Study of properties of cements and concrete mixtures with carbon nanotubes

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Abstract. The development of nanotechnology contributes to the production of a new generation of multifunctional building materials. Carbon nanotubes (CNTs) are one of the components that make it possible to obtain such materials. CNTs are so small that they are prone to aggregation. To exclude this phenomenon, it is necessary to subject the particles to ultrasonic dispersion and stabilization. The purpose of the study was determined, which is to stabilize CNT suspensions and study of the properties of cements and concrete mixtures containing stabilized CNT particles in their composition. During the research, we have established the optimal dispersion parameters ($t = 25 \pm 2\ ^{\circ}C$, $\upsilon = 44$ kHz, $\tau < 30$ min) and the stabilizer concentration (5 g/l). The tests on the compressive strength of modified cement samples showed that the complex additive, which includes polycarboxylates and CNTs, gives the maximum increase in strength in the first day by 60%, in 28 days - by 20%. The introduction of CNTs into the composition of the concrete mix increased the compressive strength by 32% on the 3rd day of hardening, and by 34-39% on the 28th day compared to the control composition without additives.

Keywords. carbon nanotubes, complex additive, stabilization, acoustic cavitation, cement stone, concrete mixtures.

1 Introduction

The development of nanotechnology contributes to the production of a new generation of multifunctional building materials. The most well-known additives of the nanoscale series are carbon nanotubes (CNTs). It is known that carbon nanotubes (CNTs) have unique properties. One of these properties is high mechanical strength. Thus, the modulus of elasticity and ultimate tensile strength of an individual nanotube significantly exceeds similar values for high-strength steel [1]. Therefore, many works in various areas of the national economy (electronics, medicine, bioengineering, etc.) are devoted to the use of carbon nanotubes [2–5]. We will dwell in more detail on the study of this issue in the construction industry.

Carbon nanotubes can be used to reinforce cement matrices. The improvement of mechanical properties depends on the interphase characteristics of the obtained materials, namely, on the interactions between CNTs and cement [6]. Due to hydration processes, nuclei of

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hydration products are formed on the CNT surface. They concentrate hydrate formations, which leads to an improvement in the mechanical characteristics of the cement matrix [7-10]. It was noted in [7] that when the proper dispersion of CNTs is achieved, hydrated products of cement, including C-S-H and $Ca(OH)_2$, interact with active CNTs. This interaction leads to a decrease in the porosity of Portland cement composites, which leads to an increase in mechanical strength. In the study [8] the results showed that the yield strength significantly increases with an increase in the number of carbon nanotubes. Viscosity was also affected by the presence of carbon nanotubes. The bending strength of mortars increases with different amounts of carbon nanotubes. Depending on the geometric characteristics of carbon nanotubes, the material shows the properties of the composite.

It was noted in [11, 12] that polymers combined with carbon nanotubes to form polymer nanocomposite particles are useful additives for cements for gas wells. The addition of nanotubes to cement improves the barrier to formation gas migration through cemented annulus. In the article [13], studies were carried out to study the effect of CNTs on cement-based materials under dynamic shock loading. It has been established that the impact resistance of backfill materials based on cement with CNTs was more significant at high dynamic load, the dynamic properties increase up to 31.86%. This suggests that CNT reinforcement is more effective when designing for impact loads.

In [14, 15], a cement composite reinforced with carbon nanotubes was considered. The composite has excellent electrical and self-sensing properties. Thus, it can be an integrated sensor for monitoring the condition of structures.

The above examples show many positive properties of composites containing carbon nanotubes. However, it is not shown how dispersions of nanotube dispersions were stabilized, which allowed them to be uniformly distributed in the composition of the composite. Therefore, in this study, attention is paid to the stabilization of CNT suspensions and the study of the properties of cements and concrete mixtures containing stabilized CNT particles in their composition.

2 Experimental

The object of research is stabilized suspensions of CNTs, which make it possible to influence the structure and properties of cements and concrete mixtures. We used carbon nanotubes synthesized by low-temperature catalytic pyrolysis of hydrocarbons (RosNOU, Moscow). Characteristics of CNTs are presented in Table 1.

Table 1. Characteristics of CNTs

parameters	values
Outer diameter, nm	20–150
Inner diameter, nm	8–10
Length, μm	3–7
Density, kg/m^3	2400–2900
Bulk density, kg/m^3	140–550
Specific surface, m^2/g	90–120
Residual magnetization, EM	0.01–0,1
Coercive force, E	10–35
saturation magnetization, EM	0.2–2.2
Quantity of other forms of carbon, %	less 0.1

To achieve the goals set, samples were prepared from Portland cement CEM 0 of «Holsim (Rus) Building Materials LLC», the chemical and mineralogical composition of which is shown in Figures 1 and 2, respectively.

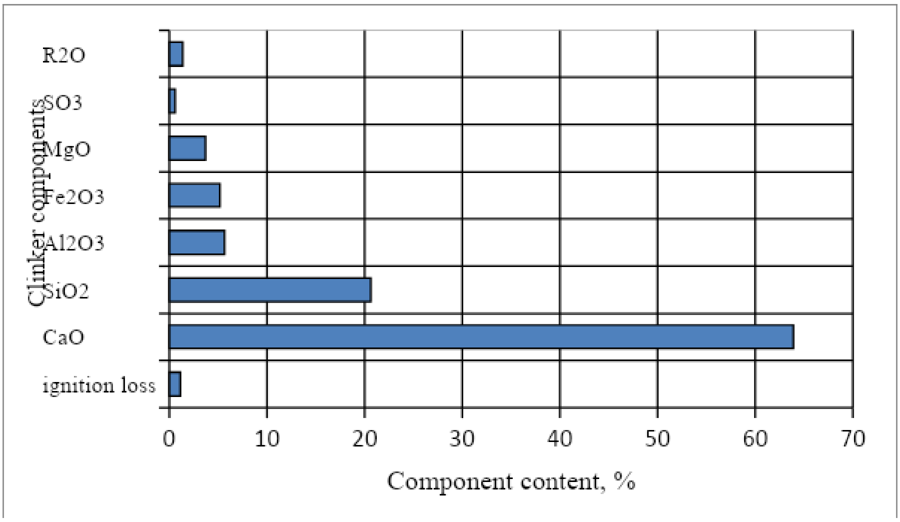


Fig.1. The chemical composition of clinker

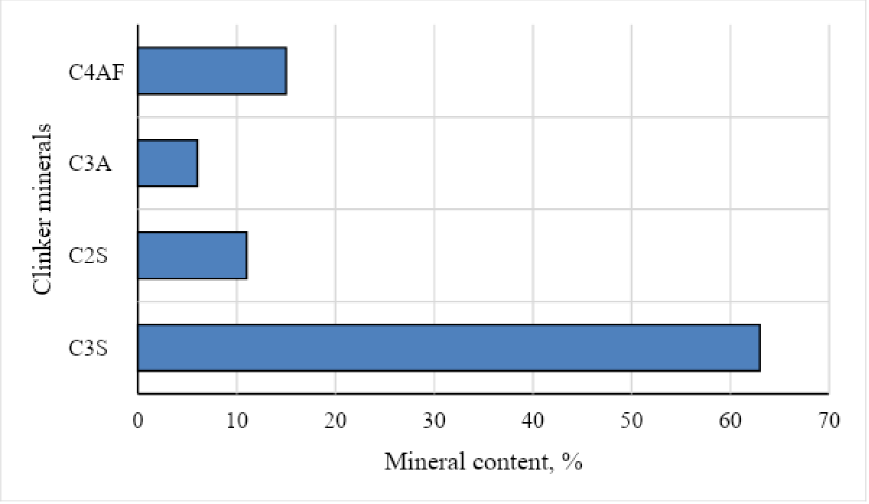


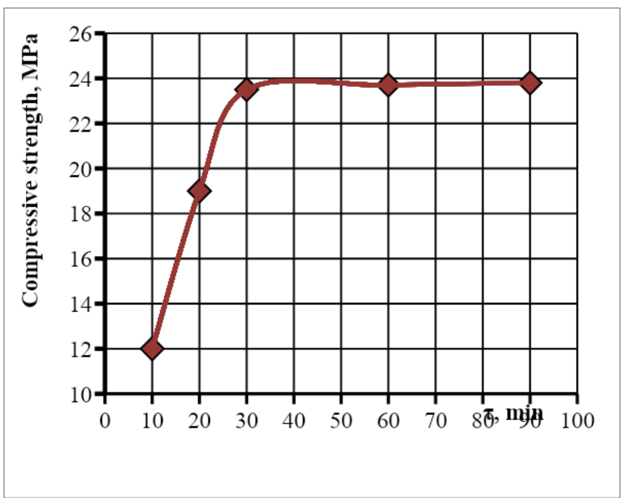
Fig.2. Mineralogical composition of clinker

Chemical and physical methods were used to achieve stabilization of CNTs: the addition of a polycarboxylate superplasticizer Melflux 2651F to the system and ultrasonic dispersion on an UZDN-1 device at a frequency of 44 kHz under thermostated conditions (t = 25 ± 2oC).

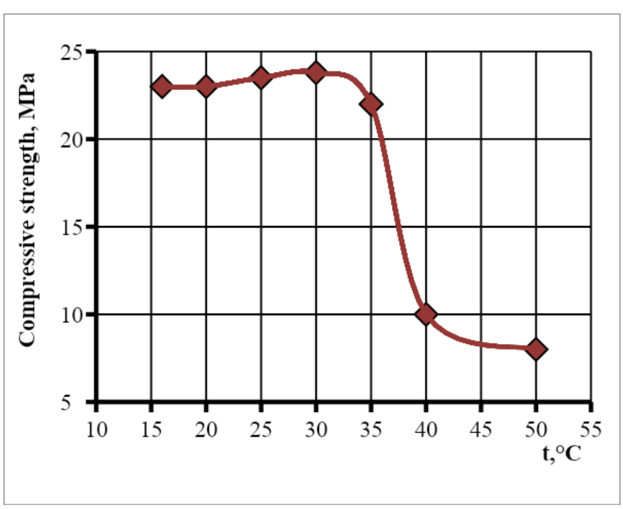
Physical and mechanical tests of materials were carried out in accordance with current national and international standards and procedures.

3 Evaluation

The use of CNTs in construction and materials science practice is limited due to their increased tendency to agglomeration. Agglomeration leads to an uneven distribution of nanoparticles in the bulk of the composite material and to insufficient adhesion to the binder matrix, which causes instability of the physical and mechanical properties and often their deterioration. For the effective use of CNTs in the production of building materials, it is necessary to provide them with sufficient homogeneity and stabilization. One of the commonly used methods for separating nanoparticles is acoustic cavitation. However, this method is not always productive. Therefore, the task was set to identify the optimal conditions for the dispersion and stabilization of CNTs. To establish the optimal dispersion time and temperature, graphs of the dependence of the strength of daily samples (containing 0.1% CNTs) on the duration of dispersion and the temperature of the dispersion medium were plotted (Fig. 3). The constructed dependency graphs made it possible to indirectly judge the most optimal dispersion conditions.



a)



b)

Fig.3. Influence of dispersion parameters of CNT suspension on the strength of daily samples: a) dispersion time, b) temperature of the dispersion medium in CNT suspension

The resulting dependence in Fig. 3a showed that the strength of daily samples reaches its maximum values when dispersed for 30 min. With further dispersion, the strength remains constant.

Fig. 3b shows that within the range of 16-30°C, the strength of the samples takes on a constant maximum value, above 30°C, the strength begins to decrease, and at 50°C it has a minimum value. At elevated temperatures, two competing processes occur simultaneously: diffusion transfer of particles due to Brownian motion and coagulation, which leads to an imbalance and even to a decrease in the dispersion efficiency.

Thus, it is recommended to carry out the dispersion of CNTs for no more than 30 min under thermostatic conditions while maintaining the dispersion temperature at t = 25±2ºC.

Stabilizers must be used to keep CNTs longer in suspension. The most ideal stabilizer is a polycarboxylic acid plasticizer, because This high molecular weight compound, being adsorbed on the CNT surface, creates a structural-mechanical barrier that prevents the coalescence of nanoparticles into agglomerates. The side hydrocarbon chain in the polycarboxylate structure causes an additional steric effect, which enhances the stabilization of CNTs in suspension.

To determine the optimal concentration of the plasticizer (which makes it possible to stabilize CNT particles in suspension), the critical micelle formation concentration (CMC) was determined using the stalagmometric method, which serves as the maximum allowable concentration value for establishing CNT stabilization. The formation of spherical micelles is observed, leading to destabilization of the nanosystem above the CMC point. In the course of the computational and graphical determinations described in [16, 17], an isotherm of the surface tension of the plasticizer was constructed (Fig. 4), showing the CMC point with a dotted line, lg Cv = 1.7, respectively, CMC is equal to the concentration of the plasticizer 7 g/l.

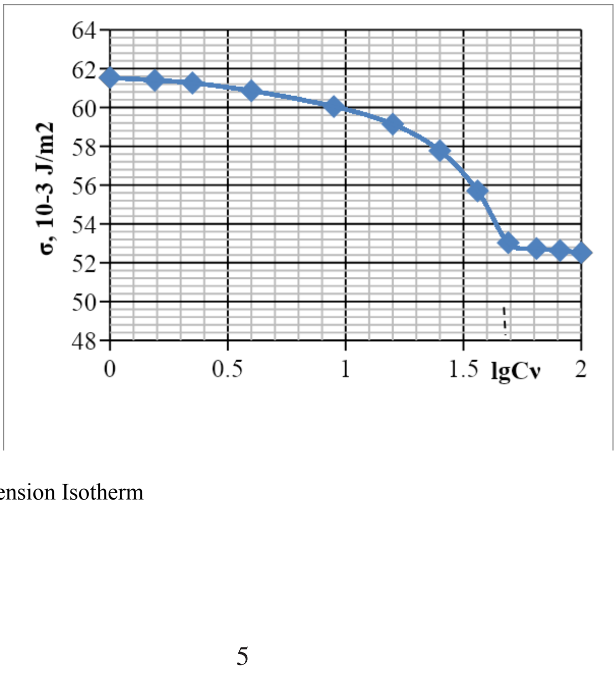


Fig.4. Plasticizer Surface Tension Isotherm

The obtained results show that it is optimal to use the concentration up to the CMC point but located close to it. It is assumed that the concentration of 5 g/l (0.5%) is located close to the CMC point, and it can provide stabilization of the CNT suspension.

To obtain cement compositions with a nanocomponent, a CNT suspension in an amount of 0.025% was introduced into the cement composition instead of mixing water, and the samples were prepared and kept in air-humidity conditions in cubes of 20x20x20 mm. After exposure, the samples were tested for compressive strength. The resulting dependencies are shown in Figs. 5.

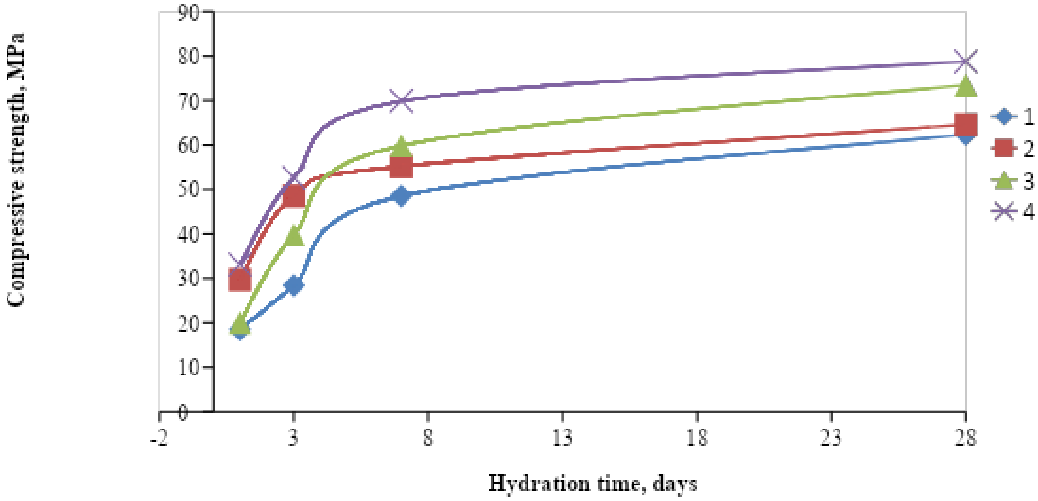
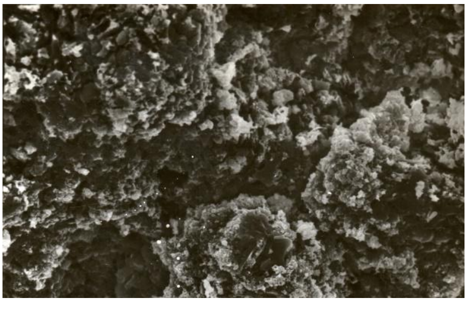


Fig.5. The strengths of samples with CNT additives with a concentration of 0.025%:
1- b / d; 2 - with CNT; 3- with plasticizer; 4- with a complex additive

The complex additive, which includes polycarboxylates and CNTs, gives the maximum increase in the strength of the samples. That is, on the first day it increases by 60%; on the third day - by 80%; on the seventh day - by 37%, on the 28th days - by 20%. CNT suspensions after ultrasonic treatment without a plasticizer also showed good results in the initial hardening period, but closer to the grade age, the increase in strength slowed down significantly, although it remained higher than the control sample. The increase was 5% at grade age,

The structure of the cement stone was shown by an electron microscopic examination of the samples. The structure of the cement stone is represented by poorly crystallized flaky calcium hydrosilicates (Fig. 6). The formation of such a structure is explained by the fact that calcium hydroxide adsorbed on the surface of stabilized CNTs doesn't crystallize into individual portlandite fields. Calcium hydroxide interacts with crystalline hydrates of the hardening system and binds to calcium hydrosilicates, which, by enveloping CNTs, bind individual phases in the composition. All this creates an increase in the strength of the samples.



a) b)

Fig.6. Electron microscopic images of hydrated samples after 28 days: a – PC without additives; b - PC + "CNT + plasticizer"

CNT with a content of 0.025% by weight of the binder was used in the selection of modified concrete compositions. Table 2 presents the main technological properties of the concrete mixture.

Table 2. – Composition and technological properties of fine-grained concrete mixtures

Consumption of materials per 1 m^3 of concrete, kg				W/C	Workability grade	Delamination by water separation, %
PC	Sand	granite siftings	CNT			
500	750	750	-	0,37	P1 (3)	0.8
			0.1375		P2 (7)	0.7
550	687	687	-	0,37	P1 (4)	0.7
			0.1375		P2 (8)	0.4

The study of the properties of the concrete mixture with the introduction of CNT shows that with the same water-cement ratio, the mobility changes, and the movement of cement grains relative to each other improves.

To ensure the quality of high-strength concrete, attention must be paid to maintaining the technological parameters of the concrete mixture over time.

Table 3. – Persistence of mobility of concrete mixtures with CNT

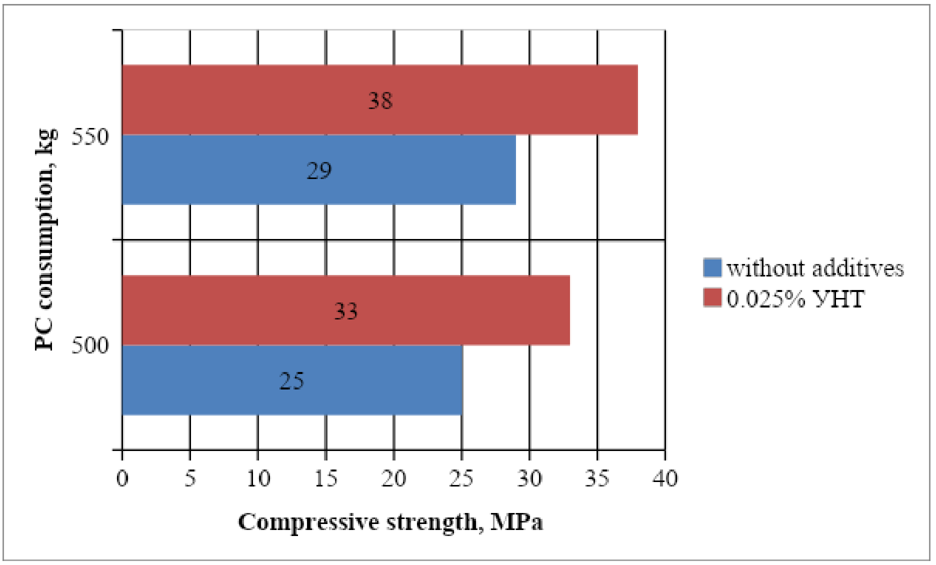
Time, h	Slump tests, cm	
	Control composition	CNT 0.025%
0.5	4	7
1.0	3	7
1.5	2	7
2.0	1	6.5

The introduction of CNTs in the optimal dosage contributes to the preservation of the concrete mixture over time by improving the delamination index.

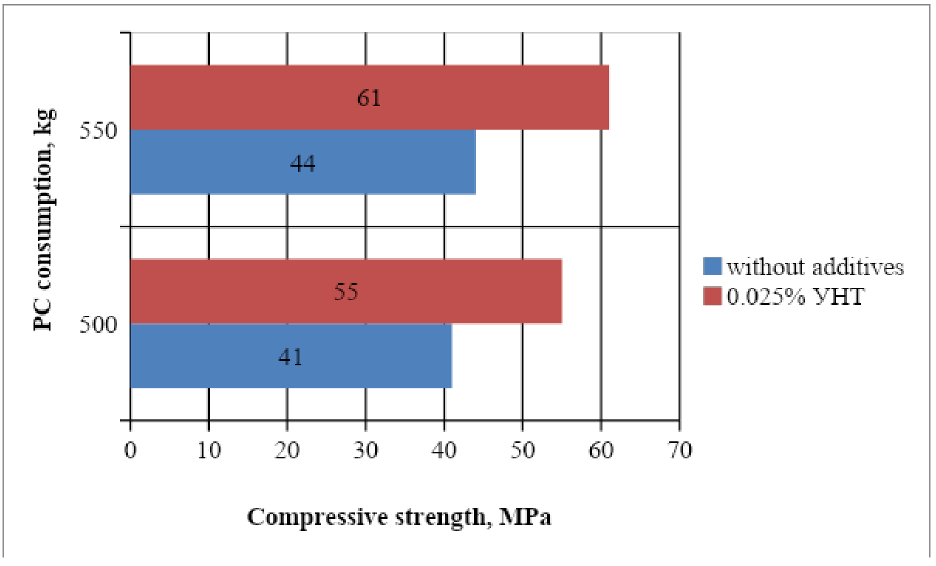
The study of this indicator within 2 hours from the moment of mixing shows the ability of the modified concrete mix to maintain its mobility compared to the control sample.

The introduction of CNT increases the compressive strength of concrete on the 3rd day of hardening by 32%, on the 28th day - by 34-39% compared with the control composition without additives (Fig. 7).

The frost resistance of concrete is associated with water absorption, which is characterized by the water saturation coefficient of pores. A decrease in the saturation coefficient at a constant porosity indicates a decrease in open porosity, which contributes to an increase in the frost resistance of the structure. Studies of the modified concrete mix for construction and operational properties are presented in fig. 8.

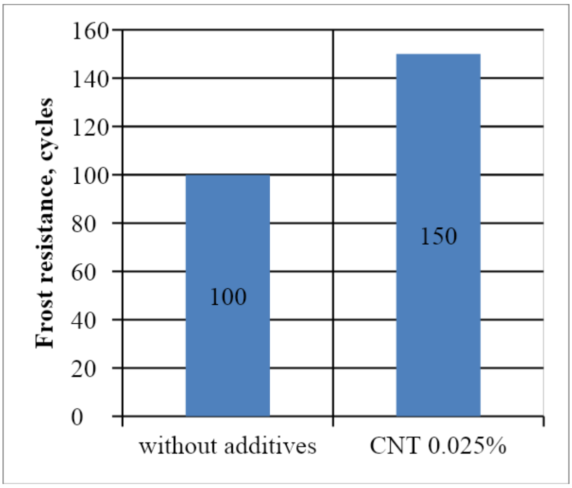

PC consumption, kg
550
500
38
29
33
25
0
5
10
15
20
25
30
35
40
Compressive strength, MPa
without additives
0.025% УНТ

a)

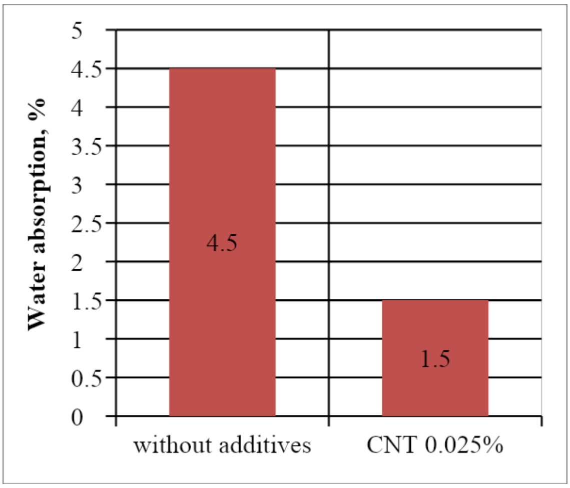

PC consumption, kg
550
500
61
44
55
41
0
10
20
30
40
50
60
70
Compressive strength, MPa
without additives
0.025% УНТ

b)

Fig.7. Physical and mechanical properties of concretes with CNTs: a) 3 days of hardening; b) 28 days hardening



a)



b)

Fig.8. Construction and operational properties of concrete with CNT: a) frost resistance, b) water absorption

An analysis of the results showed that frost resistance increased by 50 cycles when CNTs were added to concrete and water absorption decreased from 4.5 to 1.5%, which indicates an increase not only in physical and mechanical parameters, but also in construction and operational properties.

Thus, the complex effect of CNTs at different stages of concrete hardening contributes to the creation of a high-strength structure, improvement of the hydrophysical and operational performance of modified concrete.

4 Conclusions

To obtain stable research results with CNT-modified cements and concrete mixtures, it is necessary to obtain a stabilized suspension of nanoparticles. Therefore, the acoustic cavitation method was used with dispersion parameters t= 25±2ºC, υ= 44 kHz, τ< 30 min.

The stabilizer is a polycarboxylate plasticizer. The optimal content of the stabilizer (5 g/l) was established using the stalagmometric method of research.

The compressive strength tests of modified cement samples showed that the complex additive, which includes polycarboxylates and CNTs, gives the maximum increase in strength. On the first day, it increases by 60%; on the third day - by 80%; on the seventh day - by 37%, on 28 days - by 20%. CNT suspensions after ultrasonic treatment without a plasticizer also showed good results in the initial hardening period, but closer to the grade age, the increase in strength slowed down significantly, although it remained higher than the control sample. The increase was 5% at grade age.

The study of the properties of the concrete mixture with the introduction of CNT shows that with the same water-cement ratio, the mobility changes, and the movement of cement grains relative to each other improves.

The study shows that the CNT-modified concrete mix can maintain mobility for a longer time compared to the control sample.

The introduction of CNT increases the compressive strength of concrete on the third day of hardening by 32%, on day 28 - by 34-39% compared with the control composition without additives.

An analysis of construction and operational indicators showed that the frost resistance of the modified CNT concrete increased by 50 cycles, and the water absorption decreased from 4.5 to 1.5%.

Thus, the complex effect of CNTs at different stages of concrete hardening contributes to the creation of a high-strength structure, improvement of the hydrophysical and operational performance of modified concrete.

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