Cement Compositions Modified with Dispersed Magnesium Silicate Dihydrate- and Carbon-Based Additives

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Abstract: This study is based on the hypothesis that carbon black and chrysotile nanofibers, due to their ability to act as micro-reinforcement of the cement matrix and stimulate the formation of additional amounts of calcium silicate hydrates, can be used together as modifying additives in order to replace the expensive carbon nanotubes in cement-based compositions. The presented paper describes the results of experimental studies on the influence of these additives and their combinations on the physical and mechanical characteristics of the cement matrix. It was experimentally confirmed that the introduction of a complex additive based on chrysotile fibers and carbon black into the composition of the cement matrix leads to an increase in the strength of the material at the age of 28 days by 30.8% in compression and 21.6% in bending compared to the reference composition. The results of infrared spectroscopy, X-ray phase and microstructural analysis of the cement matrix are also presented. Physical and chemical analysis methods revealed a decrease in the content of the crystalline phases and the formation of amorphous hydration products in the structure of the matrix, characteristic of low-basic calcium silicate hydrates, which are responsible for the increased strength of the cement stone.

Keywords: cement stone; carbon nanotubes; carbon black; chrysotile nanofibers; X-ray phase analysis; thermal analysis; microstructure

1. Introduction

Cement-based composites are used as structural materials operating under various conditions in buildings and structures of civil, industrial and special purposes. In recent decades, studies devoted to the improvement of the properties of these materials have shifted towards the use of fine additives, including microdispersed and nanodispersed modifiers.

Much research has been aimed at unraveling the mechanism of the controlled structural formation of cement-based materials initiated by the presence of nanosized modifiers [1–3]. The research has established that the introduction of additives with a high surface area into the cement-based materials makes it possible to influence the course of the matrix structural formation and the resulting morphology of the composite, thus significantly changing the quantitative and qualitative phase composition of the material.

It is well known that in the process of cement hydration, two products are mainly formed: calcium hydroxide Ca(OH)2 and calcium silicate hydrates C-S-H. The amount of calcium hydroxide in the resulting material is much less than that of calcium silicates hydrates [4]. However, it is the presence of calcium hydroxide in the matrix that reduces
the physical and mechanical characteristics of the material due to the lamellar morphology of its crystals, between the layers of which the stone is usually fractured.

Therefore, in the process of the cement stone hardening, it is necessary to create conditions under which calcium hydroxide is intensively bound into less soluble compounds, leading to its conversion into amorphous calcium silicate hydrates—for example, tobermorite gels—preferably of lower basicity, which determine the improvement of the mechanical properties of the cement composite. The process of calcium hydroxide binding can be initiated by the introduction of ultrafine additives into the composition of the hardening cement matrix. It is preferable to choose additives which have a chemical affinity with Portland cement minerals, and which are small enough to act as additional nucleation centers for cement hydration products, which makes it possible to create a denser and less defective structure [5].

However, the use of most types of nanoadditives is limited by the so-called ‘concentration effect’, which correlates the maximum increase of the technical properties of building materials of various chemical structures and compositions (polymer, linear and mesh, bitumen-polymer, ceramics and cement binders) with the introduction of ultra-low amounts of additives (from hundredths to thousandths of a percent) [6]. This concept has lead to an assumption that the effects of nanomodification are based on the surface interactions (adsorption, chemisorption) of nanoparticles with the matrix substance, whereas the contribution of their own properties to the resulting characteristics of the composite is negligible [7]. Therefore, the most important characteristic of nanosized additives is their surface area. In this case, the task of ensuring a statistically uniform distribution of additives in the initial viscous-plastic cement paste becomes extremely important, since the effectiveness of their influence on the structural formation of the cement matrix is determined by the degree of fineness of the individual modifier particles that are used to prepare aqueous dispersions. In this case, poorly dispersed nanoadditives, when introduced into a composite, tend to agglomerate, forming flakes, clusters, or bundles due to the action of significant Van der Waals intermolecular interaction forces [8,9]. In cement compositions, these agglomerates act as weak points, preventing the formation of cement hydration products [10,11] and acting as stress concentrators [12], thus causing the destruction of the material. That is why the quality of distribution of nanoparticles in the composition of the suspension, and further in the composition of the cement matrix, has a great influence on the parameters of the obtained materials. For this purpose, when preparing suspensions of nanomodifiers, surfactants [13], sonication [14], high shear mixing [15] and other dispersing methods are traditionally applied.

Another promising solution to this problem is the development of complexes of nanoadditives of incompatible chemical compositions, which do not interact directly with each other, maintaining the stability of dispersions and ensuring the homogeneity of the properties of the modified materials.

In light of the above, the aim of this research was to study the parameters of cement matrixes modified with additives based on carbon and magnesium silicate dihydrate, introduced into the material composition together at the stage of mixture preparation. The objectives of the research included the study of the structure of the obtained composites, as well as their mechanical, physical and chemical characteristics.

2. Materials and Methods

Portland cement CEM I 32.5 N produced by OOO Timlyui Cement Plant was used as a binder. Natural river sand obtained from the sand deposit of the Kama river (Novy village, Udmurtia, Russia) was used as a fine aggregate. The size modulus of the sand was equal to 2.0. The fine aggregate-to-cement ratio was 3:1 and the water-to-cement ratio-0.45.

The development and selection of the dispersed component was based on its ability to disperse to ultra-fine sizes, and the possibility of its stabilization in the aquatic environment, with the use of surfactants. Wide availability on the market was also preferable.
The multiwalled carbon nanotubes (MWCNT) dispersion was chosen based on the wide experience of its application in recent years and its well-established ability to improve the physical, mechanical and operational characteristics of cement-based composites. Dispersions of carbon black (CB) and chrysotile fibers (ChF) have been used as an alternative to expensive MWCNT dispersion. Carbon black was selected due to its chemical similarity to MWCNT, and chrysotile fibers were selected due to their similarity to MWCNT in terms of geometry. In addition, the combined effect of chrysotile fibers and carbon black was studied. All modifying additives were added into the cement-sand mortars together with mixing water.

MWCNT stabilized with carboxymethylcellulose were introduced into the material in the form of an aqueous suspension produced by OOO Novy Dom (Izhevsk) using Graphistrength™ precursor, manufactured by the Arkema Group. The concentration of nanotubes in the suspension was 4.5 wt.%. In accordance with [16], the composition of MWCNT was represented by carbon (>90%), aluminum oxide Al₂O₃ (≤7%) and iron oxide Fe₂O₃ (≤5%). A fragment of the MWCNT dispersion microstructure, presented in Figure 1a, shows that the length of the nanotubes was approximately 200–800 nm, and the diameter was in the range of 15–80 nm.

![Figure 1. Microstructure of: (a) carbon nanotube dispersions with grafted functional groups based on carboxymethylcellulose; (b) carbon black dispersions.](image-url)

The suspension of carbon black (also known as black soot) was introduced into the composition of the material in the form of a ready-made tinting paste “CS.BK black concentrated” (Figure 1b) produced by OOO Novy Dom (Izhevsk) with soot content of 34%. The established particle size was in the range of 30–120 nm. The composition of carbon black was represented by carbon (88.6–93.7%), hydrogen (0.7–0.8%) and oxygen (5.5–10.5).

Chrysotile fibers (Figure 2) are prolonged nanotubes consisting of magnesium silicate dihydrates that can also be used for the purpose of cement-based composites modification, due to their high surface area and their ability to react chemically with the cement clinker minerals. The chemical composition of chrysotile fibers is presented in Table 1. An aqueous suspension of chrysotile fibers from the Bazhenov deposit, grade 7–370 (Figure 2a), was produced using cavitation disperser [17]. The cavitation principle is based on the separation of fiber bundles into individual fibers, using renewable water energy during the collapse of the cavitation bubbles, friction and water molecules synthesis. To stabilize the suspension of the chrysotile fibers, and to prevent the re-agglomeration of ultrafine particles, the C-3 superplasticizer based on naphthalene sulfonic acid and formaldehyde was added into the composition. The average particle size in the obtained modifier was from 30 to 100 nm (Figure 2b,c).
Some studies show that the use of chrysotile fibers may have a negative effect on people’s health. However, according to the research of Bernshtein D.M. [18], the fibrous structure of chrysotile particles ensures their complete removal from the human lungs in a natural way during breathing. The safety of chrysotile fibers application was also confirmed by the works of Neumann S.M. [19]. In addition, both in the dispersions and in the final products, chrysotile fibers are present in the bound state, which ensures the consumer’s safety and prevents any direct contact. The introduction of chrysotile fibers in doses not exceeding hundredths of a percent by weight of the binder also ensures the safety of its use. Workers in the chrysotile mining industry, and those working at plants for the manufacture of chrysotile-based products, must strictly follow the requirements of safety regulations, to help and protect them from any negative effect of this mineral exposure on their health.

The high-sensitivity measurement of the suspension’s particle size was carried out using a Shimadzu SALD-7500 laser diffraction analyzer.

Thermogravimetric analysis (TGA) of the samples was performed in the temperature range of 60–1100 °C at a heating rate of 30 °C/min, using the TGA/DSC1 Starsystem derivatograph, manufactured by Mettler Toledo.

Infrared (IR) spectral analysis was performed on a Shimadzu IRAffinity-1 spectrometer in the frequency range 400–4000 cm$^{-1}$.

The mineralogical composition of the hydration products in the structure of the cement-based composites was determined using X-ray phase analysis (XPA) on the general-purpose diffractometer DRON-3. Cobalt was used as the cathode of the X-ray tube. The obtained data was processed manually using the Grapher editor (version 2.04) and decoded using the JCPDS database [20].

To interpret the IR, TGA and XPA spectra, the data given in the Gorshkov reference book [21] was also used.

The microstructural analysis of the additives was carried out on a MIRA3 TESCAN scanning electron microscope (AdMAS Research Center, Brno, Czech Republic), and the study of the microstructure of the obtained cement-based compositions was carried out on a Quattro ESEM Thermo Fisher Scientific scanning electron microscope (Central Collective Use Center ‘Surface and New Materials’, Udmurt Federal Research Center, Ural Branch of the Russian Academy of Sciences, Izhevsk, Russia).

**Table 1. Chrysotile chemical composition.**

| Component         | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | FeO  | MgO  | CaO  | H$_2$O + 10$^5$ | H$_2$O − 10$^5$ | K$_2$O + Na$_2$O |
|-------------------|---------|-------------|-------------|------|------|------|----------------|----------------|-----------------|
| Content, wt%      | 42.60   | 0.65        | 1.04        | 0.45 | 40.77| 0.03 | 13.46          | 0.95           | traces          |

**Figure 2.** Microstructure of chrysotile fibers: (a) before processing, at 20,000-fold magnification; (b) after processing, at 50,000-fold magnification; (c) the same at 150,000-fold magnification.
To estimate the effect of the nanosized additives (MWCNT, CB, ChF) on the strength characteristics of the cement matrix, mechanical tests were carried out on standard beam samples of a cement-sand mixture with the dimensions of $160 \times 40 \times 40$ mm. A PGM-100 MG4-A hydraulic press with the maximum load of 100 kN and a loading rate of 0.5 MPa/s was used. The compositions and amounts of the individual additives introduced into the compositions were chosen in accordance with the results of the previous studies [22], which specified the optimal concentrations of the additives that led to the maximum increase in strength of samples at 28 days. In addition, samples modified with a complex additive consisting of chrysotile fibers in an amount of 0.05% by weight of cement (bwoc) and black carbon in an amount of 0.01% bwoc were studied. The ratio of the components of the additive was also established based on the results of a previous study [22].

It should be noted that when it comes to the nano-modification of cement-based composites, the comparison of nanosized additives by their mass fraction might be incorrect due to their different densities. Considering this, it seems more appropriate to use volume fractions (percentages) of these additives in the volume of the modified material, rather than their mass percentages. Besides, it may be justified and informative to evaluate the effectiveness of nanoadditives depending on their quantitative content (pieces) in the volume of cement stone, or to assess the effect of the total surface of the introduced fraction of nanoparticles on the strength parameters of the modified material.

In this research, a mixture of cement, sand and water was studied. On average, the mass of cement required to produce 1 m$^3$ of cement-sand mixture is 320 kg.

If the optimal concentration of nanostructures $C_{\text{add}}$ required for the modification of the composite is known, their mass can be determined using Equation (1):

$$m_{\text{add}} = \frac{m_{\text{cem}} \cdot C_{\text{add}}}{100}$$

In this case, the mass of the MWCNT was 7.2 g, the mass of the CB was 64 g, and the mass of the ChF was 160 g.

Carbon and chrysotile nanotubes are cylinders, the length $l$ and diameter $d$ of which are known. The volume of a single nanotube can be determined using Equation (2):

$$V_{\text{cyl}} = \frac{\pi d^2 l}{4}$$

The diameter of a carbon nanotube is around 25 nm and its length is around 200 nm, therefore its volume will be $98.1 \times 10^{-24}$ m$^3$. The median diameter of a chrysotile nanotube is 46 nm and its length is 1 µm, therefore its volume will be $1.7 \times 10^{-21}$ m$^3$.

The mass of a single modifying particle can be determined by Equation (3):

$$m_1 = V_1 \cdot \rho_1$$

where: $V_1$—volume of a single modifier particle; $\rho_1$—modifier density.

Given that the density of MWCNT is $1900 \times 10^3$ g/m$^3$ [23], the mass of one fiber will be $186.44 \times 10^{-18}$ g. The mass of a chrysotile fiber is $4080 \times 10^{-18}$ g, given that its density is $2400 \times 10^3$ g/m$^3$ [24].

Particles of carbon black are conventionally assumed to be spherical [25,26]. The volume of a spherical body is determined by Equation (4):

$$V_{\text{sph}} = \frac{1}{6} \pi d^3$$

In this case, the volume of an individual particle of carbon black is $220.8 \times 10^{-24}$ m$^3$, provided that the particle diameter is 75 nm. The mass of a carbon black particle, calculated using Equation (3), will be $397.4 \times 10^{-18}$ g, if the average density of carbon black is equal to $1800 \times 10^3$ g/m$^3$ [27].
Based on the above, the number of nanoparticles $N$ in a cubic meter of cement composite can be determined by Equation (5):

$$N = \frac{m_{\text{add}}}{m_1}$$ (5)

For multiwalled carbon nanotubes the number of nanoparticles will be $38.62 \times 10^{15}$ pcs, for carbon black—$161 \times 10^{15}$ pcs and for chrysotile fibers—$39.21 \times 10^{15}$ pcs.

The total volume of nanoparticles in 1 m$^3$ of cement-based composite can be determined by Equation (6):

$$V_{\text{part}} = V_1 \cdot N_{\text{part}}$$ (6)

In this case, the total volume of the MWCNTs was $3.79 \times 10^{-6}$ m$^3$; the total volume of the CB was $35.42 \times 10^{-6}$ m$^3$; and the total volume of the ChF was $66.6 \times 10^{-6}$ m$^3$.

The surface area of a single nanotube can be determined using Equation (7) for the calculation of the side surface of a cylinder:

$$S_{\text{cyl}} = \pi dl$$ (7)

Using Equation (7), the surface area of a carbon nanotube can be calculated to be $15.7 \times 10^{-15}$ m$^2$, and that of a chrysotile nanotube—$144.4 \times 10^{-15}$ m$^2$.

The surface area of a carbon black particle can be determined using Equation (8) for the surface area of a sphere:

$$S_{\text{sph}} = \pi d^2$$ (8)

Thus, the surface area of a carbon black particle is $35.4 \times 10^{-15}$ m$^2$.

In this case, the surface area of all modifying particles $S_{\text{sur}}$ in 1 m$^3$ of the composite was determined by Equation (9):

$$S_{\text{sur}} = S \cdot N$$ (9)

For the MWCNT it was $0.6 \times 10^3$ m$^2$; for the CB, it was $7.79 \times 10^3$ m$^2$; and for the ChF, it was $5.66 \times 10^3$ m$^2$.

In the complex additive, the amount of chrysotile introduced into the composition of the material was 0.05% bwoc, and the amount of carbon black was 0.01% bwoc. In this case, the total number of nanoparticles of the complex modifier was calculated as:

$$N_{\text{complex}} = N_{\text{ChF}} + N_{\text{CB(0.01)}} = 80.5 \times 10^{15} + 39.21 \times 10^{15} = 119.71 \times 10^{15}$$ (10)

In this case, the volume fraction (percentage) of complex modifier nanoparticles in 1 m$^3$ of cement-based composite was 0.009%, and the surface area was $46.35 \times 10^3$ m$^2$.

Summary data on the quantitative content of the modifying additives in the composition of the material are presented in Table 2.

| Parameter          | MWCNT        | CB            | ChF            | Complex                   |
|--------------------|--------------|---------------|----------------|---------------------------|
| Mass content, % bwoc | 0.005        | 0.02          | 0.05           | ChF-0.05 + CB-0.01        |
| Quantity, pcs      | $38.62 \times 10^{15}$ | $161 \times 10^{15}$ | $39.21 \times 10^{15}$ | $119.71 \times 10^{15}$ |
| Volume fraction, % | 0.0004       | 0.0035        | 0.007          | 0.009                     |
| Surface area, m$^2$ | $0.6 \times 10^3$ | $7.79 \times 10^3$ | $5.66 \times 10^3$ | $9.56 \times 10^3$ |

Thus, the quantitative parameters—the number of particles ($10^{15}$ pcs), their volume fraction and the huge area of contact with the surrounding matrix (thousands of m$^3$)—are responsible for the main effect of ultra-small dosages of nanoparticles.

An assessment of the additives’ application cost is presented in Table 3.
Table 3. The cost of the additives’ application.

| Composition                  | Price Per kg of Dispersion, € | The Content of the Dispersed Component | Concentration in the Matrix, % Bwoc. | Modification Price, €/tn of Binder |
|------------------------------|-------------------------------|----------------------------------------|-------------------------------------|-----------------------------------|
| MWCNT dispersion, including: | 20                            | 4.5%                                   | 0.005                               | 22.5                              |
| MWCNT                       | 450                           |                                        |                                     |                                   |
| CB dispersion, including:    | 7                             | 34%                                    | 0.02                                | 1.4                               |
| CB                           | 20.5                          |                                        |                                     |                                   |
| ChF dispersion, including:   | 0.14                          | 10%                                    | 0.05                                | 0.07                              |
| ChF                          | 0.8                           | 2%                                     | 0.01                                | 0.08                              |
| Complex additive, including: |                               |                                        |                                     |                                   |
| ChF dispersion               |                               |                                        |                                     | 0.85                              |
| CB dispersion                |                               |                                        |                                     | 0.15                              |
| CB                           |                               |                                        |                                     | 0.7                               |

It can be seen from the table that the cost of material modification with the MWCNT and the carbon black dispersions is 22.5 and 1.4 euros per ton of binder, respectively. Thus, the most cost-effective cement matrix modifier is a dispersion of chrysotile nanofibers (the cost per ton of binder is only 0.15 euro) at a fiber content of 0.05% bwoc, which is significantly less than the cost of the carbon-based analogues. Unfortunately, the further increase in the concentration of chrysotile additive leads to agglomeration of the dispersed component and a decrease in the strength of the composite. This issue can be overcome by use of the complex additive based on chrysotile fibers and carbon black. The cost of the cement composites modification with a complex additive is 0.85 euro per ton of binder, which enables an increase in the compressive strength of the material by about 30%.

3. Results and Discussion

To evaluate the dynamics of the composition strength development with the presence of each additive, the samples were tested on the 1st, 3rd, 7th and 28th days of hardening. The results of the study are presented in Figure 3.

Figure 3. The dynamics of the strength development of cement-based compositions depending on the type of additive introduced: (a) in compression; (b) in bending.

The graph shows that the maximum increase in strength of the cement-sand mixture at all periods of hardening was achieved with the introduction of a complex additive; however, other additives alone also contributed to the material strengthening. This may have been due to the effect of the “nucleation” of hydration products on the surface of the nanosized additives. At 28 days, a 30.8% increase in compressive strength and a 21.6% increase in bending strength was achieved when the complex additive, containing chrysotile fibers in an amount of 0.05% bwoc and carbon black in an amount of 0.01% bwoc, was introduced.
into the composition of the material. Here, the stability of dispersion over time was of significant importance, and requires additional research.

The stability of the MWCNT and carbon black-based modifiers used in this research was provided by the manufacturer OOO Novy Dom, by introducing surfactants into the composition of dispersions. The sedimentation stability of the chrysotile fibers’ suspension was determined through its visual assessment over time. It was established that the dispersion was sedimentationally unstable over time: within seven days, heavier fractions of solid particles tended to precipitate due to the low viscosity of the aqueous dispersion medium, which was insufficient to resist the forces of gravity on individual particles. However, this did not affect the aggregative stability of the modifier (the process of formation of stable and coherent aggregates of the solid phase in the suspension). In addition, it was noted that the chrysotile dispersion had good re-dispersibility, which is the ability of its particles to be evenly distributed over the entire volume of the medium with little mechanical action (for example, shaking). This was confirmed by dispersion analysis of the suspension at the age of 2 years. Figure 4 shows that after keeping the suspension for 2 years and then shaking it, the median particle size reached the value of around 26 nm, whereas its size in the initial dispersion was almost twice as big (46 nm). This can be explained by peptization (splitting under the action of a liquid medium) of the predominant ionic bonds along the fibers of large chrysotile agglomerates—rock residues, the presence of which is clearly visible in Figure 2b,c. The initial destruction of the chrysotile fibers ‘packages’ (Figure 2a) also prevented the possibility of the re-emergence of stable bonds between particles. Furthermore, the addition of C-3 superplasticizer had a stabilizing effect on the suspension, due to the creation of electrostatic repulsion forces, preventing agglomeration of particles.

Currently, there is no generally accepted method for quantifying the degree of nanomaterials dispersion in the cement matrix. In most studies, an indirect method is used, in which the dispersion degree is evaluated based on the mechanical properties of the composite materials, as well as their final structure [28].

Figure 5 shows SEM images of a cement matrix structure of the reference composition, and in the composition modified with a complex additive based on CB in an amount of 0.01% bwoc and ChF in an amount of 0.05% bwoc. The introduction of the complex additive led to a significant change in the micromorphology of the cement stone, with the replacement of a porous net of needle-like cement hydration products (Figure 5a) by an amorphous phase of calcium silicate hydrates (Figure 5b). Thus, the introduction of a complex additive provides conditions for matrix densening, with the following improvement in its strength and performance characteristics.

![Figure 4](image-url)
The results of an X-ray spectral analysis suggest that the additional amount of hydration products can be attributed to thaumasite formations (CaSiO₃·CaSO₄·CaCO₃·15H₂O), formed as a result of calcium silicate hydrates (C–S–H) reacting with calcite and unbound sulfate ions, or the reaction of ettringite with C–S–H and carbonates/bicarbonates [29,30].

Additionally, the hydrated samples were studied by means of the differential scanning calorimetry, which showed that all spectra had endothermic effects characteristic of dehydration of cement hydration products (100–200 °C), as well as calcium hydroxide (450–550 °C), and calcium silicate hydrates (above 600 °C).

The results of a thermogravimetric analysis, summarized in Table 4, reflect a decrease in the weight loss of the samples during dehydration in the temperature range of 90–200 °C, in the case of their modification with nanoadditives, which indicates the binding of free water in the structure of the material into the additional amount of hydration products.

Table 4. Results of thermogravimetric analysis.

| Composition                  | Initial Mass | 90–200 °C Mass Loss, wt.% | 450–550 °C Mass Loss, wt.% | 600–800 °C Mass Loss, wt.% |
|-----------------------------|--------------|----------------------------|----------------------------|----------------------------|
| Reference                   | 94.722       | 4.64                       | 1.74                       | 2.58                       |
| Modified with MWCNT         | 103.232      | 3.36                       | 1.05                       | 1.68                       |
| Modified with CB            | 95.69        | 3.39                       | 1.1                        | 1.7                        |
| Modified with ChF           | 108.462      | 3.26                       | 1.03                       | 1.64                       |
| Modified with a complex additive | 95.01      | 3.25                       | 1.09                       | 1.54                       |

IR spectral analysis of cement matrices of the reference composition, and the composition modified with a complex additive based on chrysotile fibers and carbon black, is shown in Figure 6.

The IR spectrum shows the presence of a strong OH⁻ group (3421.72 cm⁻¹), as well as the bound water (1662.24 cm⁻¹) in the reference composition. At the same time, when the cement-based composite was modified with a complex additive (ChF + CB), the formation of multiple peaks in the frequency range of 3400–3900 cm⁻¹ was noted. The related decrease in the amount of free water (3800–3400 cm⁻¹ and 1653.00 cm⁻¹) suggests there was a different degree of bonding of the hydroxyl group OH⁻ in the calcium silicate hydrates, as well as a decrease in the total amount of free Ca(OH)₂ due to its conversion into C-S-H. In addition, the intensity of the absorption line in the frequency range of 1008.7 cm⁻¹ decreased in the spectrum of the modified sample, and the absorption lines corresponding to C-S-H shift from 1089.78 cm⁻¹ to 1080.14 cm⁻¹, as well as from 1008.77 cm⁻¹ to 993.34 cm⁻¹. A change in the nature of the doublet with a shift of the maximum peak to a lower frequency region suggests there was a change in the basicity of the calcium silicate hydrates, which can be responsible for an increase in the strength of the cement matrix.
Figure 6. IR spectrum of the sample: (a) reference composition; (b) modified with a complex additive based on carbon black and chrysotile asbestos.

The represented shift of the absorption lines (from 1008.77 cm\(^{-1}\) to 993.34 cm\(^{-1}\)) may also have been because the polymerization of the silicon–oxygen radicals in the C-S-H phase of the modified sample significantly lagged behind compared to the reference composition; the resulting fragments of the C–S–H phase were extremely finely dispersed. This may explain the increased strength due to the formation of finely dispersed C-S-H nano-colloidal formations, which have a larger specific surface area and ‘gluing’ ability due to van der Waals surface forces. In order to analyze the mineralogical composition of the reference and the modified samples, X-ray diffraction analysis was carried out (Figure 7). The XRD spectrum of the reference composition is represented in black, and the XRD spectrum of the composition modified with a complex additive is represented in red.

Figure 7. Spectra of X-ray phase analysis of the reference composition sample (black) and a sample modified with a complex additive based on chrysotile fibers and carbon black (red).

The analysis results show that quartz SiO\(_2\) reflections dominated in the resulting spectrum (d, Å = 4.26; 3.35; 2.46; 2.13; 1.98; 1.82; 1.67; 1.54; 1.38; 1.37). The presence of unreacted clinker minerals 3CaO·SiO\(_2\) was also noted (d = 3.03; 2.87; 2.78; 2.63; 2.32; 2.19; 1.77; 1.62; 1.49).
In addition, the presence of tobermorite 5CaO·6SiO$_2$·(0-2,5)H$_2$O (d, Å = 9.70; 3.18; 3.03; 2.78; 1.83), Portlandite Ca(OH)$_2$ (d, Å = 4.92; 2.63; 1.93; 1.77; 1.45), calcite CaCO$_3$ (d, Å = 3.03; 2.28; 2.09; 1.44), and calcium hydroxysulfoaluminate—ettringite (d, Å = 9.71; 5.61; 4.70; 3.85; 3.50; 2.78; 2.57) was revealed in the phase composition of the material.

Interpretation of the changes in the diffraction lines corresponding to calcium hydroxide (d, Å = 4.92; 1.93) is difficult because in most cases they were superimposed by the corresponding reflections of tobermorite.

Identification of C-S-H phases by X-ray phase analysis is also problematic, as this hydration product is usually present in the matrix composition in an amorphous or weakly crystallized state [31]. However, the literature data [32–34] suggests that highly basic calcium silicate hydrates CSH (II) in the composition of cement-based materials usually have diffraction reflections with d = 9.70; 4.92; 3.50; 3.07; 2.78; 2.74; 2.19 Å, whereas low-basic C-S-H (I) have reflections with d = 3.07; 3.03; 2.74; 1.93; 1.82; 1.67 Å. The study of the diffraction patterns shows that the intensity of the lines corresponding to low-basic calcium silicate hydrates C-S-H (I) (d, Å = 3.07; 3.03; 1.93; 1.82) increased in the modified composition. Moreover, the reflection with d = 3.18 Å corresponding to tobermorite [21] appears only in the composition modified with a complex additive.

In addition, a decrease in the intensity of reflections corresponding to ettringite (d, Å = 5.61; 4.70; 3.85; 3.50; 2.57) is clearly visible, which may indicate a decrease in the content of crystalline phases and the formation of an amorphous-crystalline structure, which is characteristic of low-basic calcium silicate hydrates. The tendency for the formation of products with more amorphous structure in the process of cement hydration results in a smaller number of defects in the cement stone and an increase in its strength, which additionally confirms the results of microstructural, IR spectral and thermal analysis, as well as mechanical tests of the developed compositions.

4. Conclusions
1. The application of dispersed additives of various sizes, shapes and natures in cement-based composites makes it possible to regulate the process of cement hydration, and to control the morphology of cement hydration products with the formation of denser and more stable structures with improved physical and mechanical characteristics.
2. Comparison of various dispersed additives and their mixtures makes it possible to obtain effective modifying solutions at an affordable price, which contributes to the creation of strong and durable compositions.
3. It was experimentally confirmed that the introduction of a complex additive based on chrysotile nanotubes and carbon black into the composition of the cement-based composite makes it possible to achieve an increase in the strength of the material during hardening under normal conditions by 30.8% in compression and 21.6% in bending, compared to the reference composition.
4. The influence of a complex additive based on chrysotile nanofibers and carbon black on the structure and composition of the cement matrix in modified concrete was evaluated using XRD analysis, IR spectroscopy, differential thermal analysis, X-ray microanalysis and the study of the matrix microstructure in cement composites.
5. It was noted that in the structure of the cement matrix, calcium silicate hydrates of lower basicity were formed, which increased the strength of the cement stone, as well as a larger amount of amorphous hydration products, which helped to reduce the defectiveness of the cement matrix, thus strengthening it.

5. Patent

Based on the results of the work reported in this manuscript, a patent was published: Patent RU 2021123273. Yakovlev, G.; Polyanskikh, I.; Saidova, Z.; Kuzmina, N. Complex additive for silicate composite materials and method of its preparation. 2021, Bull. No. 29. 11 p.
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