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The Effect of a Carbon Nanotubes-Based Modifier on the Formation of the Cement Stone Structure

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Abstract

The present paper considers the effect of carbon nanotubes, used as the main component of a modifying comprehensive nanoadditive, on the kinetics of cement hydration, the phase composition and the strength characteristics of a cement stone. The increase in the strength characteristics of the cement stone modified by the nanoadditive was found to be due to the acceleration of the cement hydration, the formation of an optimum microstructure, in which, according to X-ray phase analysis, additional formation of low-basic calcium hydrosilicates already takes place during the initial period of hardening. Based on scanning electron microscopy, additional directional crystallization of particles of cement stone neoplasms, mainly with contacts of intergrowth, was elucidated. Accelerated curing kinetics of the nanomodified samples was observed to take place with an increase in the compressive strength of 20–30 % at the age of 28 days.

Keywords

Nanomodifier; carbon nanotubes; X-ray phase analysis; cement hydration kinetics; cement stone.

Introduction

The formation of composites for construction purposes is determined by the following factors: type and characteristics of cement (chemical and mineralogical composition, fineness of grind, presence of mineral and other additives in the cement composition); water/cement ratio value; additional mechanical and chemical activation of cement; mixing conditions and modes; temperature hardening conditions; introduction of special additives to the concrete mixture, including those ones that exert their effect at the micro- and nanostructured levels of cement stone and concrete [1].

During the last period of time (10–20 years) there has been a significant transition in technologies and properties of construction materials; new types of composites – high-tech, high-strength, and low-shrinkage – have appeared.

Simultaneously with the development of construction materials, new classes of additives have been added to the agenda. They are related to deeper mechanisms of structure formation, and can comprise nanoadditives or nanomodifiers [2].

The modification of composites using various nanomodifiers, including carbon-containing ones, seems promising, since their introduction significantly improves the physical and mechanical characteristics at low dosages of additives and allows to directly adjust the material structure of the material through the manifestation of various effects [2–5].

However, due to the high surface energy of nanoparticles when using them as nanomodifier components, they can be prone to agglomeration; the size of agglomerates can reach micrometer scales.

In principle, the nanomodification of composites can be performed in two main ways: 1) nanostructures having preset parameters and sizes are pre-synthesized, and then introduced into the raw mixture; and 2) directed nanoparticle synthesis is realized in the system, due to which the nanomodification of the material structure takes place.

When implementing the second method, the essential difficulties in introducing the nanomodifier and its uniform distribution are minimized as much as possible. If pre-synthesized nanostructures (for example, a dry component mixture) are used, they must be additionally prepared for introducing into the composite structure. The most common way is to prepare an aqueous suspension based on them.

The analysis of works [4, 5] dedicated to this subject shows that the structure and mechanical characteristics of cement composites modified by carbon nanoadditives make it possible to significantly increase the values of physical and mechanical indicators. According to the authors, these changes were achieved due to the formation of a less porous structure in nanomodified samples and a greater amount of calcium hydrosilicates compared with non-modified samples.

The effect of mixing water structured with fulleroid nanoparticles on the cement stone characteristics was considered by Pukharenko and his co-authors [6]. They established that the nanostructuring of mixing water leads to a 1.4–1.7 times decrease in the viscosity of the cement paste. The results indicate a significant qualitative increase in the indices of workability and preservation of the given mobility when maintaining a fixed consumption of cement or reducing it.

In papers [7, 8], mathematical modeling of the changes in the properties of nanomodified composites and the effect of the used carbon nanoadditives on the strength characteristics of the material were studied. The analysis of the microstructure of the nanomodified samples allowed elucidation of the formation of individual crystallites of calcium hydrosilicates located in the zone of close contact of carbon nanoparticles, which contributes to the filling of microvoids and the creation of a single structure. The dependences between the length of carbon nanotubes and the processes associated with the agglomeration of nanoparticles in the bulk of the composite structure were revealed. When "shorter" carbon nanotubes were used, the accumulation of particles was absent or not significantly observed.

The processes of concrete nanomodification using carbon nanotubes have been studied by researchers from St. Petersburg under the leadership of A. Ponomarev. The scientists have developed a modifier on the basis of a water-soluble fullerene, the application of which is directed at construction materials [9, 10]. The modifier possesses the following properties: bulk density of 600–900 kg·m^{-3}, and average cluster size of 300 nm. Using this material in cement mixtures (0.15 % of cement mass) leads to a change in mobility in the range from M1 to M5, substantially increasing the strength parameters in the range of 25–40 %.

The analysis of the results of studies [11, 12] showed an increase in the physical and mechanical characteristics of construction composite samples when using a multifunctional additive dispersion based on multiwalled carbon nanotubes at the dosage level of 0.006 % of the binder (gypsum, cement), thereby contributing to an increase in the strength at early stages of hardening (day 7) and being about 55 % in comparison with reference compounds.

Thus, the aim of the present paper is to study the effect of carbon nanotubes used as a modifying comprehensive nanoadditive on the kinetics of cement hydration, the phase composition and the strength characteristics of a cement stone.

Materials and methods

In the present work, the experimental data on employing the above-mentioned comprehensive nanoadditive to modify the cement stone are presented.

“Taunit”-series multiwalled carbon nanotubes (**CNTs**) produced at NanoTechCenter Ltd. (Tambov, Russia) were used as the main component of the additive. The outer and inner diameters of these CNTs are 40 and 5 nm, respectively, their density is 560 kg·m^{-3}, and the average length of single nanotubes is 2 microns (Fig. 1).

The nanomodifier used herein represents a colloidal system (Table 1), the synthesis of which was carried out by ultrasonic treatment of the CNTs in an aqueous medium additionally containing surfactants.

The procedure for obtaining modifying additives and optimum formulations was used based on previously developed parameters [13]. The impact of ultrasound to the system was carried out on an IL-100-6/4 ultrasonic device; the optimum dispersion time was 20–30 min, and the amplitude of oscillations was at the frequency of 22 kHz (Table 1). The dispersibility of the CNTs and the stability of the resulting dispersions were monitored on a KFK-3 photocolorimeter at the wavelength of 500 nm. The distribution of the nanomaterials in the aqueous suspension was estimated from the optical density of colloidal solutions [14]. Polyvinylpyrrolidone was the main surfactant contributing to the preservation of the system in the sedimentation-stable state. The optimum ratio of the components (carbon nanomaterials : surfactants on a dry matter basis was 1 : 2).

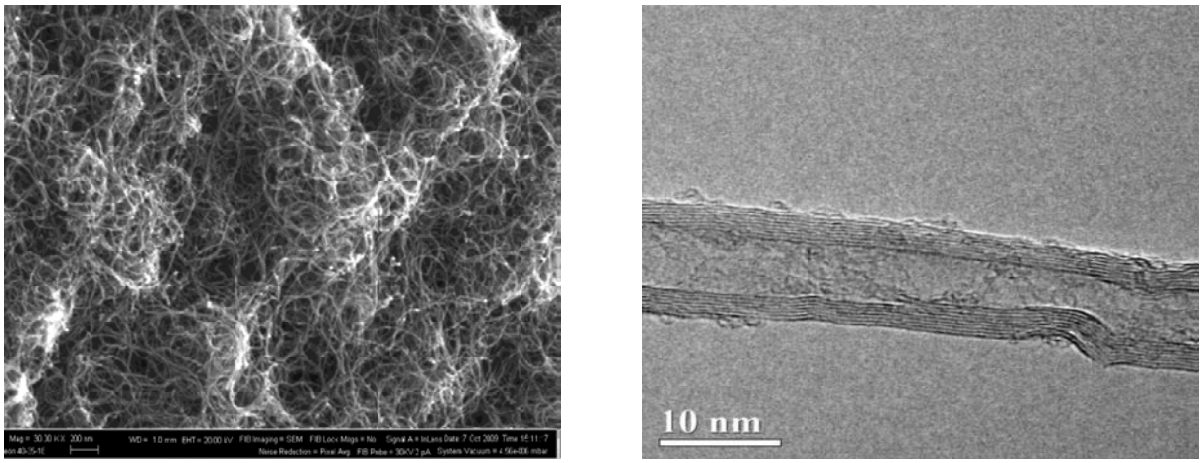
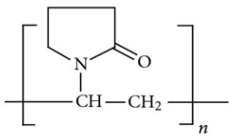
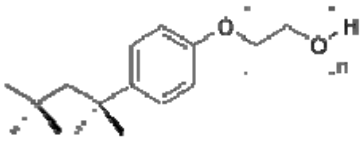
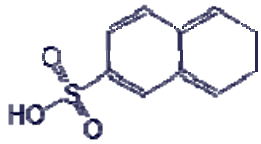
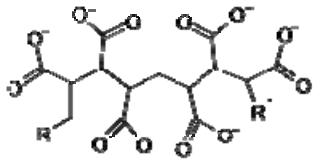
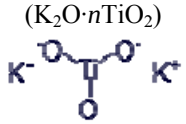


Fig. 1. SEM and TEM images of the "Taunit"-series CNTs

Table 1

Compositions, forms and methods of nanomodifier preparation

Nanomodifier	Composition	Chemical formula of surfactants used	Preparation methods
Colloidal solution (SMM, SM24)	"Taunit"-series CNTs – 0.0001 – 1%, Surfactant – 0.0002 – 2%, Water – the rest	Polyvinylpyrrolidone $(C_6H_9NO)_n$  Octylphenol ethoxylate (Triton X-100) $(C_{34}H_{62}O_{11})$  Naphthalene lingosulfonates (S-3 plasticizer) $R_n C_{10}H_{7-n}SO_3M$  Polycarboxylate esters 	Ultrasonic treatment Sonication time – 20–30 min; Frequency – (22 ± 10) % kHz
Colloidal solution (SMTK)	"Taunit"-series CNTs – 0,0001 – 1 %; Surfactant – 0,1–3 %; Water – the rest	Potassium polytitanate $(K_2O{\cdot}nTiO_2)$ 	

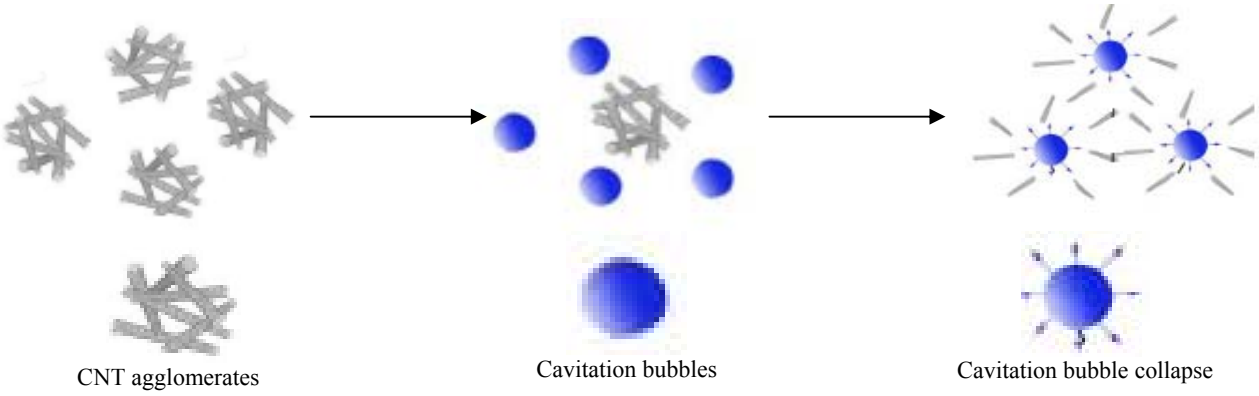


Fig. 2. Interaction between CNTs and surfactants as a result of sonication in an aqueous medium

The use of the surfactants is due to the need for reducing the coagulation effect in the suspension and the decrease in the surface interphase energy, which greatly simplifies the dispersion process (Fig. 2).

The suspensions were stabilized due to the formation of an adsorption layer onto the surface of the CNTs by means of the surfactant medium. This layer prevents CNT convergence, thereby saving the unique properties of nanostructures (adsorption, chemisorptions, topological effect). In this case, the activated water with the CNTs represented mixing water for the cement hardening system. Thus, the problem of uniform distribution of nanostructures in the construction composite was solved. Based on preliminary experimental studies, the optimum concentration dosage of the comprehensive carbon nanoadditive in the cement composition was determined, which was found to be 0.0001–0.0007 % of cement weight [15, 16].

This concentration interval experimentally obtained for the nanomodifier application corresponds to a qualitative change in the physical and mechanical characteristics of the modified composite and promotes the production of a sedimentation-stable CNTs-based suspension with optimum use and storage parameters (not more than three days). It can be assumed that the availability of such a dosage interval is associated with high chemical activity and a large reactively active surface area of the carbon nanomodifiers. It is most likely that conditions, under which chemically active carbon nanostructures retain a part of the required mixing water, are created when increasing the CNTs dosage. In this case, the formation of water deficiency possibly takes place for the mineral hydration of the binder material.

The dosage intervals applied for the nanoadditives have also been confirmed by other authors [17–20].

In the experimental studies, CEM I 42.5 Portland cement (Russian Standard GOST 31108–2003) and the above-mentioned nanoadditives (the dosage of 0.0006 %) were used for the production of a cement paste having a water/cement (**W/C**) ratio of 0.33. The kinetics parameters of the cement hydration process were studied under normal conditions, the duration of the process was 1, 3, 7, 14 and 28 days. The phase composition of the reference and nanomodified cement stones was monitored by X-ray diffractometry (CuKα radiation, $\lambda = 1.5406$ Å, D2 Phaser Bruker diffractometer); the data were processed automatically using the PDWin 4.0 software. The hydration degree was calculated [21] according to the following formula:

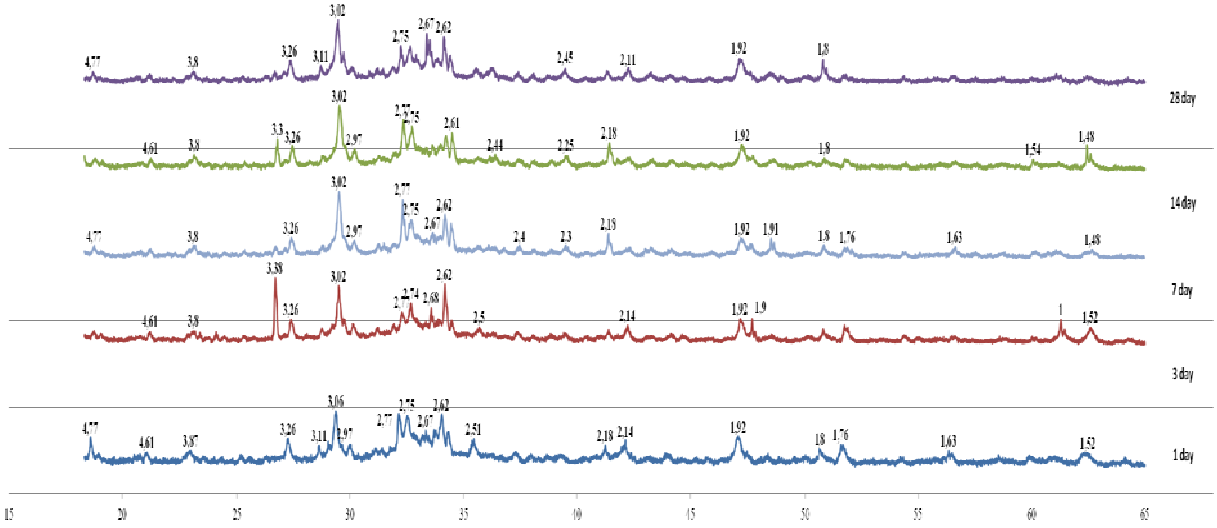
$$C_h(\mathrm{C_3S}) = \left(1 - \frac{I_{\mathrm{mod}}}{I_0}\right)100\,\%, \qquad (1)$$

where I_{mod} is the intensity of the diffraction maximum at $d = 2.75$ Å of the $3CaO{\cdot}SiO_2$ (C_3S) phase of samples having different composition and cement hydration time; I_0 is the intensity of the diffraction maximum at $d = 2.75$ Å of the $3CaO{\cdot}SiO_2$ (C_3S) phase of the initial cement.

The compressive strength of the cement stone was determined after 1, 3, 7, 14 and 28 days of hardening under normal conditions. The samples (size $5 \times 5 \times 5$ cm) were tested using an IP-500M-Auto system. To ensure statistical reliability of the physical and mechanical test results, the number of the samples in the series was 9–12. It was determined that the intra-series coefficient of variability of the strength evaluation results did not exceed 7–10 %.

Results and discussion

The generalization of the experimental data shows that in the systems containing the nanomodifying additives the cement hydration process is substantially accelerated (Fig. 3, Table 2): for a daily hardening time, the hydration degree for samples 3 and 4 reaches the values of about 50 %, which in the reference system is achieved only on the 28th day.



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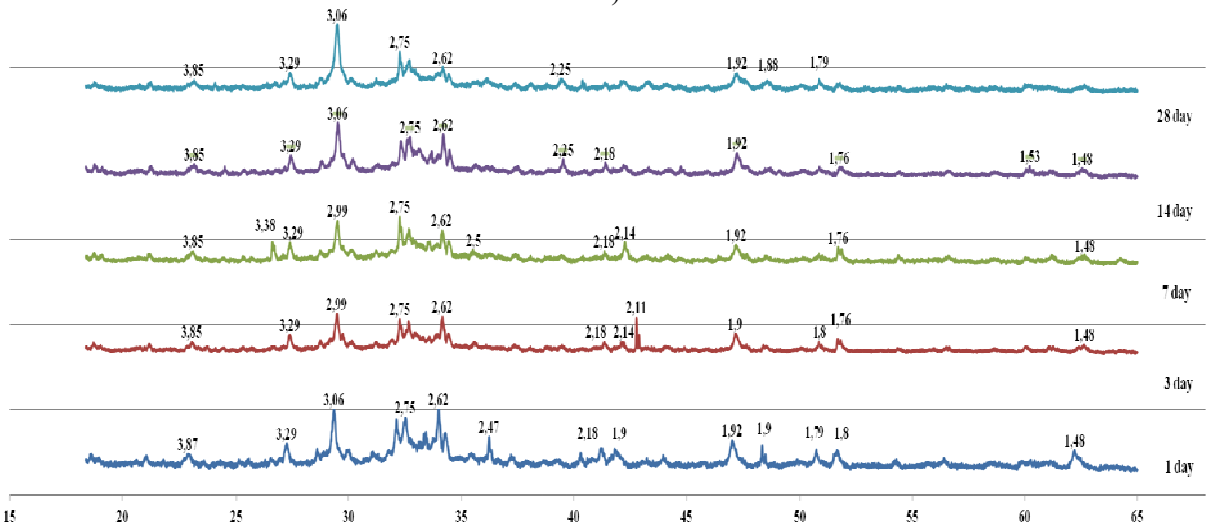


b)

Fig. 3. X-ray diffractometry studies of the cement stone hydration:

a – reference sample: $2CaO{\cdot}SiO_2$ (d = 3.8; 3.38; 2.51; 2.61; 1.9; 1.8); $3CaO{\cdot}SiO_2$ (d = 3.02; 2.75; 2.61; 2.18; 1.76;); $Ca(OH)_2$ (d = 3.11; 2.62; 1.92; 1.79; 1.48;); $2CaO{\cdot}SiO_2{\cdot}H_2O$ (d = 4.77, 4.61; 3.87; 3.26; 2.18); $2CaO{\cdot}SiO_2{\cdot}0.5H_2O$ (d = 2.77; 2.67; 2.5; 1.8; 1.61; 1.52)

b – SM24 nanomodifier: $2CaO{\cdot}SiO_2$ (d = 3.8; 3.38; 2.51; 2.18; 1.9; 1.48); $3CaO{\cdot}SiO_2$ (d = 3.02; 2.75; 2.61; 2.18; 1.76;1.48); $Ca(OH)_2$ (d = 2.62; 1.92; 1.79); $2CaO{\cdot}SiO_2{\cdot}H_2O$ (d = 3.28; 3.87; 3.85; 3.11; 2.18; 2.11); $2CaO{\cdot}SiO_2{\cdot}0.5H_2O$ (d = 3.29; 2.99; 2.67; 2.5; 2.25)

Table 2

Degree of the cement stone hydration when using the nanomodifiers

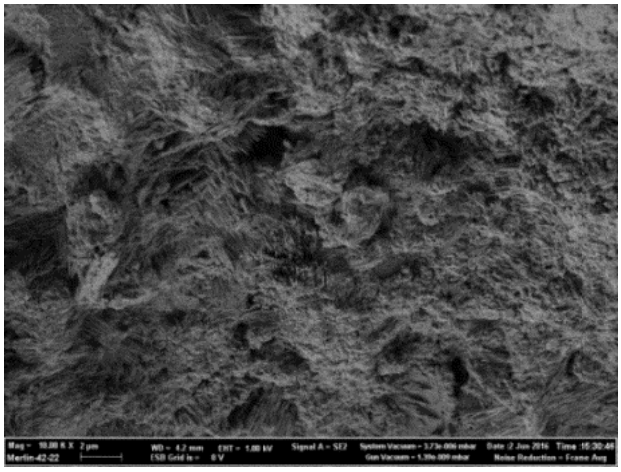
No.	System	CNT content in nanomodifier, %	Degree of hydration				
			Day 1	Day 3	Day 7	Day 14	Day 28
1	Cement-Water	0	30.0	32.9	34.6	38.5	46.8
2	Cement-Water-SMM		53.9	59.2	65.2	63.5	64.0
3	Cement-Water-SMTK	0.0006	21.4	28.0	60.6	63.1	63.1
4	Cement-Water-SM24		46.8	51.1	51.4	55.0	62.3

From on the results of the X-ray phase analysis of the reference and nanomodified cement stone samples, it can be assumed that the change in the intensity peak ratio on the diffractograms recorded for the modified samples may be due to the blocking action of the nanomodifier, at which part of calcium ions remains in the solution and further does not interact with other substances, possibly leading to the formation of smaller crystals covering vacant pores of the cement stone [22, 23]. The X-ray diffractometry studies of the modified samples allowed to observe the calcium hydrosilicate phases of various compositions ($(CaO)_x \cdot SiO_2 \cdot 8H_2O$, $2CaO \cdot SiO_2 \cdot H_2O$, $CaO \cdot SiO_2 \times \times H_2O$) on all the X-ray patterns. In this case, the diffractometric peaks are wider, thereby indicating the formation of a fine-crystalline structure. When increasing the hardening time, the availability of the ettringite phase can be fixed, confirming the CNT effect on the morphology of the resulting cement stone.

The microstructure of the reference and nanomodified fine-grained concrete samples was elucidated by electron microscopy (Fig. 4).

It was established that an increased interaction of some adhesion contacts and directional crystallization of the neoplasm particles take place in the composite modified with the comprehensive nanomodifier.

When using the CNTs-based nanomodifiers, the composite structure is more densely packed with the particles, thereby making it possible to conclude that the physical and mechanical characteristics of the material increase (Fig. 5) as a result of the formation of an ordered structure and neoplasms with an altered morphology of the crystalline hydrates. This is confirmed by the presence of needle crystals (the size of individual crystals reaches 3–5 microns), which presumably perform discrete nanostructuring of the cement systems, combining the neoplasms into a single conglomerate and acting the reinforcing role



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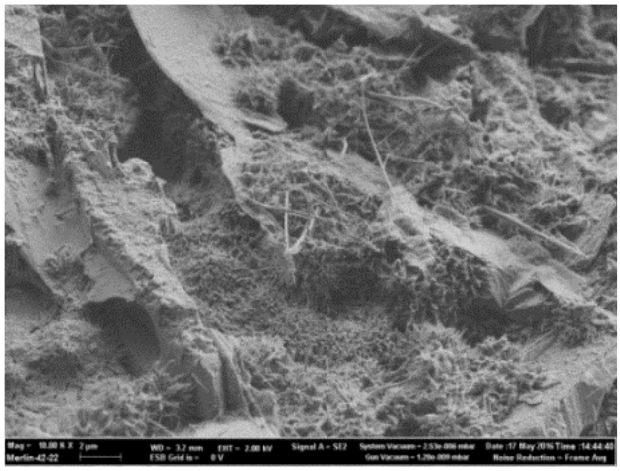

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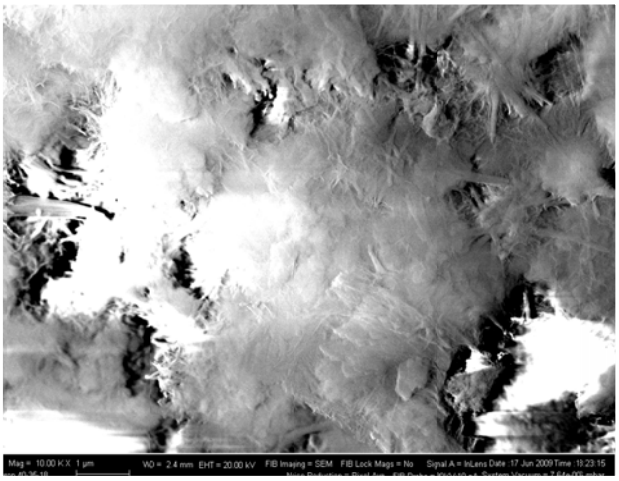

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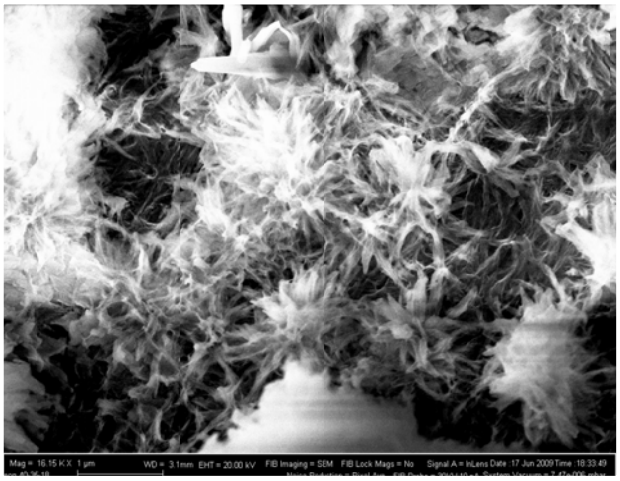

d)

Fig. 4. Microstructure of the nanomodified fine-grained concrete samples:
a, *c* – reference sample (cement-water-sand); *b*, *d* – nanomodified sample (cement-water-sand-SM24)

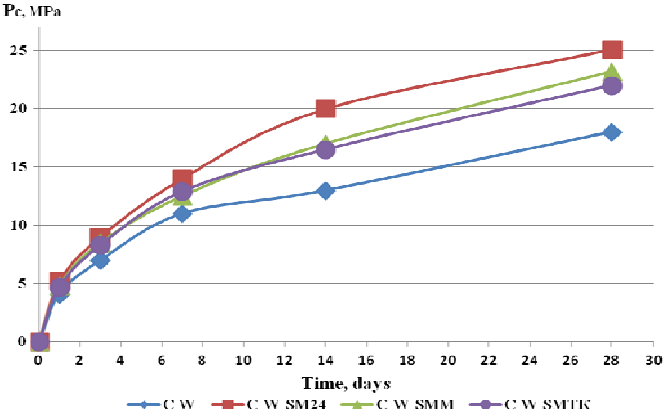

Fig. 5. Kinetics of gaining the strength obtained for the cement stone when using the nanomodifiers:
Systems: C-W (cement-water), C-W-SM24 (cement-water-SM24), C-W-SMM (cement-water-SMM), and C-W-SMTK (cement-water-SMTK)

in the concrete structure. Besides, agglomeration of the nanofiller from a set of spheric nanoparticles can also be observed, which characterizes the degree of activity of the carbon nanoparticles and their surface forces. The formation of the crystalline hydrates on the CNT surface leads to the creation of an extra supramolecular structure that has its direction and CNTs-like surface possessing its own substructure [24–26].

All the nanomodified samples obtained showed an increase 30–50 % in the specific surface area in comparison to the reference composition. It should be noted that the specific surface area values determine the dispersity of the material and geometric characteristics of the pore channels; on the other hand, these factors are key elements for the formation of a qualitative and durable material structure.

When modifying the cement stone structure with the nanoadditives, the nanomodification efficiency can be determined not only by the hydration kinetics change but also by the strength kinetics change (strength gain rate, duration of reaching "release" and achievable limit values of the cement stone strength). The studies carried out demonstrated acceleration in gaining the strength for all the nanomodified samples, as well as an increase of 20–30 % in the compressive strength.

Conclusion

The effect of the CNTs-based comprehensive nanomodifier on the kinetics of cement hydration, phase composition and strength characteristics are considered herein.

It was established that when the nanomodifier is introduced, the cement hydration process is accelerated, and the optimum microstructure of the cement stone is formed. At the same time, scanning electron microscopy confirmed the formation of extra directional crystallization of cement stone neoplasm particles, mainly with intergrowth contacts.

The X-ray diffraction analysis showed a change in the phase composition of the nanomodified samples, with an extra formation of low-base calcium hydrosilicates even at an early stage of hardening.

The studies conducted on the kinetics of gaining the strength of the nanomodified cement stone demonstrated an increase of about 20–30 % in the compressive strength at the age of 28 days for all the samples.

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