Structural Modification of New Formations in Cement Matrix Using Carbon Nanotube Dispersions and Nanosilica

B. M. Khroustalev¹, S. N. Leonovich¹, G. I. Yakovlev¹, I. S. Polianskich¹, O. Lahayne³,
J. Eberhardsteiner³, G. Skripkiunas⁴, I. A. Pudov², E. A. Karpova³

¹Belarusian National Technical University (Minsk, Republic of Belarus),
²Kalashnikov Izhevsk State Technical University (Izhevsk, Russian Federation),
³Vienna University of Technology (Vienna, Austria),
⁴Vilnius Gediminas Technical University (Vilnius, Lithuania)

Abstract. Complex nanodispersed systems with multi-walled carbon nanotubes and nanodispersed silica have a significant impact on the processes of hydration, hardening and strength gain of construction composites predetermining their durability. While using a scanning electron microscope with an attachment for X-ray microanalysis and a device for infrared spectral analysis investigations have shown that the main effect of the cement matrix modification in the case of adding complex nanodispersed systems is provided by direct influence of hydration processes with subsequent crystallization of new formations. It has been noted that while adding carbon nanotube dispersion and nanosized silica a binding matrix is structured in the form of an extremely dense shell from crystalline hydrate new formations on the surface of solid phases that provides strong binding matrix in cement concrete. The addition effect of carbon nanotubes has been analyzed and quantitatively assessed through an investigation for every case of one sample with nanotubes and one sample without them with the help of a nanoindenter and scanning electron microscope. It is necessary to solve rather complicated challenging task in order to assess quantitatively the addition effect of CNT on material characteristics at a micromechanical level. At the same time it is possible to investigate surface of a concrete sample with one-micron resolution. In this case it is necessary to prepare samples for nanoindentation with exclusion of all CNT defectable effects that have been shown by a SEM. So in this case more adequate method for assessment must be a picoindenter, which combines a test method for nanoindentation with an optical SEM potential. Such equipment is in the stage of in-situ testing process at the Vienna University of Technology. The investigation is based on the fact that the main modification effect of mineral binding matrix while using incorporated complex nanodispersed systems and nanosilica is ensured by a direct influence of hydration processes and subsequent crystallization of new formations. Scanning electron microscopy and X-ray microanalysis with detection in IR spectra have revealed that adding of multi-walled carbon nanotubes dispersion together with nanodispersed silica provides structuring of rather dense shell of hydrated new formations along cement matrix on the surface of solid phase. The structured interfacial layers form separate cells in the modified cement matrix that ensures a formation of extremely filled system and predetermines structural strengthening of the modified cement matrix due to formation of spatial packaging. Consequently, the main factor increasing characteristics of cement concrete which is modified with carbon nanotubes and nanosilica is a structural modification of calcium hydrosilicates with relation to composition and morphology of new formations.

Keywords: nanodispersed system, multi-walled carbon nanotubes, nanosilica, scanning electron microscope, X-ray microanalysis, hydration, cement concrete

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Структурная модификация новообразований в цементной матрице с использованием дисперсии углеродных нанотрубок и нанокремнезема

Акад. НАН Беларуси, докт. техн. наук, проф. Б. М. Хрусталев1, доктора техн. наук, профессора С. Н. Леонович1, Г. И. Яковлев2, канд. техн. наук, доц. И. С. Полянских2, канд. наук О. Лахайин3, докт. наук, проф. И. Эгерхардштайнер4, докт. наук, проф. Г. Скрипкинна5, канд. техн. наук, доц. И. А. Пудов2, студ. Е. А. Карпова2

1) Белорусский национальный технический университет (Минск, Республика Беларусь),
2) Ижевский государственный технический университет имени М. Т. Калашникова (Ижевск, Российская Федерация),
3) Венский технический университет (Вена, Австрия),
4) Вильнюсский технический университет имени Гедиминаса (Вильнюс, Литва)

Реферат. Комплексные нанодисперсные системы с многослойными углеродными нанотрубками и нанокремнеземом имеют значительное влияние на процессы гидратации, твердения, набора прочности строительных композитов, предопределяя их долговечность. Исследования с использованием сканирующего электронного микроскопа и X-лучевого микроанализа с обнаружением в инфракрасном спектре показали, что главный эффект модификации в случае добавления комплексных нанодисперсных систем обеспечивается направленным влиянием процессов гидратации с последующей кристаллизацией новообразований. Установлено, что при добавлении дисперсии углеродных нанотрубок и нанокремнезема формируется структурная матрица в виде чрезвычайно плотной оболочки из кристаллогидратов новообразований на поверхности твердой фазы, что обеспечивает прочную вяжущую матрицу в цементном бетоне. Эффект добавления углеродных нанотрубок анализировался и количественно оценивался исследованием в каждом случае одного образца с нанотрубками и одного без них с помощью наноиндентора и сканирующего электронного микроскопа. Чтобы количественно оценить эффект добавки углеродных нанотрубок на характеристики материала на микроанализ, лучевой микроанализ, гидратация, цементный бетон

Ключевые слова: нанодисперсная система, многослойные углеродные нанотрубки, нанокремнезем, сканирующий электронный микроскоп, X-лучевой микроанализ, гидратация, цементный бетон

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Introduction

Carbon nanotubes (CNT) were first synthesized in 1952 (fig. 1) by the members of Institute of Physical chemistry and Electrochemistry of Russian Academy of Sciences, L. V. Radushkevich and V. M. Lukyanovich [1]. The main properties of CNT were systematically described by Sumio Iijima who discovered them in 1991 as a by-product of fullerene synthesis [2]. The authors of the given study have synthesized carbon nanotubes using an original technology presented in patent [3] the technique of which is described in article [4]. The produced nanostructures were used to modify the structure of non-autoclaved cellular concrete. It was also shown that CNT increase the strength of aerated concrete by 70 %, while the stabilization of the pore structure with...
their size and the decrease of the average density of aerated concrete are noted [5]. Further studies [6, 7] found that adding CNT changes not only the structure but also the composition of calcium hydroxysilicates (CHS) that form the main values of the properties of dense cement concrete.

Calcium hydroxysilicates are the main components of set cement at the nanoscale. The nature of their structure determines the values of strength and durability of cement concrete. There are some works which present the results of the studies of the changes in the morphology of crystalline hydrates based on calcium hydroxysilicates due to adding nanodispersed modifiers based on carbon nanosystems to the hardening cement matrix [8–10]. Using a nanodispersed modifier can control the kinetics of the interaction between cement minerals and mixing water, influence the composition and structure of CHS, increase the degree of polycondensation of silicon-oxygen anions of calcium hydroxysilicates. Thus, in the process of modification of cement matrix with CNTs one of the main issues is the directed regulation of the processes of polycondensation of silicon-oxygen anions in order to strengthen the borders of the contact areas and provide the increased strength, water- and frost-resistance of concrete.

In the review of the works about the use of CNTs [11–13] it is noted that most researchers limit the role of nanotubes to the nanoreinforcing of the set cement structure considering the microstructures containing carbon nanotubes, which are in physical contact with CHS or located in microcracks. The amount of the modifying nanotubes exceeds 0.05% of weight of the binder, which is apparently caused by their insufficient dispersing, despite using various dispersing methods and applying surfactants for aqueous dispersions.

A lot of works suggest using two or more nanosystems for the modification of cement concrete, nanosilica being used as the second additive in most cases [14–17], which due to the synergistic effect from being used with CNTs intensifies the processes of CHSs forming, densifying the structure of set cement. At the same time, these systems can significantly change the structure of the interphase boundaries in cement composites due to the crystallization of new CHS formations on the surface of the solid phase with the formation of dense shells that connect the components of cement concrete. This dramatically increases the role of nanosilica which binds calcium hydroxide to form CHS contributing to extra densifying of lowly cohesive new formations.

Thus, adding nanosized particles to the concrete composition enables the control of the processes of hydration and formation of the hardening cement structure at the nanoscale, providing the directed formation of the required macrostructure to achieve the required properties of concrete.
At the same time the nature of self-organization of the cement concrete microstructure is not clear, nanosystems being added, especially CNT that provide the formation of high-strength set cement from the originally lowly cohesive new crystalline hydrate formations.

**Materials and Methods**

Multi-walled carbon nanotubes (MWCNT) were used as an aqueous dispersion of Vulvek 100 “Novy Dom”, LLC (Izhevsk) prepared on the basis of Graphistrength™ Masterbatch CW2-45 premix produced by Arkema Group Co. French company. The premix containing 55 % of carboxymethyl-cellulose and 45 % of MWCNT was dispersed in a high-speed bead mill mixer.

The binder used was Portland cement of CEM I 42.5N JSC “Nevyansk Cementnik”; the fine aggregate – ditch sand from Selychinskoye deposit (Udmurtia) meeting the requirements of GOST 8736; coarse aggregate – ballast stone from river gravel of 5–20 mm fraction meeting GOST 8267 from Kama deposit.

The amorphous finely-dispersed silica includes a mixture comprising 90 % of microsilica MK-85 (Tula) with an average particle size of 300 nm and 10 % of synthetic nanosilica Nanosilika (Cairo) with an average particle size of 15 nm.

The microstructure of the produced samples was studied with a scanning electron microscope JSM-7600F of JEOL company and Phenom G2 Pure. The analysis of set cement by means of infra-red spectroscopy was conducted with a FT-IR spectrometer of Spektrum One in the frequency range of 4000–650 cm⁻¹.

The water resistance of the samples was determined by means of a “wet spot” test on the certified unit, as well as “VIP-1.2” device concerning the air permeability of the concrete samples. The frost-resistance tests were carried out by means of accelerated method using heat-cold chamber KTH-74.

**Results and Discussion**

The main task, the solution of which determines further development of technology of cement concrete modification by means of carbon nanotubes, is to produce a stable dispersion that would not be broken down for a long time due to the CNT coagulation. This task is solved by dispersing CNTs in aqueous solutions of surfactants when exposed to ultrasound [9, 18]. Using high-speed bead mill can improve dispersing MWCNT and apply the produced dispersions on an industrial scale [7]. At the same time, in such dispersion the amount of nanotubes does not exceed 20–25 %, the remaining volume of the particles is located in the range of several micrometers (fig. 2a). The additional processing of this dispersion with ultrasound provides dispersing nanotubes to nanometer size (the average particle size is 25 nm). Thus, according to the average particle size (fig. 2b), nanotubes do not only separate, but also are destructed and possibly broken down.

**Fig. 2.** Distribution of multi-walled carbon nanotubes in aqueous dispersion:

a – after processing in a high-speed bead mill; b – after additional ultrasound processing
The analysis of the influence of dispersion on mechanical properties of set cement in the composition of fine concrete shows the increase in strength, which is in direct proportion to the duration of ultrasonic processing of dispersion (fig. 3). The conducted studies show that the concentration of nanotubes in the set cement matrix can be limited to 0.001 % from the weight of Portland cement, and the strength values of the set cement will not yield to the values shown in fig. 3.

Taking into account the destruction of multi-walled CNTs with such combined dispersing technology, it is necessary to interpret the strength increase of the cement matrix as in this case the traditional reference to nanoreinforcing of the cement matrix by means of carbon nanotubes is not correct enough. The main effect of the modification of set cement in this case is provided by structuring the new crystalline hydrate formations based on CHS. At the same time due to the contact interactions of the structured boundary layers the spatial frame cells are formed in the structure of the modified matrix. A large number of point contacts ensure the formation of extremely filled system in which the collective transfer to adhesion in a short-range order leads to the hardening of the structure of the modified binding matrix due to the formation of spatial packing of CHS (fig. 4). This leads to a dense and strong mineral matrix that provides durable composite material for construction purposes.

Therefore, it is necessary to pay attention to the microstructure of the new formations in the set cement matrix and, above all, to the composition and morphology of CHS. In the process of cement setting crystalline hydrates cover the surface of the solid phase in the composition of cement concrete with a thin layer of 3–10 microns of dense new formations (fig. 5a, b) forming high-strength shells that combine the components of concrete in a frame. Carbon nanotubes being denuded, in the case of formation of shrinkage cracks, the nanotube surface is overgrown with calcium hydroxilicates (fig. 5c). In certain cases carbon nanotubes can provide “self-healing” of cracks with new formations, crystallization of which is stimulated with nanotube surface.

To determine the composition of the cement matrix adjacent to the surface of basalt fiber, X-ray microanalysis of new formations was conducted. Its results are presented in fig. 6. Based on the results of X-ray microanalysis, it can be argued that around the basalt fiber there are dense structured shells from the new formations of sheet structure (calcium hydroxide) coated with amorphous calcium hydroxilicates. The presence of carbon in the composition confirms the presence of carbon nanotubes in the studied microvolume.
Fig. 5. Microstructure of the cement matrix modified with carbon nanotubes in cement concrete with dense new formations: a – on the surface of quartz sand; b – the surface of basalt fiber [19]; c – carbon nanotubes in a shrinkage crack coated with calcium hydrosilicates.

Fig. 6. Results of X-ray microanalysis of new formations on the surface of basalt fiber [19]

Using an complex additive comprising MWCNT dispersion along with nanosilica leads to the densification of the structure of set cement in the space between the structured shells (Fig. 7a), new hydrosilicate formations appearing as clusters in the presence of silica fume (Fig. 7b), and additionally densifying the binding matrix in the composition of cement concrete (Fig. 7c). Such structure leads to a significant increase in the cement strength in the composition of the modified concrete.

Fig. 7. The microstructure of cement concrete modified with the complex additive (“DC-5” with 8% of nanosilica): a – densification of crystalline structure with new hydrosilicate formations; b – fragment of microstructure with densifying bunch-like new formations; c – fragment of microstructure with a particle of nanosilica.
Infrared spectral analysis of the check sample (fig. 8a) and the samples modified with a complex additive (fig. 8b) confirms the intensification of hydration of Portland cement along with the formation of additional calcium hydroxides (increase in the intensity of the absorption lines 1085 and 1089 cm$^{-1}$). The formation of calcium hydroxides of different basicity is also confirmed with an additional absorption line of 1033 cm$^{-1}$.

Thus, the use of complex additives with multi-walled carbon nanotubes and nanosized silica significantly changes the set cement structure in the modified concrete due to the directed crystallization of new formations based on calcium hydroxides, stimulating their crystallization of the surface of solid phase components of concrete. At that, not only the morphology of new formations, but their mineralogical composition changes, as well as the basicity of calcium hydroxides, which in its turn determines their strength characteristics [20].

**Experimental Results**

To check the actual influence of the CNTs on the characteristics of the concrete, samples without CNTs (type A) and with CNTs (type B) were subjects to several series of experiments performed at the Institute for Mechanics of Materials and Structures at Vienna University of Technology: They were examined by the help of a nanoindenter and with a scanning electron microscope (SEM).

*Results of nanoindentation on two concrete samples.* For this test series, one sample of type A and B have been used. One each of the two samples an extensive test series was performed with a Hysitron Triboindenter, analogous to test series conducted before on other concrete samples [21, 22]. For each single measurement, the force was increased over 10 s up to a maximum value of approximately 1200 µN, kept constant for 5 s and then again linearly decreased over 10 s. If the force is plotted as a function of the depth, we get curves as in fig. 9.

Actually, the indentation depth $h$ is a function of the force $F$, which is given by the indenter, but usually $F(h)$ is plotted instead of $h(F)$. The elastic material parameters, such as Young’s modulus $E$ and the hardness $H$ can be calculated based on the curve sector with decreasing force [23].

![Fig. 8. IR-spectra of the cement matrix in the check sample (a) and the sample modified with a complex additive (b) (MWCNT dispersion with nanosilica)](image-url)
For performing the indents, first the top side of each sample was polished to get a smooth test surface, which is necessary as a reference for measuring the indentation depth as precise as possible. As can be seen in fig. 10, the remaining height fluctuations in the pictured area were in the range of a few microns. (It was only possible to reduce the roughness to a certain degree, because during the polishing smaller parts of the material, but also parts in the range of 1 mm and more crumbled away from the samples. This way, not only the roughness was increased locally, but also the whole sample became smaller and smaller.)

With every indent, Young’s modulus $E$ as well as the hardness $H$ of the material is quantified at the respective reading point. An area of 100×100 µm was examined on both samples with a grid of 40×40 indentions, resulting in a total sum of 1600 measurement on every sample. (Each of these test series took about 3 days.) Fig. 11a shows the results for sample type $A$ and fig. 11b shows the analogous results for sample type $B$. In the same way the hardness can be plotted, but the pattern for this parameter is rather similar to the pattern of the modulus, though the variation of the results is even higher, as demonstrated in tabl. 1.

![Fig. 10. Scan of an area of 60×60 µm of the polished surface of sample type $B$, as done with the imaging mode of the nanoindenter](image)

**Table 1**

|                        | Type $A$         | Type $B$         |
|------------------------|------------------|------------------|
| Young’s modulus $E$, GPa | $47,80 \pm 31,20$ | $56,30 \pm 38,70$ |
| Hardness $H$, GPa       | $2,56 \pm 3,09$  | $3,82 \pm 6,04$  |

While for the modulus, the standard deviation is in the range of 65 % of the mean values, for the hardness the standard deviation even exceeds the mean values, though test areas have been chosen, which appeared relatively homogeneous in the optical microscope attached to the nanoindenter, as shown in fig. 12.

![Fig. 11. Young’s modulus on sample type $A$ (a) and type $B$ (b), as calculated on the basis of a 40×40 grid of indents](image)
The distribution of $E$, as given in figs. 11a and 11b, suggests that it is not a mere statistical distribution. Instead there are areas with significantly higher (or lower) modulus, compared to the average. For example, there is a zone in the lower left part of fig. 4, where $E$ is higher than 100 GPa throughout and reaches maximum values of 250 GPa.

These variations of $E$ and $H$ probably result from the spatial distribution of the various phases of the material. This distribution is also reflected in the histograms of Young’s modulus, as given in fig. 13.

While there is a distinct global maximum for the distribution at approximately 30 GPa (type $A$) and 36 GPa (type $B$), it would be challenging to identify any local maxima and therefore to distinguish the various phases, based on this test series. There is also no systematic pattern in the distribution of $E$, and there are no significant structures visible in the optical images of the inspected areas, which clearly reflect the measured distribution of the modulus. Especially it wasn’t possible to detect any elongated structures, which might have been caused by nanotubes. One reason for that might be the distance of 2.5 µm between two indents, which is roughly the tenfold of the presumed diameter of the nanotubes. Other possible reasons will be discussed at the end of this paper.

To check if it is in principle feasible to detect nanotubes with the indenter, one concrete sample of each type has been inspected by the help of a Scanning Electron Microscope.

Results of microscopic determination of concrete samples. For this part of the work, an analytical high-resolution FEGSEM of the type FEI Quanta 200 FEGSEM has been used, which is available at the Vienna University of Technology [24]. Again, the two concrete cubes inspected by the SEM were both polished on the top side, but because of the roughness of the material and its tendency to brittle, only a part of the visible surface of the prepared side was effectively polished, while on the rest of the top side there was a relatively rough fracture surface left. These disparities are also visible of the images obtained by the SEM.

In the middle of fig. 14a there is a relatively smooth area, which is obviously the result of the polishing process. (On closer inspection, flimsy scratches are visible, all running in the same direction, which is a typical byproduct of the polishing process.) Contrary to that, the surface in fig. 14b is much rougher and completely irregular. A similar distinction was found for the sample of type $B$; see fig. 15a and 15b.

The images in fig. 15a to 15b were done with the same magnification ($\times 1000$) and also otherwise with the same parameters. While the polished area on the left half of fig. 15a has a similar appearance to the polished one in fig. 14a, there are elongated structures visible in the unpolished area of fig. 15a as well as in fig. 15b, which are not visible in fig. 14b. With higher magnification ($\times 10000$), these structures can be identified as nanotubes (fig. 16a). While in the unpolished areas the nanotubes are clearly visible, especially in zones of cracks and pores, it seems that they are destroyed by polishing the surface, or that they are covered with attrition material and therefore neither visible in the SEM nor detectable by the nanoindenter.

This process would explain why the mean values of $E$ and $H$, as identified by the test series with the nanoindentor and as listed in tabl. 1, are rather similar for concrete types $A$ and $B$, since the absolute concentration of Nanotubes in the concrete material is only a fraction of a percent.
CONCLUSIONS

1. The research has found that the main effect of the modification of mineral binding matrices using complex nanodispersed systems comprising MWCNT and nanosilica is ensured with the directed influence on the hydration processes and the subsequent crystallization of new formations. Scanning electron microscopy and X-ray microanalysis confirmed with IR-spectra have revealed that adding multi-walled carbon nanotubes dispersion together with nanodispersed silica provides the structuring of the binding matrix along with the perfect dense shell of hydrated new formations on the surface of solid phases. The structured interfacial layers form the special frame cells in the modified cement matrix which ensures the formation of extremely filled system predetermining the strengthening of the structure of the modified binding matrix due to the formation of the spatial packaging. Consequently, the main factor increasing the characteristics of cement concrete modified with carbon nanotubes and nanosilica is the structural modification of calcium hydroxides concerning both the composition and the morphology of new formations.

2. To quantify the effect of the addition of the CNT on the characteristics of the material on a micromechanical level proved to be a challenging
task, though. While it is possible to inspect the surface of a concrete sample with a resolution in a range of 1 micron, the necessary process of preparation of the samples for the nanoindentation probably obliterates all detectable effects of the CNTs, as shown by a SEM. Therefore, a more adequate examination method in this case would be a so-called picoindentor, which basically combines the test method of a nanoindentor with the optical potential of a SEM. Such an instrument is right now at the stadium of field testing at the Vienna University of Technology, though, and hopefully will be available at a later date.

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