Evaluation of the efficiency of lightweight concrete modified with additives based on nanostructures

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Abstract. The paper presents the results of studies on assessing the effectiveness of the modification of lightweight concrete with nanostructures. The results of these experimental studies show that the introduction of additives based on nanostructures, such as dispersions of carbon nanotubes and silica nanoparticles, improves the physical-mechanical characteristics of lightweight foam concrete (LWFC), even at low additive concentrations. As a result of chemical and physical interactions, nanosilica (NS) accelerates the pozzolanic reaction between cement and nanosilicate in the concrete mixture, filling the gaps. CNTs affect the hydration process and effectively increase the grain growth of calcium silicate hydrate (C-S-H). The presented experimental studies not only demonstrate the possibility of modifying construction materials with nanostructures in order to improve the physical and mechanical properties of the LWFC but also provide potential modification mechanisms that help in designing and manufacturing high-tech lightweight concrete of various compositions.

1. Introduction

Modern technologies for the production of construction materials are aimed at using nanosystems and providing for employing those materials, the basic properties of which are manifested at the nanoscale level. Firstly, this is due to the excellent physical-mechanical characteristics of nanomaterials. When developing composites for construction purposes, the following types of nanomaterials are actively studied and applied: nanosilica and carbon nanostructures such as graphene, fullerenes and carbon nanotubes (CNTs), etc. The use of CNTs leads to an increase in the physical-mechanical characteristics of construction composites, durability, moisture resistance and crack resistance, as well as a reduction in the consumption of expensive components, which makes this material attractive for the construction materials industry. At the present stage of nanotechnology development, the study of the effectiveness of CNTs-modified concretes is of particular scientific and practical importance. Modification with chemical additives, especially based on CNTs, improves the properties of lightweight foam concrete (LWFC), which usually consists of cement, sand, foaming agent and water [1]. The concrete body has a large number of pores with a diameter of 1-3 mm; therefore, its density usually ranges from 200 to 2000 kg/m³.

A large number of research and scientific experience have shown that ultra-light foam concrete (ULFC) is not stable [2-3]. The instability inescapable of foam concrete often leads to a low mechanical characteristic such as compression and fracture strength, which limits the material
applications. Various studies have estimated the compressive and fracture strength of foam concrete. Besides, more and more researchers in the field of materials science are trying to improve the physical-mechanical characteristics of construction materials, like compressive and tensile strength of ULFC using various fibers as modifiers. Moreover, the curing conditions not only significantly affect the mechanical properties of foam concrete, but also significantly affect its fracture energy. The properties of LWFC are significantly affected by the microstructural properties and are related to the distribution of bubbles and the development of hydrated products [4-7]. Foam concrete possesses excellent properties such as low density, thereby leading to a decrease in the structural dead load and operating costs. In addition, due to its textured surface and microstructure unit, it improves soundproofing and thermal conductivity, but the strength gradually decreases as the density decreases. However, in such a medium, at low density values (\(< 1000 \text{ kg/m}^3\)), the above positive characteristics of the LWFC can be better manifested. Low-density LWFC elements are used in non structural applications and partitions in buildings in road construction and concrete floors, and for higher density it may be used in structural applications such as composite wall systems [8-10]. The flexural strength increases by the presence of the fibers of LWFC, but it also effectively reduces drying shrinkage [8,11].

Over the last years, investigators have shown that the addition of CNTs dispersions improves the compressive and fracture strength of concrete/foam concrete [12-15]. The nanoscale reinforcement potentially possesses the quality of the filler, contributing to the formation of a more dense material; besides, it makes it possible to slow down and prevent the development of cracks at the early stages of hardening, as well as to improve the quality of the phase boundary matrix aggregate as a whole. As a result, using CNTs can produce more durable and stiff concrete [16]. Concrete is a fragile material with a binder in the form of cement paste, which has a porous structure, including micro- and mesopores. The properties of the concrete mix and their changes mainly depend on the hydration of cement. The use of CNTs in cement composites, for the most part, is aimed at creating a reinforcing effect at the nanoscale level [17]. Some researchers have attempted to disperse CNTs using various methods: mechanical processing and surface modification. Surface modification methods using various acids can lead to destructive phenomena in concrete/foam concrete. The methods for dispersing CNTs employing surfactants can block the CNTs effect on the structure of foam concrete. Thus, the use of these conventional processes of dispersing CNTs in concrete/foam concrete is limited [18-20].

Considering the aforementioned, the aim of the present research was to study the efficiency of the modification of LWFC using various nanostructures.

2. Experimental part

In order to assess the effect of nanostructures on the physical-mechanical properties of LWFC, experimental studies were carried out with various nanomodifiers. The nano-SiO$_2$ (NS) was added to the cement composition in a dry format a ratio of 1, 1.5, 2, 2.5, and 3 % by weight of cement in order to determine the effect of the additive on the physical and mechanical properties. It was found that the optimal ratio is 2.5 %, while the pozzolan reaction between the cement and the NS is activated, and the nanosilica particles fill the gaps of C-S-H gel and contribute to a denser bond with C-S-H, which makes the matrix of the binder paste denser. Table 1 and figure 1 show the NS properties and XRD, respectively.

The following materials were used in the experiment with the nanomodifiers of lightweight concrete based on CNTs: Portland-type cement (M500, Eurocement, Belgorod, Russia), gradient sand as fine aggregate (collected in Tambov, Russia), as well as ordinary tap water (the water/cement ratio was 0.4); besides, a foaming agent acquired from MAXPEN (Voronezh, Russia) was used to obtain LWFC. Taunit-24 CNTs were manufactured at NanoTechCenter Ltd. (Tambov, Russia). Table 2 demonstrates their properties, and figure 2 presents their SEM images. Polyvinylpyrrolidone (PVP) was used as a surfactant to prepare the dispersion. Figure 3 shows the microsized agglomeration of the CNTs.
Table 1. Physical properties of the NS.

| Property         | Value         |
|------------------|---------------|
| Particle Size    | 30-100 nm     |
| Density          | 2.220 kg/m³   |

Figure 1. X-Ray diffraction pattern of the NS powder.

Table 2. Properties of the Taunit-24 CNTs.

| Properties                                  | Values       |
|---------------------------------------------|--------------|
| External diameter (nm)                      | 20-50        |
| Inner diameter (nm)                         | 10-20        |
| Length (µm)                                 | ≥2           |
| The total amount of impurities,%            |              |
| initial                                     | ≤10          |
| after cleaning                              | ≤1           |
| Surface Area m²/g                           | ≥160         |
| Density, g / cm³                            | 0.3-0.6      |
The water-cement ratio was chosen depending on two parameters: sample density and compressive strength [22]. Polyvinylpyrrolidone was dissolved in (100 mL) of water and stirred with a magnetic stirrer for 10 min. Then the CNTs were added and mixed for 5 min by hand in a glass beaker. Ultrasonic treatment of the solution was carried out for 15 min at a frequency of 60 kHz [23]. Figure 4 shows the ultrasonic device and the CNTs dispersion after the sonication procedure.

Figure 2. SEM images of the Taunit-24 CNTs [21].
In accordance with the ratio of the components shown in table 3, the mixing process was carried out by mixing the cement with the sand, and then the mixing water was added to prepare the solution. The CNTs dispersion was added to the solution mixture. After that, the foaming agent was added to the mixture to obtain the LWFC.

Table 3. Mixture preparations.

| Cement (g) | Sand (g) | Foam (g) | Mix No. With CNTs | Mix No. With NS | **CNTs (%)** | **NS (%)** |
|------------|----------|----------|-------------------|----------------|--------------|------------|
| 1200       | 1200     | 6        | Mix 0 CNTs 0      | Mix 0 NS 0     | 0            | 0          |
| 1200       | 1200     | 6        | Mix 1 CNTs 0.0004 | Mix 1 NS 1     | 1            | 1          |
| 1200       | 1200     | 6        | Mix 2 CNTs 0.0006 | Mix 2 NS 1.5   | 2            | 2.5        |
| 1200       | 1200     | 6        | Mix 3 CNTs 0.0008 | Mix 3 NS 2     | 2            | 2.5        |
| 1200       | 1200     | 6        | Mix 4 CNTs 0.001  | Mix 4 NS 2.5   | 3            | 3          |

* W/C=0.4
** In reference to cement mass.

After the mixing, the concrete mixture was placed into a prism mold (40 x 40 x 160 mm). The samples were removed after 24 h of molding, and then were immersed into the water to cure at a temperature of 23°C±2°C according to State Standard of the Russian Federation No. 31108-2016. The average of three prisms was tested according to State Standard of the Russian Federation No.310.4-81) to determine the flexural strength and then the compressive strength at the age of 28 days. The testing machine was uniaxial (IP-M testing machine) with a capacity of 2000 kN, the applied loading rate was 0.4 MPa/s.

3. Results and discussion

The results of the experimental studies with the NS modifier showed an increase in the compressive and flexural strength of the LWFC. It was also found that the additives based on the NS and the CNTs slightly increase (by 3 %) the density of the concrete compared to the reference sample, and clearly increase the compressive and tensile strength. Figure 5 shows the distribution of the NS in the concrete matrix.

![Figure 4. Ultrasonic device and CNTs before mixing with water (a); CNTs after mix with water (b).](image_url)
As a rule, resistance to the flexure under load, especially for the foam concrete which has many pores, leads to a low flexural strength value. The physical-mechanical characteristics of the concrete are enhanced by the addition of CNTs, since the strength of the C-S-H gel in the cement is enhanced by the presence of the CNTs. The reason for improving the mechanical properties of the concrete may be that the CNTs in the concrete form a structure that is resistant to cracking under load, especially in terms of flexural strength. Adding the nanomodifiers to concrete will reduce the consumption of cement, which will reduce the cost of lightweight concrete products. The increase in the compressive strength indicates that agglomeration of the nanotubes in cement products is minimized due to the proper dispersion of the CNTs. The agglomeration is primarily opposed to the ultrasonic processing and magnetic stirring, if the nanotubes are not completely dispersed, the mechanical properties of concrete may not be improved. Figure 6 shows the distribution of the CNTs in the concrete body (matrix). The CNTs have a large specific surface area, which, in turn, provides interaction at the interface. The availability of the connecting cracks is one of the weakest links in the heterogeneous concrete mixture. The introduction of the CNTs fills this space and prevents the crack spreading. Figures 7 and 8 show the effect of NS and CNTs on mechanical properties.

**Figure 5.** SEM images: samples without (a) and with (b) the NS.

**Figure 6.** SEM images: samples without (a) and with (b) the CNTs.
The structure of concrete, as a rule, has pores, which are classified as internal pores in cement C-S-H, they are formed in the process of hydration and external pores. Testing of samples for water absorption was carried out according to State Standard of the Russian Federation No.31108-2016. Figure 9 presents the results of assessing the effect of the content of CNTs on water absorption. There is a decrease in water absorption of CNTs at (0.0008%) by weight of cement, due to the formation of a denser structure.

4. Conclusion
Nanomodifiers to the LWFC based on NS and CNTs can control and direct the process of hydration hardening, due to the formation of various structures affecting the packing density of the cement matrix. It was also found that the contents of CNTs (Taunit 24) and NS even in small doses in the ranges of (0.0004 - 0.0012 % and 1, 1.5, 2, 2.5 and 3%, respectively) can affect the microstructure, and, accordingly, the physical-mechanical properties of the LWFC, such as compressive strength (increase up to 68%) and flexural strength (increase up to 34 %), as well as water absorption (decrease by 8%). Increasing the strength characteristics of the lightweight concrete will reduce the consumption of cement.
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