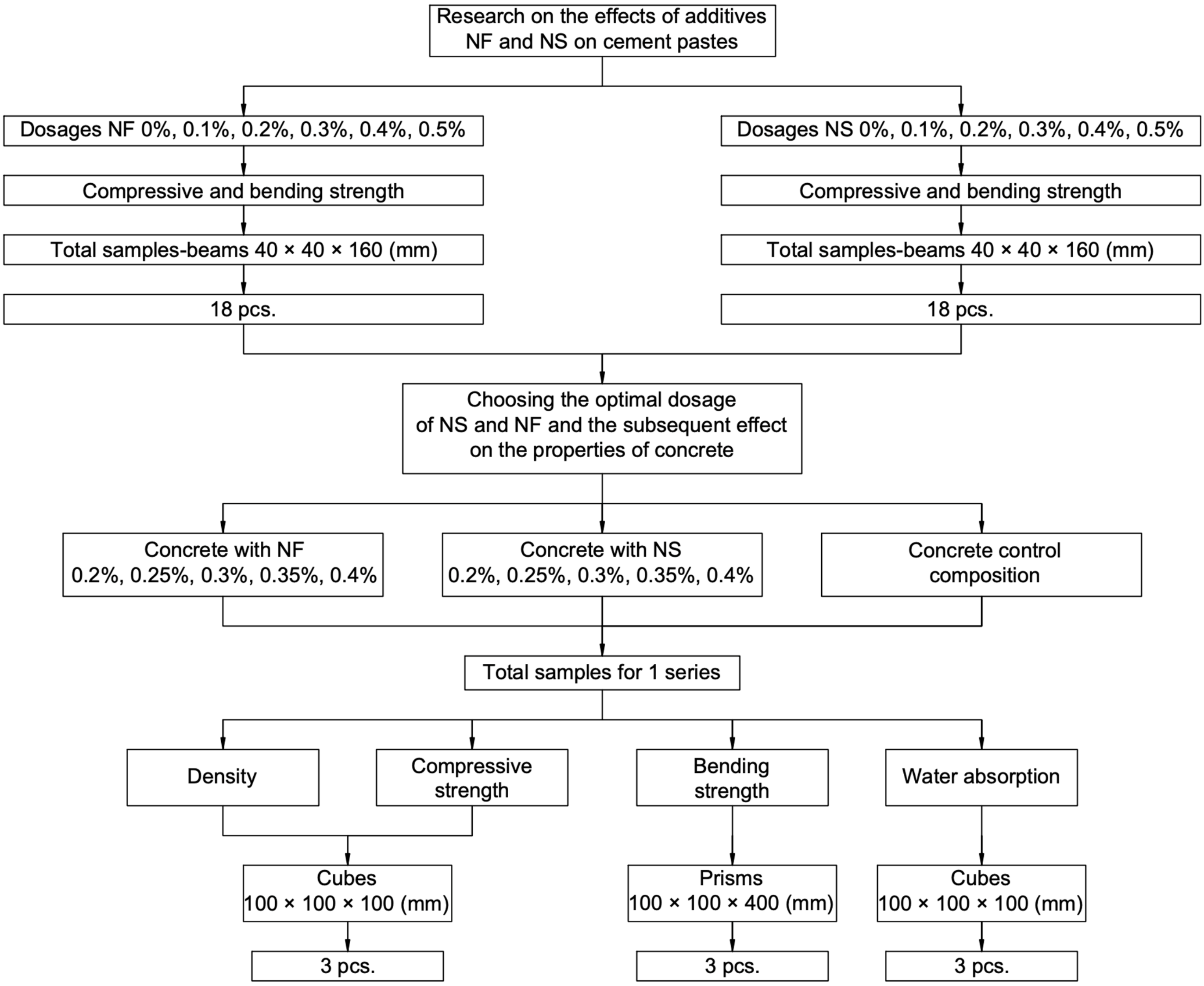


Figure 5. Experimental research program.

3. Results and Discussion

Figures 6 and 7 illustrate the relationships between the modifications made with NF and NS additives and the resulting changes in the strength properties of cement pastes.

The correlation between the compressive strength of cement paste (R) and the dosage of nanoadditives is graphically presented in Figure 6.

The impact of the NF and NS on the compressive strength of cement paste (R) shown in Figure 6 can be expressed by Equations (7) and (8):

$$R_{NF}^{CP} = 49.538 - 5.328\,x + 223.0\,x^2 - 805.1\,x^3 + 770.8\,x^4, \quad R^2 = 0.948 \tag{7}$$

$$R_{NS}^{CP} = 49.510 - 6.084\,x + 123.7\,x^2 - 422.7\,x^3 + 395.8\,x^4, \quad R^2 = 0.985 \tag{8}$$

where R^2 is the coefficient of determination.

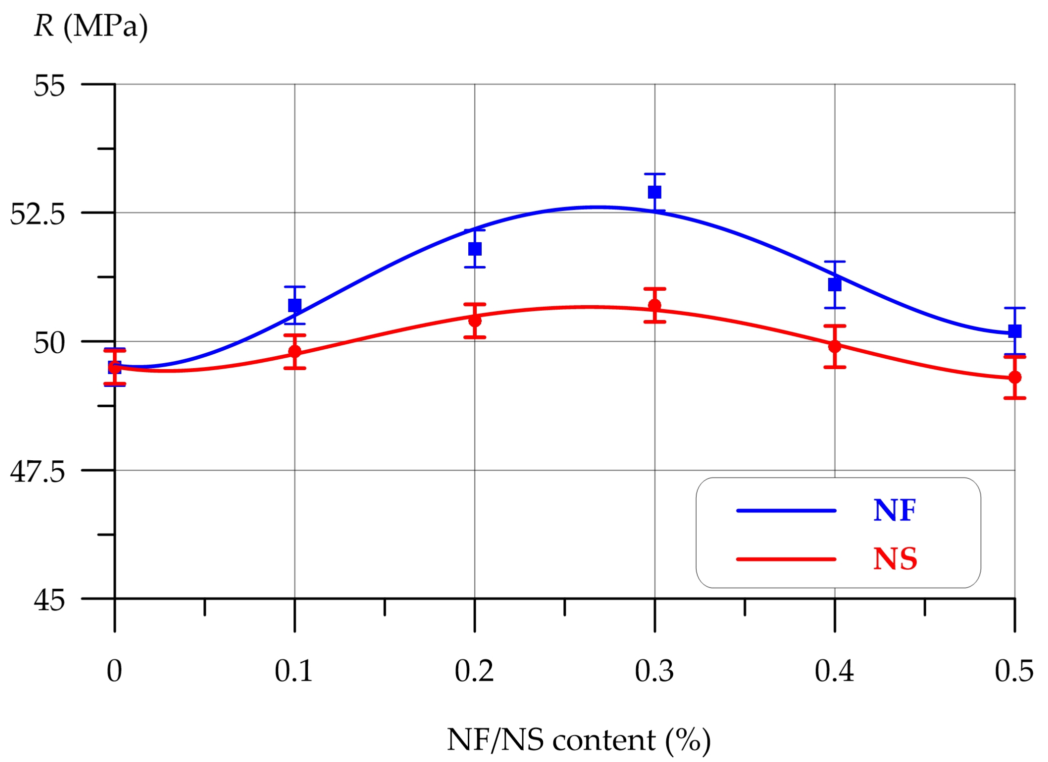


Figure 6. Change in compressive strength of cement paste (*R*) modified with different amounts of NF and NS additives.

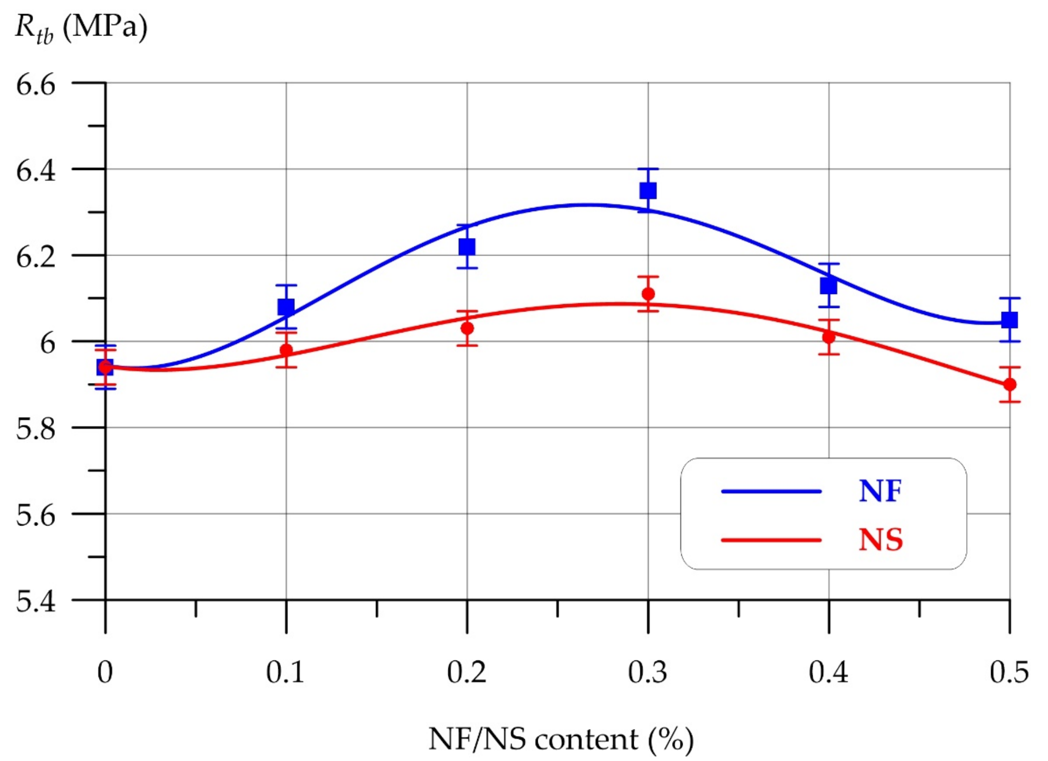


Figure 7. Change in flexural strength of cement paste (R_{tb}) modified with different amounts of NF and NS additives.

Figure 6 clearly demonstrates that the NF additive outperforms NS in terms of effectiveness. At a level of 0.3%, the highest values of the increase in compressive strength were noted for NF and NS, with percentages of 6.87% and 2.42% respectively. In general, the dependence of the change in the compressive strength of concrete modified with NF is as follows. At dosages of 0.1%, 0.2% and 0.3%, a stable increase was observed with a peak at around 0.3%, and the increases were 1.62%, 4.65% and 6.87%, respectively. Starting from 0.4%, the effectiveness of the additive decreased, and at 0.4% and 0.5%, the values of the increase in compressive strength were 3.23% and 1.41%, respectively. The dependence of the change in the compressive strength of cement pastes modified with NS was of a similar nature. There were stable increases in compressive strength at 0.1%, 0.2%, and 0.3% NS by 0.61%, 1.82%, and 2.42%, respectively. Further, at 0.4% NS, the increase in compressive strength was 0.81%, and at 0.5%, a completely negative effect was observed with a decrease in compressive strength by 0.40%.

Comparison of the efficiency of these two nanoadditives at different dosages shows that the difference in compressive strength between the composites on these additives increases from 0 to 5% in favor of NF with an increase in their dosage from 0 to 0.3% and then gradually decreases from 5% to 2% with an increase in the dosage of nanoadditives from 0.3% to 0.5%. As a rule, nanomaterial particles are tiny and easily agglomerate, which allows them to fill the pores of concrete, thereby improving its compactness. However, if the level of particle agglomeration is too high, the filling effect may be weakened. This effect explains the decrease in the effectiveness of nanoadditives at dosages of more than 0.3%. Nanoadditive particles agglomerate and cannot be evenly distributed throughout the entire volume of the cement composite and fully manifest themselves.

The relationship between the change in flexural strength of cement paste (R_{tb}) and NF/NS content, as shown in Figure 7, exhibits a similar pattern to the relationship between the change in compressive strength.

The impact of the NF and NS on the flexural strength of cement paste (R_{tb}) shown in Figure 7 can be expressed by Equations (9) and (10):

$$R_{tb\,NF}^{CP} = 5.944 - 0.877\,x + 29.68\,x^2 - 107.1\,x^3 + 104.2\,x^4, \quad R^2 = 0.947 \tag{9}$$

$$R_{tb\,NS}^{CP} = 5.942 - 0.622\,x + 12.25\,x^2 - 38.0\,x^3 + 31.3\,x^4, \quad R^2 = 0.945 \tag{10}$$

where R^2 is the coefficient of determination.

The introduction of NF in amounts of 0.1%, 0.2%, and 0.3% provided an increase in bending strength by 1.85%, 4.71%, and 6.90%, respectively. At 0.4% and 0.5% NF, the effectiveness of the additive decreased, and the increases in flexural strength were 3.20% and 1.85%, respectively. The addition of NS in amounts of 0.1%, 0.2%, and 0.3% provided increases in bending strength by 0.67%, 1.52%, and 2.86%, respectively. At 0.4% NS, the increase in flexural strength was 1.18%, and at 0.5%, a decrease in flexural strength of 0.67% was recorded.

Consequently, an initial evaluation of the impact of NF and NS on the characteristics of cement composites indicated that these additives have a favorable influence on the strength properties of the composite. It would be logical to test the results obtained by studying the influence of NF and NS on the properties of concrete. For this purpose, the most optimal and effective range of dosages was selected. Modification of concrete with NF and NS additives was carried out at dosages of 0.2%, 0.25%, 0.3%, 0.35%, and 0.4%.

Next, Figures 8–11 present the results of experimental studies of concrete modified with NF and NS additives. Figure 8 shows the dependence of concrete density (ρ) on various amounts of NF and NS additives.

The impact of the NF and NS on the concrete density (ρ) shown in Figure 8 can be expressed by Equations (11) and (12):

$$\rho_{NF} = 2343.1 + 844.2\,x - 1457.1\,x^2, \quad R^2 = 0.973 \tag{11}$$

$$\rho_{NF} = 2364.2 + 657.7\,x - 1142.8\,x^2, \quad R^2 = 0.970 \tag{12}$$

where R^2 is the coefficient of determination.

It should be noted that Equations (11) and (12) are valid for the range 0.2–0.4% NF/NS.

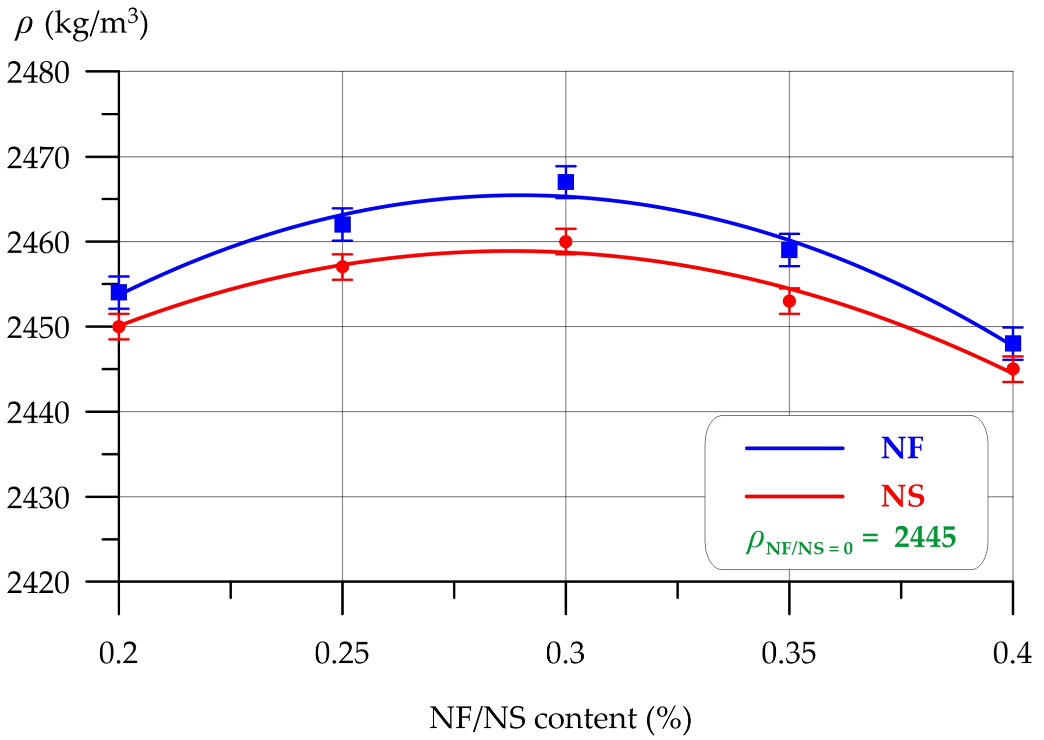


Figure 8. Change in the density of concrete (ρ) modified with different amounts of NF and NS additives.

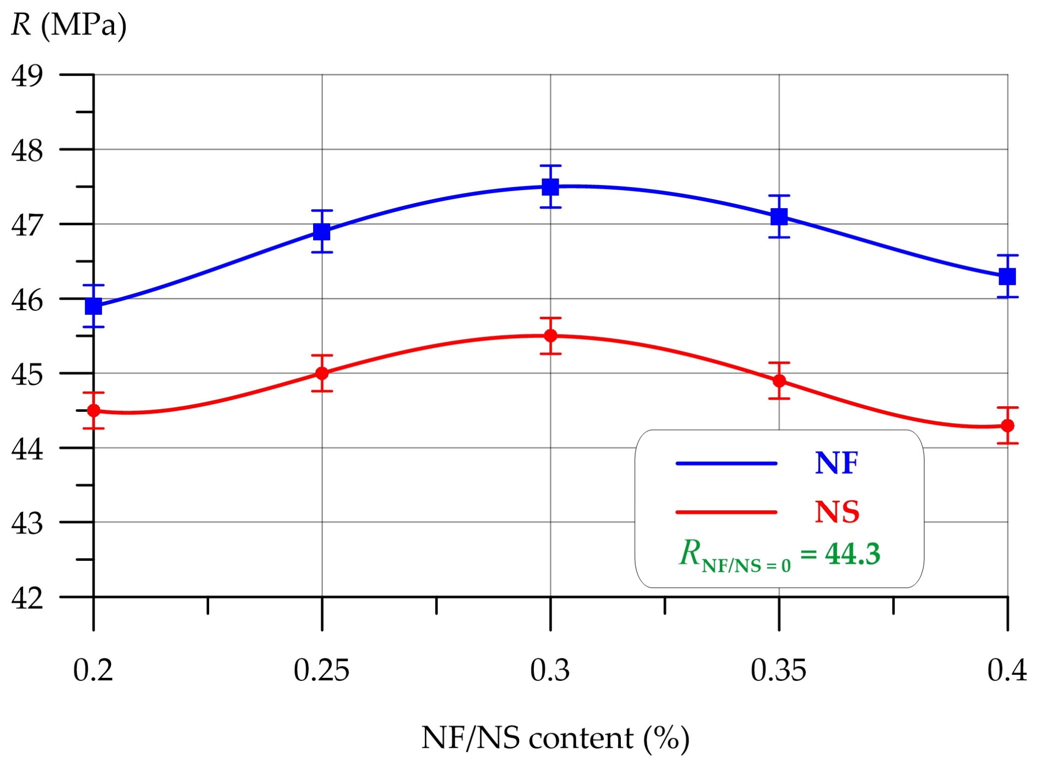


Figure 9. Change in compressive strength of concrete (R) modified with different amounts of NF and NS additives.

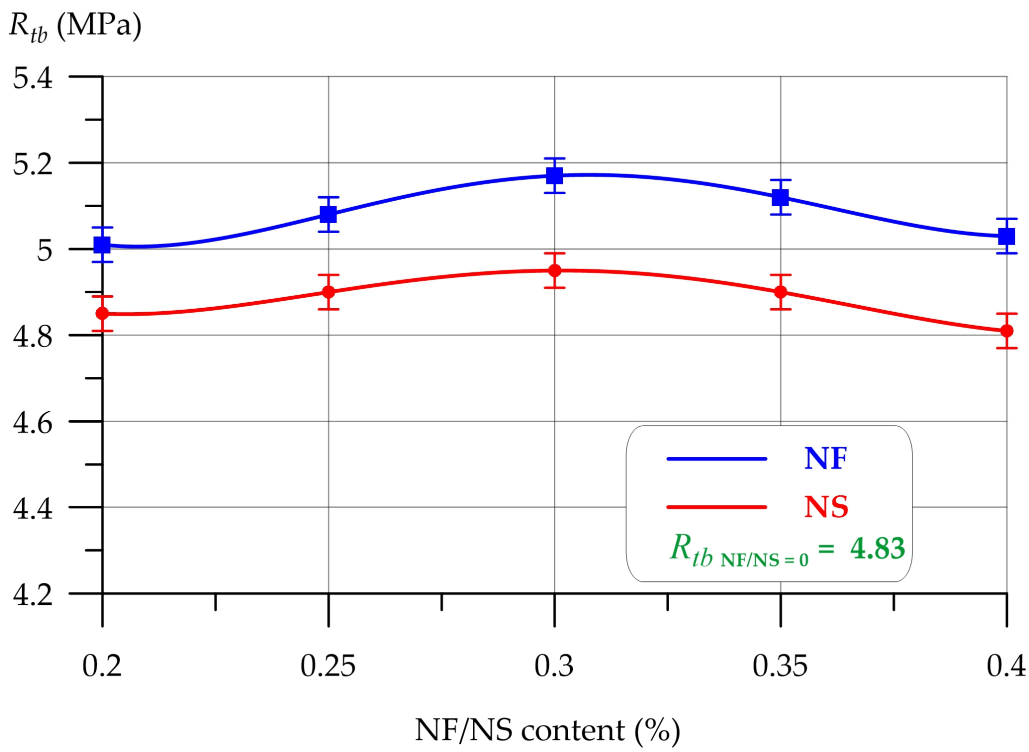


Figure 10. Change in flexural strength of concrete (R_{tb}) modified with different amounts of NF and NS additives.

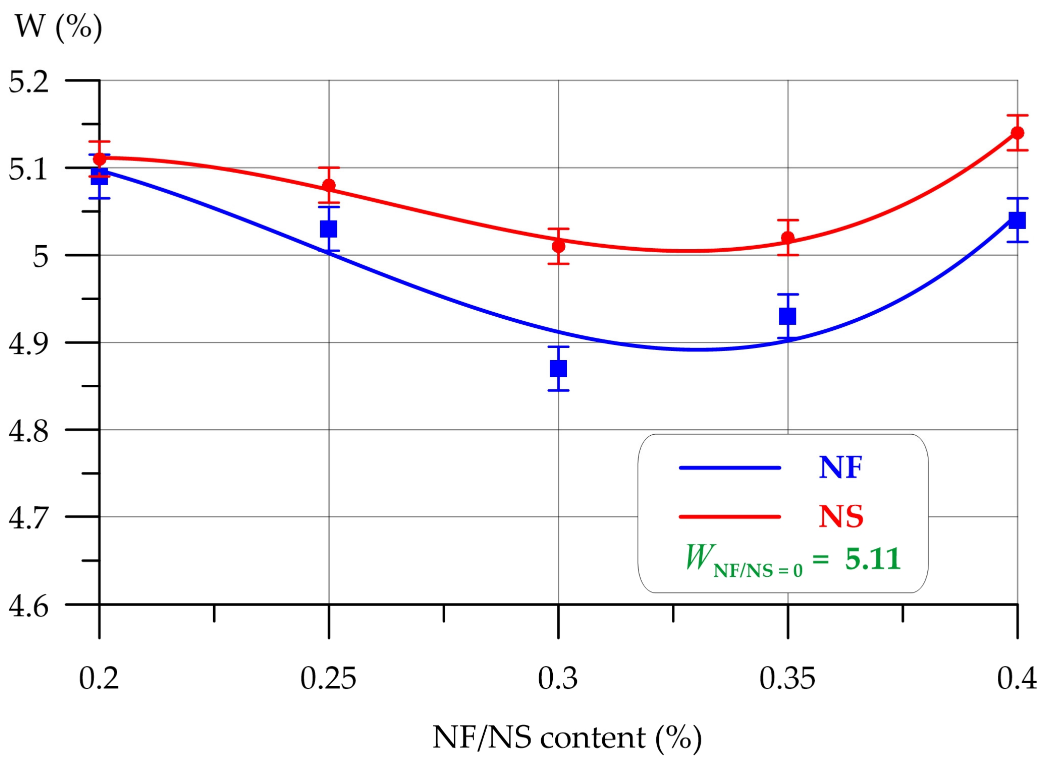


Figure 11. Change in water absorption of concrete (*W*) modified with different amounts of NF and NS additives.

The use of NF and NS additives did not have a significant effect on the change in concrete density. However, there was a slight dependence. Concrete modified with NF had a slightly higher density compared to concrete modified with NS additive. The density of concrete of the control composition and compositions with 0.2%, 0.25%, 0.3%, 0.35%, and 0.4% NF was 2445 kg/m^3 and 2454 kg/m^3, 2460 kg/m^3, 2467 kg/m^3, 2459 kg/m^3, and 2448 kg/m^3, respectively. For concrete modified with the NS additive in similar dosages, the density values were 2450 kg/m^3, 2457 kg/m^3, 2460 kg/m^3, 2453 kg/m^3, and 2445 kg/m^3, respectively.

The compressive strength of the concrete (R) is depicted in Figure 9, illustrating its dependence on different quantities of NF and NS additives.

The impact of the NF and NS on the compressive strength of concrete (R) shown in Figure 9 can be expressed by Equations (13) and (14)

$$R_{NF} = 91.9 - 730\,x + 4100\,x^2 - 9600\,x^3 + 8000\,x^4, \quad R^2 = 0.999 \tag{13}$$

$$R_{NS} = 141.5 - 1431\,x + 7663\,x^2 - 17600\,x^3 + 14666\,x^4, \quad R^2 = 0.999 \tag{14}$$

where R^2 is the coefficient of determination.

It should be noted that Equations (13) and (14) are valid for the range 0.2–0.4% NF/NS.

Figure 9 provides visual evidence that the modifying additives NF and NS contributed positively to the compressive strength of concrete. Higher increases in compressive strength served as evidence for the superior effectiveness of the NF additive over the NS additive in modifying concrete. The increases in compressive strength for concretes with 0.2%, 0.25%, and 0.3% NF content were 3.61%, 5.87%, and 7.22%, respectively. Further, with an increase in NF to 0.35% and 0.4%, the efficiency decreased, and the increments were 6.32% and 4.51%. For concretes modified with NS in amounts of 0.2%, 0.25%, 0.3%, 0.35%, and 0.4%, the increases in compressive strength compared to the control composition were 0.45%, 1.58%, 2.71%, 1.35%, and 0%, respectively.

The relationship between the flexural strength of concrete (R_{tb}) and various quantities of NF and NS additives is illustrated in Figure 10.

The impact of the NF and NS on the flexural strength of concrete (R_{tb}) shown in Figure 10 can be expressed by Equations (15) and (16):

$$R_{tb\,NF} = 17.23 - 178.1\,x + 939.7\,x^2 - 2120\,x^3 + 1733\,x^4, \quad R^2 = 0.999 \tag{15}$$

$$R_{tb\,NS} = 12.25 - 108.7\,x + 577.3\,x^2 - 1306.7\,x^3 + 1066.7\,x^4, \quad R^2 = 0.999 \tag{16}$$

where R^2 is the coefficient of determination.

It should be noted that Equations (13) and (14) are valid for the range 0.2–0.4% NF/NS.

As in the case of compressive strength, modification of concrete with NF and NS additives had a positive effect on flexural strength. According to the experimental data presented in Figure 10, it is clear that the NF additive provided a greater increase in flexural strength compared to the NS additive. For both types of supplements, 0.3% was the best dosage. When modifying concrete with the NF additive in amounts of 0.2%, 0.25%, 0.3%, 0.35%, and 0.4%, the increases in flexural strength were 3.73%, 5.18%, 7.04%, 6.00%, and 4.14%, respectively. NS was less effective, and at 0.2%, 0.25%, 0.3%, and 0.35%, the flexural strength increases were 0.41%, 1.45%, 2.48%, and 1.45%, respectively. Note that at 0.4% NS, a slight decrease in bending strength was recorded, which amounted to 0.41%.

Figure 11 shows the dependence of concrete water absorption (W) on different amounts of NF and NS additives.

The impact of the NF and NS on the water absorption of concrete (W) shown in Figure 11 can be expressed by Equations (17) and (18):

$$W_{NF} = 4.03 + 16.15\,x - 74.0\,x^2 + 100\,x^3\,, \quad R^2 = 0.893 \tag{17}$$

$$W_{NS} = 3.55 + 19.7\,x - 79.14\,x^2 + 100\,x^3, \quad R^2 = 0.990 \tag{18}$$

where R^2 is the coefficient of determination.

It should be noted that Equations (13) and (14) are valid for the range 0.2–0.4% NF/NS.

According to the data in Figure 11, it is clear that modification with NF and NS additives also had a positive effect on the water absorption of concrete composites. As in the case of strength properties, the NF additive performed better in comparison with the NS additive. Adding NF to concrete in amounts of 0.2%, 0.25%, and 0.30% provided a stable reduction in water absorption values, which decreased by 0.39%, 1.57%, and 4.70% compared to the control composition. With the introduction of 0.35% and 0.4% NF, an inverse relationship was observed, and the values of reduction in water absorption were 3.52% and 1.37%. For concrete modified with NS in amounts of 0.2%, 0.25%, 0.3%, and 0.35%, water absorption values decreased by 0, 0.59%, 1.96%, and 1.76% compared to the control composition. At 0.4% NS, an increase in water absorption of 0.59% was recorded in comparison with the control composition.

The determination of physical and mechanical properties of cement pastes and concretes modified with NF and NS additives leads to the following conclusions.

- The use of NF and NS additives has a positive effect on the compressive strength and flexural strength of cement pastes. The NF additive provides a greater increase in compressive and flexural strength compared to the NS additive. For both types of additives, the most optimal dosage is fixed at 0.3%. The maximum values of increases in compressive and flexural strength of cement pastes modified with 0.3% NF were 6.87% and 6.90%, respectively. The maximum values of increases in compressive and flexural strength of cement pastes modified with 0.3% NS were 2.42% and 2.86%, respectively.
- Modification of concrete with NF and NS additives does not have a significant effect on the change in concrete density. The maximum density value was recorded for concrete with 0.3% NF—2467 kg/m^3.
- NF and NS additives provide an increase in the strength properties of concrete. The maximum values of increases in compressive and flexural strength of concrete with 0.3% NF were 7.22% and 7.04%, respectively. For concrete with 0.3% NS, the increases in compressive and flexural strength were 2.71% and 2.48%, respectively.
- NF and NS additives slightly reduce the water absorption of concrete, NF to a greater extent than NS (4.7% versus 1.96%, respectively), and maximum reductions were also recorded with an additive dosage of 0.3%.

In a broad sense, the findings from experimental studies on the physical and mechanical properties of cement composites have concluded that the most efficient concentration of NF and NS additives is 0.3%. Therefore, it would be logical to perform X-ray phase analysis on concrete samples of the control composition and compositions with 0.3% NF and 0.3% NS. Figure 12 shows diffraction patterns of concrete with a control composition (Figure 12a), concrete with an NF content of 0.3% (Figure 12b), and concrete with an NS content of 0.3% (Figure 12c).

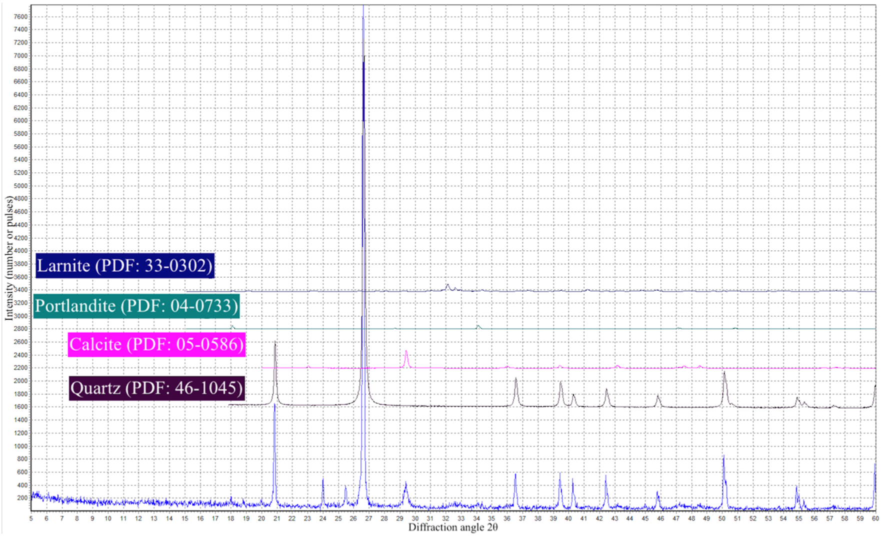
The concrete of the control composition was analyzed using X-ray phase analysis, which revealed the presence of quartz, calcite, larnite, and portlandite.

The phase composition of concrete modified with 0.3% NF was characterized by the presence of phases such as quartz, calcite, portlandite, larnite, and olivine-Ca.

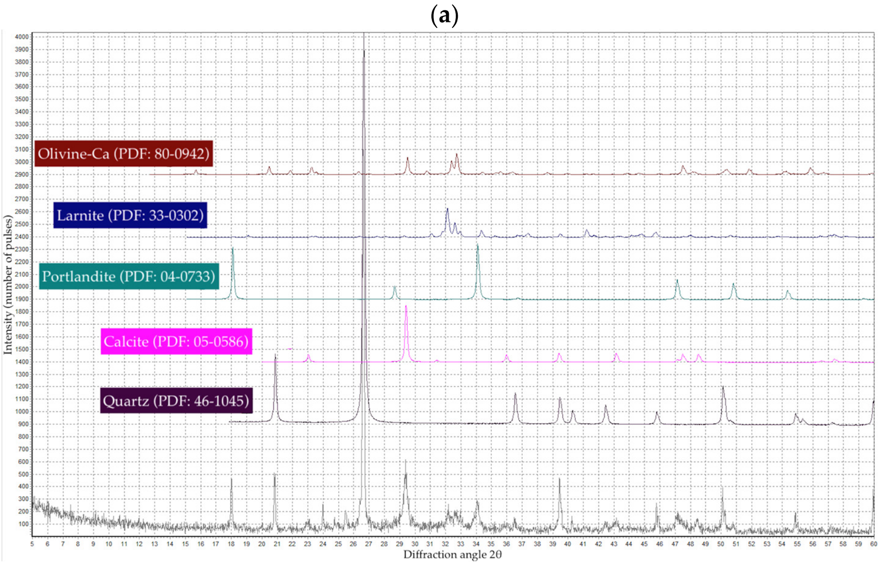
The phase composition of concrete modified with 0.3% NS was characterized by the presence of phases such as quartz, calcite, portlandite, larnite, and olivine-Ca.

Based on the results of the X-ray phase analysis, it was established that compositions with 0.3% NF and NS, like the control composition, were characterized by the presence of four main phases—quartz, calcite, portlandite, and larnite—and were distinguished by the presence of such a phase as olivine-Ca.

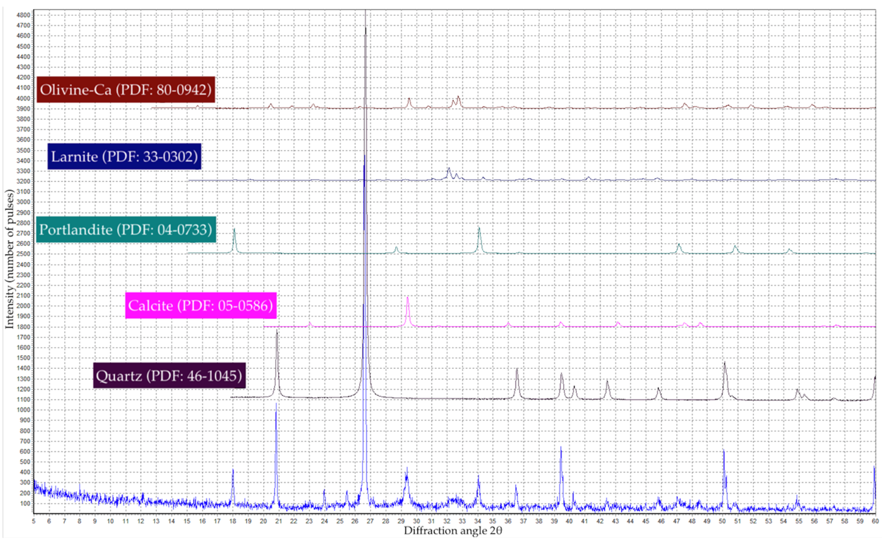
Photographs depicting the microstructure of concrete samples are displayed in Figures 13–15. Figure 13 represents the control composition, while Figures 14 and 15 represent concrete with 0.3% NF and NS content.



(**a**)

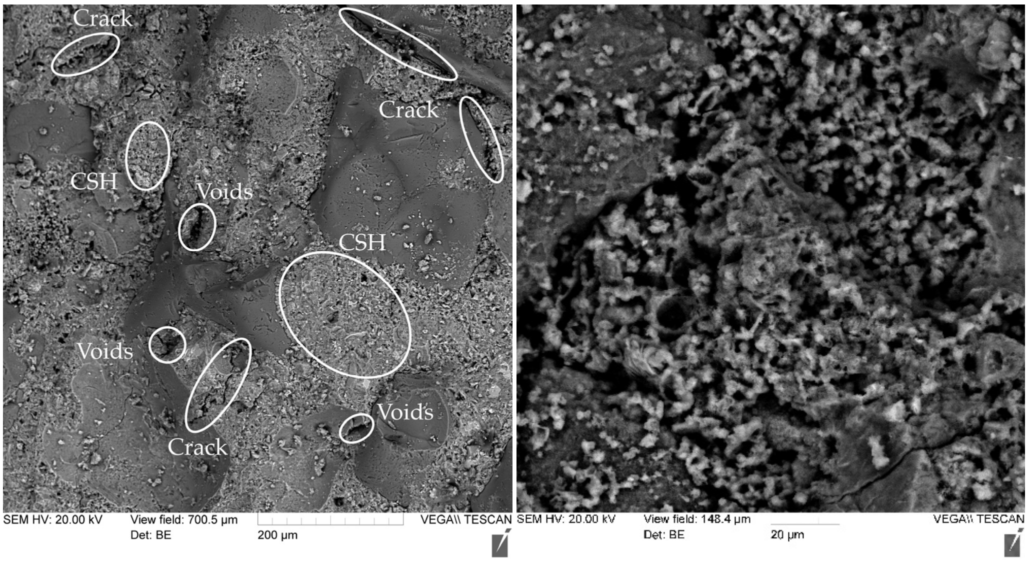


(**b**)



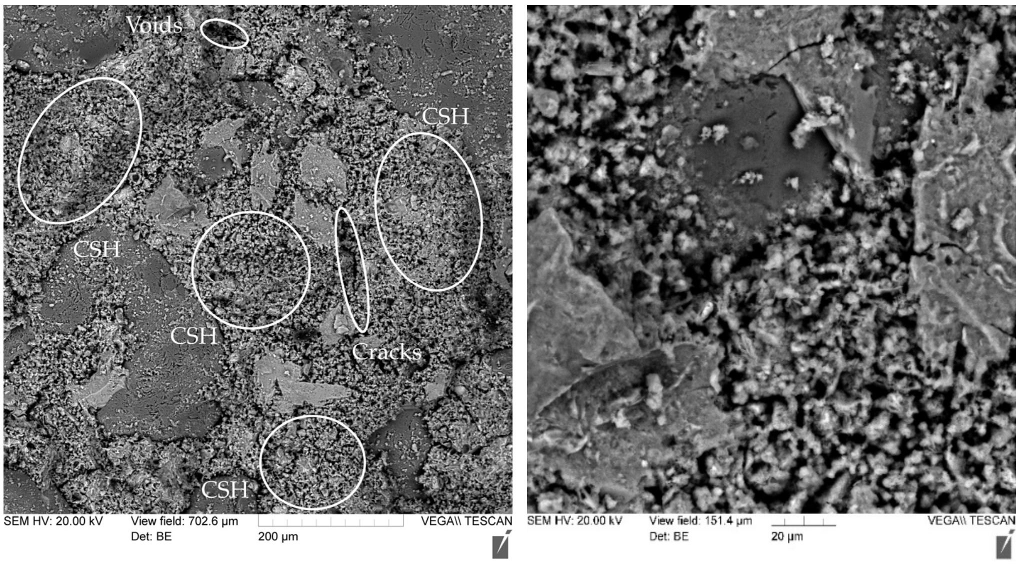
(**c**)

Figure 12. Diffraction pattern of concrete: (**a**) control composition, (**b**) containing 0.3% NF, (**c**) containing 0.3% NS.



(**a**) (**b**)

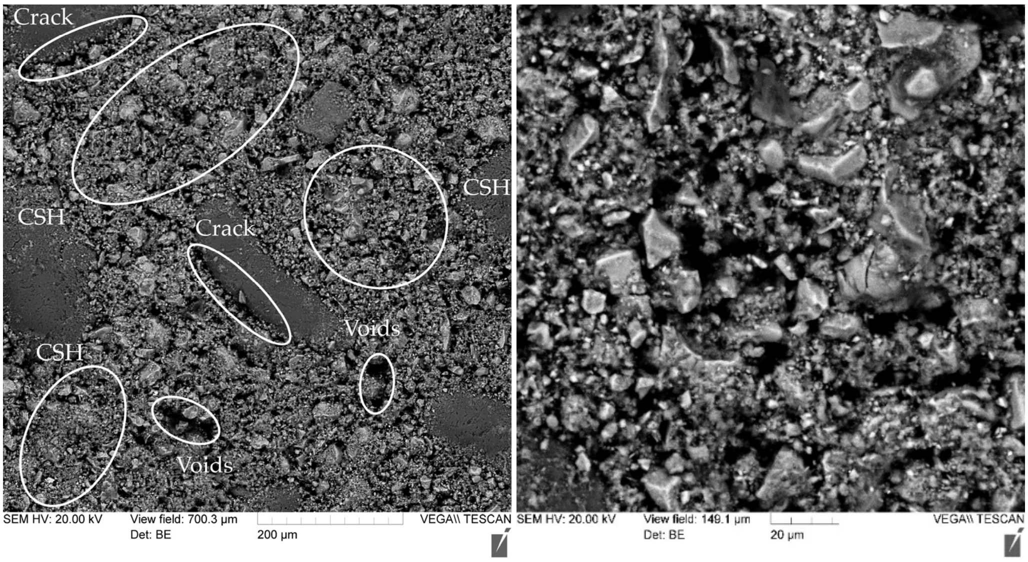
Figure 13. Photographs of the microstructure of concrete samples of the control composition: (**a**) with a magnification of 300×; (**b**) at 1500× magnification.



(**a**) (**b**)

Figure 14. Photographs of the microstructure of concrete samples modified with 0.3% NF: (**a**) with a magnification of 300×; (**b**) at 1500× magnification.

The results of microstructural analysis presented in Figures 13–15 are in good agreement with the results obtained during the experiments. The microstructure of concrete samples modified with 0.3% NF (Figure 14) is characterized by a large accumulation of zones of calcium hydrosilicates (CSH) in comparison with the microstructure of concrete of the control composition (Figure 13) and the composition modified with 0.3% NS (Figure 15). In concrete samples without NF and NS, there are many pores and voids (Figure 13). When adding nanomodifiers in the form of NF and NS, the number and size of pores and voids are significantly reduced, and the CSH zones become more uniform (Figures 14 and 15). In addition, nanoadditives, reacting with calcium hydroxide, form additional CSH zones to fill large pores and voids, leading to an improvement in the microstructure of the matrix. NF and NS can also fill nanosized pores and voids in the matrix, which further improves the microstructure, making it denser. These phenomena are in good agreement with the microstructural changes observed in similar studies [14,15,53]. Thus, microstructural studies confirm that nanomodification of cement composites with NF and NS additives in relatively small dosages from 0.2% to 0.35% contributes to changes in the structure of the composite at the microlevel due to such processes as accelerating hydration, increasing the proportion of high-density CSH and reducing the number of non-hydrated cement particles, which is also confirmed in [54–56].



(**a**) (**b**)

Figure 15. Photographs of the microstructure of concrete samples modified with 0.3% NS: (**a**) with a magnification of 300×; (**b**) at 1500× magnification.

The improvement in the properties of cement pastes and concretes when they are modified with nanoadditives in the form of nanofibrils from synthesized wollastonite with a high characteristic ratio of 1:250–1:400 and needle-shaped and hollow nanospheres from Al_2O_3 corundum is explained by the mechanism of interaction of particles of these additives with cement paste during the hydration process. Thus, the increase in compressive and flexural strength and the decrease in water absorption of cement composites with the introduction of the optimal amount of NF additive is explained by its good physical properties and needle-like shape. Wollastonite has a high elastic modulus, the values of which vary from 300 to 530 GPa, and good corrosion resistance [28]. Due to their needle-like shape, NFs act as reinforcing fibers in the cement matrix. During the hydration process, the released $Ca(OH)_2$ reacts with the SiO_2 in the wollastonite nanofibers to form CSH. Accordingly, when nanofibrils from synthesized wollastonite are introduced into a cement composite, they act as a strengthener of the microstructure of the cement matrix and filler, as a result of which the structure of cement composites becomes denser, with fewer capillary pores [57–59]. The effect of the mechanism of action of the NF additive during the hydration process of the cement binder is clearly presented in Figure 16.

As for the use of hollow Al_2O_3 corundum nanospheres as a modifying additive, they showed lower efficiency in comparison with nanofibrils from synthesized wollastonite. Small increases in strength properties up to 2.71% can be explained by the fact that at the optimal dosage, NS acts as a filler. Typically, nanomaterial particles are tiny and easily agglomerated, allowing them to fill the pores of concrete, thereby improving its compactness. However, if the level of particle agglomeration is too high, the filling effect may be weakened. It is this effect that explains the decrease in the effectiveness of the NS nanoadditive at dosages of more than 0.3%. NS particles agglomerate and cannot be evenly distributed throughout the entire volume of the cement composite and cannot fully manifest themselves [60–62].

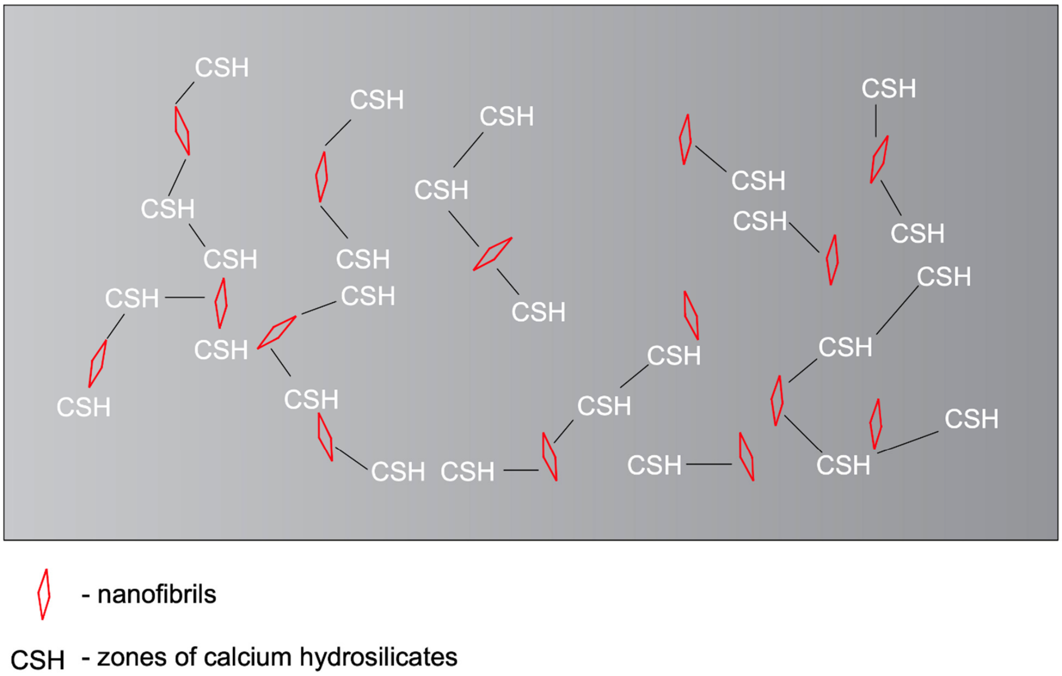


Figure 16. Schematic visualization of the mechanism of action of the NF additive during the hydration process of the cement binder.

Let us conduct a comparative analysis of modifying additives in the form of nanofibrils from synthesized wollastonite and hollow nanospheres from corundum (Al_2O_3) produced by LLC NPK Nanosystems (Rostov-on-Don, Russia) with additives for concrete made from similar raw materials (Table 5).

Table 5. Comparative analysis of the effectiveness of nanoadditives.

Reference Number	Additive Name	Best Dosage	Result Obtained
[63,64]	Wollastonite microfibers	10%	Replacing part of the cement with wollastonite fibers improves composite fracture toughness by up to 33%, mechanical properties and durability.
[65]		30%	The introduction of wollastonite microfiber up to 30% instead of part of the fine aggregate helps improve the properties of the mixtures, making them more fluid, and also improves the strength properties of the composites themselves.
[66,67]		Up to 15%	Modification of concrete with wollastonite microfibers improved their strength properties and water absorption.
[68,69]			The introduction of wollastonite microfiber increases the resistance of concrete to aggressive acids and alkalis
[70]	Nano-Al_2O_3	1%	Modification of UHPC with the addition of nano-Al_2O_3 improves the fluidity of concrete mixtures and the strength of hardened composites.
[37,71]			The introduction of nano-Al_2O_3 particles provides an increase in compressive strength of up to 20%, increases resistance to aggressive environments and reduces water absorption.
[72]	Micro-powder Al_2O_3	Up to 10%	Increases compressive strength, reduces shrinkage and chloride migration.

Based on the results of a comparative analysis of the nanosized additives NF and NS produced by LLC NPK Nanosystems (Rostov-on-Don, Russia) with modifying additives based on wollastonite and Al_2O_3, according to their effectiveness criteria, we can draw the following conclusions. Wollastonite for modifying cement composites is mainly used as a partial replacement for cement and in the form of microfibers [63–69]. Wollastonite microfibers can be introduced in large quantities up to 30% into cement composites and at the same time obtain composites with improved strength properties and durability. In our case, the use of nanosized wollastonite fibers did not provide such significant increases in the strength properties of cement composites. At the most optimal dosage of 0.3%, the increase in strength properties was 7.22% or less. However, it is worth noting that with a relatively small consumption of the NF additive, the recorded increases in compressive and bending strength and a decrease in water absorption were quite good. Accordingly, the use of nanofibrils from synthesized wollastonite in the technology of cement composites has great promise and requires additional research aimed at studying the durability properties of concretes modified with NF. Modification of concrete by adding hollow corundum nanospheres (Al_2O_3) turned out to be not so effective. The maximum increases in strength characteristics were 2.71% or less. In comparison with the studies carried out in [68,69], the modification of cement composites with nano-Al_2O_3 and Al_2O_3 micro-powder showed more significant results: increases in compressive strength of up to 20% were observed. In this regard, the addition of hollow corundum nanospheres has low prospects for further use, and further research on modifying concrete with this additive is impractical.

The work performed represents a fundamentally new approach to the modification of concrete using nanoadditives. The difference between the work performed and work related to the most popular nanoadditives, such as nanosilica [9,10,12–14,53] and carbon nanotubes [15–19,29,33], is that the components of concrete were activated by nanoparticles of a specified shape. In particular, nanospheres have a spheroidal shape, which implies modification of the concrete structure by the least effective type of nanomodifying additives. However, it was necessary to confirm this thesis experimentally. The experiments showed that nanospheres with a confirmed spheroidal shape do have a minimal effect on the structure of concrete, and information about this helps to systematize the knowledge base on concrete nanomodifiers. At the same time, our study analyzed the effect of nanofibrils, i.e., nanosized needle-like structures, that allowed creating additional bonds between concrete components at the nanolevel. Compared to known additives such as carbon nanotubes and nanosilica, nanofibrils are still inferior in their effectiveness [12–19]. However, it should be emphasized that the experiments conducted are the first in this direction, and in accordance with future stages of development of nanoparticle science, a new knowledge base will certainly appear concerning the use of nanofibrils in concrete and other construction conglomerates of various types. Thus, this study is not intended to compete with known nanoadditives, but to supplement theoretical and practical ideas about a large-scale system of nanomodifying additives in concrete.

4. Conclusions

The influence of additives of nanofibrils from synthesized wollastonite and hollow nanospheres from corundum on the properties of cement paste and concrete was studied. Studies of the phase composition of concrete and its microstructure have been carried out.

(1) The introduction of NF and NS into the cement paste in an amount of 0.1% to 0.4% improves their strength properties. For both types of additives, the optimal dosage is 0.3%. The maximum values of increases in compressive and bending strength with the NF modification were 6.87% and 6.90%. For cement pastes with NS, the increment values were 2.42% and 2.86%. The NF additive is more effective than NS in cement paste.

(2) Modification of NF and NS concretes in amounts from 0.1% to 0.5% does not have a significant effect on the density of hardened composites. Small increases in density were observed for composites with the highest strength properties. The maximum density value was recorded for concrete with 0.3% NF and amounted to 2467 kg/m^3.

(3) The optimal amount of NF in concrete varies between 0.2% and 0.4%. The maximum values of increases in compressive and flexural strength of concrete at 0.3% NF were 7.22% and 7.04%, and water absorption decreased by 4.70%. The optimal amounts of NS in concrete varied from 0.2% to 0.35%. The maximum values of increases in compressive and bending strength of concrete were recorded at 0.3% NS—2.71% and 2.48%. Water absorption decreased by 3.13%. The NF supplement is more effective compared to NS.

(4) Concrete of the control composition, like concrete, with the additions of 0.3% NF and NS, includes four main phases—quartz, portlandite, calcite, larnite. Concrete with 0.3% NF and NS differs from concrete of the control composition by the presence of the olivine-Ca phase.

(5) The results of microstructural analysis confirm the performance of NF and NS additives at the micro-level of the concrete composite structure. The structure of modified concrete is characterized by a large presence of clusters of calcium silicate hydrate zones.

Thus, the results of experimental studies demonstrate the possibility of using nanofibrils from synthesized wollastonite and hollow nanospheres from corundum as modifying nanoadditives in the technology of cement composites. A more effective and promising additive is nanofibrils from synthesized wollastonite, the use of which in the technology of cement composites has great promise and requires additional research in the direction of studying the durability of concrete. For a more complete assessment of the behavior of concrete modified with nanofibrils and nanospheres, it is recommended that such properties as freeze–thaw resistance, chloride penetration, resistance to wetting and drying, and corrosion resistance be studied. Research in this direction can fill a fairly large scientific gap in the field of cement composites modified with nanomaterials. The practical implications of this study include the possibility of using concrete modified with nanofibrils with improved mechanical characteristics in building structures (load-bearing and non-load-bearing) operating in non-aggressive conditions and mild climatic zones.

Author Contributions: Conceptualization, S.A.S., E.M.S., D.E., V.V. and A.C.; methodology, S.A.S., E.M.S. and M.K.; software, S.K., D.E. and A.C.; validation, A.C., S.K. and D.E.; formal analysis, A.C., S.A.S., E.M.S. and M.K.; investigation, D.E., M.K., B.M., S.A.S., E.M.S., A.N.B. and A.C.; resources, L.R.M., S.A.S., E.M.S. and B.M.; data curation, V.V., S.K. and A.C.; writing—original draft preparation, S.A.S., E.M.S. and A.N.B.; writing—review and editing, S.A.S., E.M.S. and A.N.B.; visualization, S.A.S., E.M.S. and A.N.B.; supervision, B.M. and L.R.M.; project administration, B.M. and L.R.M.; funding acquisition, S.A.S., E.M.S. and A.N.B. All authors have read and agreed to the published version of the manuscript.

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References

1. Gil, L.; Bernardo, J. An approach to energy and climate issues aiming at carbon neutrality. *Renew. Energy Focus.* **2020**, *33*, 37–42. [CrossRef]
2. Udumulla, D.; Ginigaddara, T.; Jayasinghe, T.; Mendis, P.; Baduge, S. Effect of Graphene Oxide Nanomaterials on the Durability of Concrete: A Review on Mechanisms, Provisions, Challenges, and Future Prospects. *Materials* **2024**, *17*, 2411. [CrossRef]
3. Georgiev, S.V.; Mailyan, D.R.; Solovyeva, A.I. Determining the Most Efficient Method of Strengthening the Reinforced Concrete Columns under Different Loading Levels. *Mod. Trends Constr. Urban Territ. Plan.* **2024**, *3*, 7–14. [CrossRef]
4. Soloviev, A.N.; Binh, D.T.; Chebanenko, V.A.; Lesnyak, O.N.; Kirillova, E.V. Vibration analysis of a composite magnetoelectroelastic bimorph depending on the volume fractions of its components based on applied theory. *Adv. Eng. Res. (Rostov-on-Don)* **2022**, *22*, 4–13. [CrossRef]

5. Mohtasham Moein, M.; Rahmati, K.; Saradar, A.; Moon, J.; Karakouzian, M. A Critical Review Examining the Characteristics of Modified Concretes with Different Nanomaterials. *Materials* **2024**, *17*, 409. [CrossRef]
6. Guangcong, N.; Tiraturyan, A.N.; Uglova, E.V.; Vorobev, A.V. Study on Dynamic Response Characteristics of Different Asphalt Pavement Structures Based on ALF Test. *Adv. Eng. Res. (Rostov-on-Don)* **2023**, *23*, 241–256. [CrossRef]
7. Al-Noaimat, Y.A.; Chougan, M.; Al-kheetan, M.J.; Al-Mandhari, O.; Al-Saidi, W.; Al-Maqbali, M.; Al-Hosni, H.; Ghaffar, S.H. 3D printing of limestone-calcined clay cement: A review of its potential implementation in the construction industry. *RINENG* **2023**, *18*, 101115. [CrossRef]
8. Shcherban', E.M.; Stel'makh, S.A.; Beskopylny, A.; Mailyan, L.R.; Meskhi, B.; Varavka, V. Nanomodification of Lightweight Fiber Reinforced Concrete with Micro Silica and Its Influence on the Constructive Quality Coefficient. *Materials* **2021**, *14*, 7347. [CrossRef]
9. Wan, L.; Zhao, Y.; Maopei Yu, M.; Tian, Y.; Yipeng Wang, Y. Durability and Mechanical Properties of Nano-SiO_2 and Polyvinyl Alcohol Fiber-Reinforced Cementitious Composites Subjected to Saline Freeze–Thaw Cycles. *Materials* **2024**, *17*, 2542. [CrossRef]
10. Zhou, Y.; Zhuang, J.; Lin, W.; Xu, W.; Hu, R. Creep and Shrinkage Properties of Nano-SiO_2-Modified Recycled Aggregate Concrete. *Materials* **2024**, *17*, 1904. [CrossRef]
11. Golewski, G.L. Determination of Fracture Mechanic Parameters of Concretes Based on Cement Matrix Enhanced by Fly Ash and Nano-Silica. *Materials* **2024**, *17*, 4230. [CrossRef] [PubMed]
12. Luo, J.; Wang, S.; Quan, X.; Xu, J.; Li, J.; Liu, K.; Xu, F.; Hong, Z. Nano-SiO_2 Recycled Concrete Anti-Sulfate Performance and Damage Mechanism Research. *Buildings* **2023**, *13*, 1429. [CrossRef]
13. Zhang, M.; Tian, Z.; Cui, J. Carbonation Resistance of Marine Concrete Containing Nano-SiO_2 under the Action of Bending Load. *J. Mar. Sci. Eng.* **2023**, *11*, 637. [CrossRef]
14. Wang, K.; Guo, J.; Zhang, P.; Meng, Q. The Counterbalance of the Adverse Effect of Abrasion on the Properties of Concrete Incorporating Nano-SiO_2 and Polypropylene Fiber Based on Pore Structure Fractal Characteristics. *Fractal Fract.* **2022**, *6*, 392. [CrossRef]
15. Rafieizonooz, M.; Jay Kim, J.-H.; Kim, J.-S.; Jo, J.-B. Effect of Carbon Nanotubes on Chloride Diffusion, Strength, and Microstructure of Ultra-High Performance Concrete. *Materials* **2024**, *17*, 2851. [CrossRef]
16. Wu, H.; Liu, X.; Ma, X.; Liu, G. Effects of Multi-Walled Carbon Nanotubes and Recycled Fine Aggregates on the Multi-Generational Cycle Properties of Reactive Powder Concrete. *Sustainability* **2024**, *16*, 2084. [CrossRef]
17. Zhu, F.; Wu, X.; Lu, Y.; Huang, J. Strength Estimation and Feature Interaction of Carbon Nanotubes-Modified Concrete Using Artificial Intelligence-Based Boosting Ensembles. *Buildings* **2024**, *14*, 134. [CrossRef]
18. AlAraj, R.R.; Tamimi, A.K.; Hassan, N.M.; Fattah, K.P. Mechanical Performance of Cementitious Materials Reinforced with Polyethylene Fibers and Carbon Nanotubes. *Fibers* **2024**, *12*, 1. [CrossRef]
19. Moses Karakouzian, M.; Visar Farhangi, V.; Ramezani Farani, M.; Joshaghani, A.; Zadehmohamad, M.; Ahmadzadeh, M. Mechanical Characteristics of Cement Paste in the Presence of Carbon Nanotubes and Silica Oxide Nanoparticles: An Experimental Study. *Materials* **2021**, *14*, 1347. [CrossRef]
20. Kolour, H.H.; Ashraf, W.; Landis, E.N. Hydration and Early Age Properties of Cement Pastes Modified with Cellulose Nanofibrils. *Transp. Res. Rec.* **2020**, *2675*, 9. [CrossRef]
21. Goncalves, J.; El-Bakkari, M.; Boluk, Y.; Bindiganavile, V. Cellulose nanofibres (CNF) for sulphate resistance in cement based systems. *Cem. Concr. Compos.* **2019**, *99*, 100–111. [CrossRef]
22. Zhang, X.; Lei, C.; Li, Z.; Zhang, A.; Zhao, W.; Zhang, W.; Xu, J.; Guo, P. Effect of Cellulose Nanofibrils on the Physical Properties and Frost Resistance of Pervious Concrete. *Materials* **2022**, *15*, 7906. [CrossRef] [PubMed]
23. Mejdoub, R.; Hammi, H.; Boufi, S. Nanofibrillated cellulose as nanoreinforcement in Portland cement: Thermal, mechanical and microstructural properties. *J. Compos. Mater.* **2016**, *51*, 17. [CrossRef]
24. Onuaguluchi, O.; Panesar, D.K.; Sain, M.M. Properties of nanofibre reinforced cement composites. *Constr. Build. Mater.* **2014**, *63*, 119–124. [CrossRef]
25. Goncalves, J.R.A.; Boluk, Y.; Bindiganavile, V.S. Cellulose nanofibres mitigate chloride ion ingress in cement-based systems. *Cem. Concr. Compos.* **2020**, *114*, 103780. [CrossRef]
26. Guo, A.; Sun, Z.; Sathitsuksanoh, N.; Feng, H. A Review on the Application of Nanocellulose in Cementitious Materials. *Nanomaterials* **2020**, *10*, 2476. [CrossRef]
27. Nair, N.A.; Sairam, V. Research initiatives on the influence of wollastonite in cement-based construction material—A review. *J. Clean. Prod.* **2021**, *283*, 124665. [CrossRef]
28. Dutkiewicz, M.; Yücel, H.E.; Yıldızhan, F. Evaluation of the Performance of Different Types of Fibrous Concretes Produced by Using Wollastonite. *Materials* **2022**, *15*, 6904. [CrossRef]
29. Lee, D.; Lee, S.-C.; Kwon, O.-S.; Yoo, S.-W. Shear Behavior of High-Strength and Lightweight Cementitious Composites Containing Hollow Glass Microspheres and Carbon Nanotubes. *Buildings* **2024**, *14*, 2824. [CrossRef]
30. Kalla, P.; Misra, A.K.; Gupta, R.C.; Csetényi, L.J.; Gahlot, V.K.; Arora, A. Mechanical and durability studies on concrete containing wollastonite–fly ash combination. *Constr. Build. Mater.* **2013**, *40*, 1142–1150. [CrossRef]
31. Gouse Mohiuddin, M.D.; Malagavelli, V.; Balguri, P.K. Influence of wollastonite—GGBS on properties of ternary blended self compacting concrete. *Mater. Today Proc.* **2022**, *62*, 3027–3032. [CrossRef]

32. Mandrawalia, A.K.; Gaur, A. Compressive and sorptivity characteristic of concrete modified with wollastonite fibre and waste granite fines. *Mater. Today Proc.* **2021**, *42*, 1012–1016. [CrossRef]
33. Zhou, L.; Yin, J.; Wang, W.; Liu, F.; Xiao, M.; Yang, Y.; Cui, H. Effect of Vibration Mixing on the Mechanical Properties of Carbon Nanotube-Reinforced Ultra-High-Performance Concrete. *Buildings* **2024**, *14*, 2545. [CrossRef]
34. Chu, H.; Wang, Q.; Zhang, W. Optimizing ecological ultra-high performance concrete prepared with incineration bottom ash: Utilization of Al_2O_3 micro powder for improved mechanical properties and durability. *Constr. Build. Mater.* **2024**, *426*, 136152. [CrossRef]
35. Meddah, M.S.; Praveenkumar, T.R.; Vijayalakshmi, M.M.; Manigandan, S.; Arunachalam, R. Mechanical and microstructural characterization of rice husk ash and Al_2O_3 nanoparticles modified cement concrete. *Constr. Build. Mater.* **2020**, *255*, 119358. [CrossRef]
36. Nazari, A.; Riahi, S. Improvement compressive strength of concrete in different curing media by Al_2O_3 nanoparticles. *Mater. Sci. Eng. A* **2011**, *528*, 1183–1191. [CrossRef]
37. Li, C.; Cao, Y.; Li, G.; Liang, Q.; Wu, X.; Wu, G.; Wang, F.; Du, Q.; Wang, Y.; Qi, S.; et al. Modified cementitious materials incorporating Al_2O_3 and SiO_2 nanoparticle reinforcements: An experimental investigation. *Case Stud. Constr. Mater.* **2023**, *19*, e02542. [CrossRef]
38. Beskopylny, A.N.; Stel'makh, S.A.; Shcherban', E.M.; Razveeva, I.; Kozhakin, A.; Pembek, A.; Kondratieva, T.N.; Elshaeva, D.; Chernil'nik, A.; Beskopylny, N. Prediction of the Properties of Vibro-Centrifuged Variatropic Concrete in Aggressive Environments Using Machine Learning Methods. *Buildings* **2024**, *14*, 1198. [CrossRef]
39. Bhojaraju, C.; Di Mare, M.; Ouellet-Plamondon, C.M. The impact of carbon-based nanomaterial additions on the hydration reactions and kinetics of GGBS-modified cements. *Constr. Build. Mater.* **2021**, *303*, 124366. [CrossRef]
40. Antunes, M.; Santos, R.L.; Horta, R.B.; Colaço, R. Influence of Silica Modulus on the Activation of Amorphous Wollastonitic Hydraulic Binders with Different Alumina Content: Study of Hydration Reaction and Paste Performance. *Materials* **2024**, *17*, 3200. [CrossRef]
41. Zhu, Z.; Xu, L.; Deng, M.; Lu, S.; Guo, Z.; Yan, L.; Wang, Y. Influence of Different Types of Fillers on the Performance of PMMA-Based Low-Temperature Rapid Repair Mortar. *Materials* **2024**, *17*, 2871. [CrossRef] [PubMed]
42. Dieguez, M.; Ruiz, A.I.; Cuevas, J.; Alonso, M.C.; García-Lodeiro, I.; Fernández, R. Evaluation of Fillers for Magnesium Potassium Phosphate Cement (MKPC) for the Encapsulation of Low and Intermediate Level Metallic Radioactive Wastes. *Materials* **2023**, *16*, 679. [CrossRef]
43. Pan, J.; Zou, R.; Jin, F. Experimental Study on Specific Heat of Concrete at High Temperatures and Its Influence on Thermal Energy Storage. *Energies* **2017**, *10*, 33. [CrossRef]
44. *GOST 6139*; Sand for Testing Cement. Specifications. Standartinform: Moscow, Russia, 2020. Available online: https://docs.cntd.ru/document/1200174753 (accessed on 17 June 2024).
45. *GOST 30744*; Cements. Methods of Testing with Using Polyfraction Standard Sand. State Construction Committee of Russia, GUP CPP: Moscow, Russia, 2001. Available online: https://docs.cntd.ru/document/1200011363 (accessed on 17 June 2024).
46. *EN 12390-7:2019*; Testing Hardened Concrete—Part 7: Density of Hardened Concrete. iTeh Standards: Etobicoke, ON, Canada, 2019. Available online: https://standards.iteh.ai/catalog/standards/cen/811a0cf3-55e3-495a-b06e-5c302d5f2806/en-12390-7-2019 (accessed on 17 June 2024).
47. *EN 12390-1:2021*; Testing Hardened Concrete—Part 1: Shape, Dimensions and Other Requirements of Specimens and Moulds. iTeh Standards: Etobicoke, ON, Canada, 2021. Available online: https://standards.iteh.ai/catalog/standards/cen/d1c9ccee-2e5a-425e-a964-961da95d2f99/en-12390-1-2021 (accessed on 17 June 2024).
48. *EN 12390-2:2019*; Testing Hardened Concrete—Part 2: Making and Curing Specimens for Strength Tests. iTeh Standards: Etobicoke, ON, Canada, 2019. Available online: https://standards.iteh.ai/catalog/standards/cen/ae7e6a86-1cbc-455e-8b2a-8964be9087f9/en-12390-2-2019 (accessed on 17 June 2024).
49. *EN 12390-3:2019*; Testing Hardened Concrete—Part 3: Compressive Strength of Test Specimens. iTeh Standards: Etobicoke, ON, Canada, 2019. Available online: https://standards.iteh.ai/catalog/standards/cen/7eb738ef-44af-436c-ab8e-e6561571302c/en-12390-3-2019 (accessed on 17 June 2024).
50. *EN 12390-4:2019*; Testing Hardened Concrete—Part 4: Compressive Strength—Specification for Testing Machines. iTeh Standards: Etobicoke, ON, Canada, 2019. Available online: https://standards.iteh.ai/catalog/standards/cen/10b1c613-819b-42d7-8f94-480cd37a666a/en-12390-4-2019 (accessed on 17 June 2024).
51. *EN 12390-5:2019*; Testing Hardened Concrete—Part 5: Flexural Strength of Test Specimens. iTeh Standards: Etobicoke, ON, Canada, 2019. Available online: https://standards.iteh.ai/catalog/standards/cen/5653c2c7-55a9-4bcb-8e13-5b1dfb0e3baf/en-12390-5-2019 (accessed on 17 June 2024).
52. *GOST 12730.3*; Concretes. Method of Determination of Water Absorption. Gost Standard: Moscow, Russia, 2020. Available online: https://docs.cntd.ru/document/100177301 (accessed on 17 June 2024).
53. *BS 1881-122:2011+A1:2020*; Testing Concrete Method for Determination of Water Absorption. European Standards: Plzen, Czech Republic, 2020. Available online: https://www.en-standard.eu/bs-1881-122-2011-a1-2020-testing-concrete-method-for-determination-of-water-absorption/ (accessed on 17 June 2024).
54. Peng, X.; Wang, Q.; Wu, J. Effect of Nanosilica on the Strength and Durability of Cold-Bonded Fly Ash Aggregate Concrete. *Sustainability* **2023**, *15*, 15413. [CrossRef]

55. Beskopylny, A.N.; Stel'makh, S.A.; Shcherban, E.M.; Mailyan, L.R.; Meskhi, B.; Beskopylny, N.; Elshaeva, D.M.; Kotenko, M. The Investigation of Compacting Cement Systems for Studying the Fundamental Process of Cement Gel Formation. *Gels* **2022**, *8*, 530. [CrossRef]
56. Beskopylny, A.N.; Stel'makh, S.A.; Shcherban, E.M.; Mailyan, L.R.; Meskhi, B.; Smolyanichenko, A.S.; Varavka, V.; Beskopylny, N.; Dotsenko, N. Influence of Electromagnetic Activation of Cement Paste and Nano-Modification by Rice Straw Biochar on the Structure and Characteristics of Concrete. *J. Compos. Sci.* **2022**, *6*, 268. [CrossRef]
57. Klyuev, A.V.; Kashapov, N.F.; Klyuev, S.V.; Zolotareva, S.V.; Shchekina, N.A.; Shorstova, E.S.; Lesovik, R.V.; Ayubov, N.A. Experimental studies of the processes of structure formation of composite mixtures with technogenic mechanoactivated silica component. *Constr. Mater. Prod.* **2023**, *6*, 5–18. [CrossRef]
58. Volodchenko, A.A. Efficient Silicate Composites of Dense Structure using hollow microspheres and Unconventional Aluminosilicate Raw Materials. *Constr. Mater. Prod.* **2023**, *6*, 19–34. [CrossRef]
59. Shcherban', E.M.; Stel'makh, S.A.; Mailyan, L.R.; Beskopylny, A.N.; Smolyanichenko, A.S.; Chernil'nik, A.A.; Elshaeva, D.M.; Beskopylny, N.A. Structure and Properties of Variatropic Concrete Combined Modified with Nano- and Micro-silica. *Constr. Mater. Prod.* **2024**, *7*, 3. [CrossRef]
60. Meskhi, B.; Beskopylny, A.N.; Stel'makh, S.A.; Shcherban', E.M.; Mailyan, L.R.; Beskopylny, N.; Chernil'nik, A.; El'shaeva, D. Insulation Foam Concrete Nanomodified with Microsilica and Reinforced with Polypropylene Fiber for the Improvement of Characteristics. *Polymers* **2022**, *14*, 4401. [CrossRef]
61. Gordienko, P.S.; Yarusova, S.B.; Kozin, A.V.; Ivin, V.V.; Silant'ev, V.E.; Lizunova, P.Y.; Shornikov, K.O. Synthetic wollastonite-based material and its effect on the functional properties of fine-grained concrete. *Perspekt. Mater.—Adv. Mater.* **2017**, *9*, 40–48.
62. Kuldasheva, A.H. Experimental studies toughness characteristic concrete on base vollastone cheese. *Vestn. MGSU* **2011**, *7*, 627–630.
63. Beskopylny, A.N.; Stel'makh, S.A.; Shcherban', E.M.; Mailyan, L.R.; Meskhi, B.; Varavka, V.; Beskopylny, N.; El'shaeva, D. A Study on the Cement Gel Formation Process during the Creation of Nanomodified High-Performance Concrete Based on Nanosilica. *Gels* **2022**, *8*, 346. [CrossRef]
64. Doner, S.; Lyngdoh, G.A.; Nayak, S.; Das, S. Fracture response of wollastonite fiber-reinforced cementitious composites: Evaluation using micro-indentation and finite element simulation. *Ceram. Int.* **2022**, *48*, 15493–15503. [CrossRef]
65. Balotiya, G.; Gaur, A.; Somani, P.; Sain, A. Investigating mechanical and durability aspects of concrete incorporating Wollastonite and bottom ash. *Mater. Today Proc.* 2023, *in press*. [CrossRef]
66. Jindal, A.; Ransinchung, R.N.G.D.; Jindal, A. Behavioral study of self-compacting concrete with wollastonite microfiber as part replacement of sand for pavement quality concrete (PQC). *IJTST* **2020**, *9*, 170–181. [CrossRef]
67. Soliman, A.M.; Nehdi, M.L. Effects of shrinkage reducing admixture and wollastonite microfiber on early-age behavior of ultra-high performance concrete. *Cem. Concr. Compos.* **2014**, *46*, 81–89. [CrossRef]
68. Ransinchung, G.D.N.D.; Kumar, B.; Kumar, V.G. Assessment of water absorption and chloride ion penetration of pavement quality concrete admixed with wollastonite and microsilica. *Constr. Build. Mater.* **2009**, *23*, 1168–1177. [CrossRef]
69. Zhang, X.; Bai, Y.; Luo, Q. Exploring synergistic effects and hydration mechanisms in metakaolin-blended cement system with varying metakaolin and wollastonite content. *Constr. Build. Mater.* **2024**, *425*, 135962. [CrossRef]
70. Xu, B.; Cau Dit Coumes, C.; Lambertin, D.; Lothenbach, B. Compressive strength and hydrate assemblages of wollastonite-blended magnesium potassium phosphate cements exposed to different pH conditions. *Cem. Concr. Compos.* **2023**, *143*, 105255. [CrossRef]
71. Chu, H.; Wang, Q.; Gao, L.; Jiang, J.; Wang, F. An Approach of Producing Ultra-High-Performance Concrete with High Elastic Modulus by Nano-Al_2O_3: A Preliminary Study. *Materials* **2022**, *15*, 8118. [CrossRef]
72. Li, C.; Li, G.; Chen, D.; Gao, K.; Mao, Y.; Fan, S.; Tang, L.; Jia, H. Influencing mechanism of nano-Al_2O_3 on concrete performance based on multi-scale experiments. *Constr. Build. Mater.* **2023**, *384*, 131402. [CrossRef]