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Study the effect of carbon nanoparticles in concrete

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Abstract. Carbon nanoparticles, whether in the form of nanotubes, fibers or graphenoids, can under suitable application improve mechanical as well as durability properties of cement composites. The use of carbon nanoparticles in concrete is limited by their relatively high cost but also by the difficulty of their dispersion in concrete. The experimental research was focused on the issue of dispersion of carbon nanotubes (CNT) and the effect of CNT in concrete. Concrete with different doses of multi-walled CNT (0.0015 % and 0.012 % from the weight of cement) was prepared. The dispersion of CNT, superplasticizing admixture based on polycarboxylate ether, and water was carried out using ultrasonic cavitator. The impact of various doses of CNT on the strength of concrete after 7 and 28 days and frost resistance of concrete after 100 cycles was observed. The best results were achieved with the addition of 0.012 % CNT of cement weight, representing a dose of 43.2 g per 1 m³ of concrete. The increase in compressive strength was 11.9 %, 17.3 % in flexural strength, 15.2 % in the tensile splitting strength and 26.9 % is the tensile strength of concrete surface layers after 28 days compared to the reference samples without CNT. Changes in properties of concrete with the addition of CNT were observed also in the case of frost resistance of concrete (8 % increase in the coefficient of frost resistance of concrete with the addition of 0.012 % CNT of cement weight).

1. Introduction
The beginning of the new millennium is the era of nanomaterials and nanotechnologies. The term nanomaterials can be used to describe bulk materials, nanocrystalline layers or nanocrystals. Nanocrystals are grains of particle size in the order of 1–100 nm, representing only a few hundred atoms or molecules. Carbon nanomaterials are a significant direction of modern technology. Carbon nanotubes, fullerenes, and most recently also graphene, are nanomaterials that have interesting mechanical, physical and chemical properties. They can find use in various fields, such as medicine, electronics, but also in the construction industry.

Carbon is the basic building block of all organic compounds. It is stable in several molecular structures that we call allotropes. Among the most famous allotropes that occur in nature is graphite. Graphite can also be called amorphous carbon or fullerene. It is also a modification of carbon with a molecular – crystalline structure and is characterized by spherical formations with 60 carbon atoms. The more rare carbon allotropes include crystalline carbon, known as diamond [1].

Carbon nanotubes were discovered in 1991 by prof. Sumio Iijimo. A unique feature of these structures is their electronic, mechanical, optical and chemical properties [2].

There are different types of CNT that can be manufactured in different ways. The most common techniques for the production of carbon nanotubes today are: arc discharge, laser ablation, chemical excretion and flame synthesis. CNT cleaning can also be divided into several main techniques: oxidation, acid treatment, annealing, sonication, filtering and functionalization techniques [2].
Carbon nanotubes (CNT – carbon nanotube) are an allotropic modification of carbon. It is a substance composed solely of carbon atoms. CNT are elongated formations with a diameter of 1 to 100 nanometres and a length of 100 micrometres. Typically, two types are used: single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT) [3]. SWCNT have a diameter of 1.2 – 1.4 nm, MWCNT typically have a diameter of 1.2 – 20 nm, usually they have 5 – 20 layers spaced about 0.34 nm [4].

The development of cement-based materials is directed towards high compressive strength cement composites [5,6] and cement composites with special properties in extreme conditions [7]. However, such composites also exhibit a very brittle fracture. This results in composites sensitive to micro-cracks at an early stage of volume changes due to high autogenous stresses [8]. These properties of cement-based materials are serious drawbacks that limit design and affect long-term durability of structures. Carbon nanoparticles represent possibilities to reduce the undesirable brittleness of cement matrices. Compared to conventional fine fibers, the CNT exhibits significantly higher strength and stiffness, which should improve overall mechanical behaviour. It is also expected that the high CNT slenderness ratio will effectively stop the spread of micro-cracks. If the CNT is evenly dispersed, the spacing between the individual reinforcement fibers is reduced due to their diameter.

2. Aim of research work
With good application, the carbon nanoparticles improve mechanical and durability properties of cementitious composites. The so far published studies differ in terms of the recommended amount of specific type nanoparticles into concrete and in the question of a suitable method of applying nanoparticles to concrete.

The first stage of experimental research was therefore focused on the issue of dispersion of nanoparticles and the evaluation of nanoparticles dispersion in concrete. The correct dispersion of nanoparticles is often very problematic [9,10]. Commercial nanoparticles, although manufactured and supplied in sizes below 100 nm, are typically showing as large agglomerates of 1 to 100 in size. The agglomeration reduces the specific surface of nanoparticles, this preventing the full utilization of these materials in order to improve the desired properties of concrete and other cement mixtures. In addition, the formation and presence of agglomerates prevents proper dispersion of nanoparticles within the matrix, resulting in the formation of attenuated zones in the matrix of the final product. The ideal dispersion can be described as a state in which nanoparticles are completely separated from each other and there are no clumps or agglomerates found in them. The first step in properly dispersing nanoparticles should be to use sufficient energy to break down aggregates and agglomerates into smaller sizes. After breaking the agglomerates, the next step is to stabilize the fragments and prevent their re-agglomeration.

In the next phase of experimental work, concrete with various doses of carbon nanotubes (in the order of thousands of percent of the weight of cement) were produced. It was necessary to define the exact technological process of preparation of concrete with nanoparticles. Subsequently, the effect of different doses of nanotubes on concrete properties was monitored. Concrete compressive strength, flexural strength, tensile splitting strength, surface layer tensile strength of concrete and frost resistance of concrete were determined over 100 cycles.

3. Experimental part

3.1. Used materials
- Cement. Portland cement CEM I 42.5 R was used.
- Aggregates. Three fractions of aggregate were used: silica sand with a fraction of 0 – 4 mm, aggregates 4 – 8 mm and 8 – 16 mm biotic granodiorite.
- Water. The dispersion of carbon nanotubes was carried out in demineralized water. This water is stripped of all the minerals contained in the water by filtration. During the production of...
concrete, drinking water was used as mixing water, which according to EN 1008 Mixing water for concrete meets the requirement for testing [11].

- Plasticizer. To improve the consistency of the concrete and to stabilize the stirred nanotubes during dispersion, the superplasticizing admixture COATEX ETHACRYL HF S.C. 40% was used. This admixture is based on polycarboxylate ether. Additionally, Sika ViscoCrete 4035 superplasticizing admixture was added to the concrete.

- Carbon nanotube. Carbon nanotubes manufactured by Yurui (Shanghai) Chemical Co., Ltd were used. There tubes were made using a 95 % purity chemical vapour deposition (CVD) method. The properties of carbon nanotubes are summarized in table 1.

| Table 1. Selected properties of carbon nanotubes TNM7. |
|-----------------------------------------------------|
| Properties                                      | Value               |
| Name                                           | TNM7                |
| Colour                                         | Black               |
| Type                                           | MWCNT               |
| Length                                         | 10 – 20 µm          |
| Inside diameter                                | 5 – 12 nm           |
| Outside diameter                               | 30 – 50 nm          |
| Bulk density                                   | 0.22 g·cm⁻³         |
| Specific weight                                | 2.1 g·cm⁻³          |
| Specific surface                               | > 60 m²·g⁻¹         |
| Specific electrical conductivity                | 100 S·cm⁻¹          |

3.2. Mix design
Carbon nanotubes as dispersed reinforcement are dosed up to 0.1 %. For this experiment, doses of 0.0015 % and 0.012 % by weight of the cement were selected. Each dose of nanotubes was dispersed in a solution containing the surfactant. Dosage of these substances is an empirical issue. It is reported that the amount of surfactants ranges from 10 % to 700 % by weight of CNT. In this case, a 400 % CNT weight dose was chosen, i.e. the ratio of surfactant: CNT = 4:1.

Determination of concrete properties was performed after 7 and 28 days. For each batch, a reference batch was created, which had the same dose of all raw materials, the only difference was it didn’t contain carbon nanotubes. The recipe is shown in table 2.

| Table 2. Composition of concrete per 1 m³. |
|-------------------------------------------|
| Materials                                | Amount per 1 m³  |
| CEM I 42.5 R                             | 360 kg           |
| Sand 0-4 mm                               | 840 kg           |
| Aggregate                                 |                   |
| Coarse aggregate 4-8 mm                   | 205 kg           |
| Coarse aggregate 8-16 mm                  | 900 kg           |
| Water                                     | 153 kg           |
| Plasticizer Sika Viscocrete 4035 (SP)     | 2.5 g (0.69 % z m.) |
| Plasticizer Ethacryl HF                   | 172.8 g (0.048 % z m.) |
| CNT 0.0015                                | 5.4 g (0.0015 % z m.) |
| CNT 0.012                                 | 43.2 g (0.012 % z m.) |

3.3. Preparation of suspense
The first step was the weighing of the superplasticizing additive, carbon nanotubes and water. The dispersion was carried out using the BandelinSonopuls HD 3200 ultrasonic cavitator. The suspense was then mixed in a magnetic homogenizer and then dispensed into concrete.
3.4. Production of concrete
According to the recipe, individual raw materials were weighed. The laboratory mixer plate with forced circulation was first dosed with weighed aggregate, from the coarsest fraction to the finest. The aggregate was briefly mixed, then cement was added and once again the dry ingredients were mixed briefly for better homogenization. Additionally, water with superplasticizing additive was added. After sufficient stirring, the already dispersed CNT was poured into the mixture and subsequently thoroughly mixed again. The concrete slump test was carried out on fresh concrete. Test specimens with measurements of 100 × 100 × 400 mm were produced.

4. Results of experimental work and discussion
4.1. Consistency of fresh concrete
The slump test was performed just after the mixing of each concrete batch. The concrete recipe has been designed to the S3 consistency of concrete in the slump test. The results were 120 to 130 mm Slump [12].

4.2. Strength of concrete after 7 and 28 days
Compressive strength, flexural strength, tensile splitting strength and concrete surface layer tensile strength were determined on samples after 7 and 28 days. Tests were performed according to standards EN 12390–3, EN 12390–5, EN 12390–6, CSN 731318 [13-16]. The results are shown in the following table 3 and in figure 1.

Table 3. Concrete compressive strength, flexural strength, tensile splitting strength and concrete surface layer tensile strength after 7 and 28 days.

| Concrete | Compressive strength [MPa] | Flexural strength [MPa] | Tensile splitting strength [MPa] | Concrete surface layer tensile strength [MPa] |
|----------|-----------------------------|-------------------------|----------------------------------|-----------------------------------------------|
|          | 7 days 28 days               | 7 days 28 days           | 7 days 28 days                   | 7 days 28 days                                |
| REF      | 50.0 58.0                    | 5.0 5.2                  | 3.1 3.3                          | 1.9 2.6                                       |
| CNT0.0015| 51.5 62.1                    | 5.3 6.0                  | 3.1 3.4                          | 1.9 3.0                                       |
| CNT0.012 | 52.4 64.9                    | 5.5 6.1                  | 3.2 3.8                          | 2.0 3.3                                       |

Figure 1. Changes in concrete strength after 28 days relative to the strength of the reference sample without the addition of CNT.

4.3. Frost resistance of concrete
The frost resistance of concrete was performed according to CSN 731322 [17]. Results are given in table 4.
Table 4. Flexural strength before and after 100 freezing cycles.

| Concrete | Flexural strength [MPa] | Coefficient of frost resistance |
|----------|-------------------------|--------------------------------|
| REF      | 7.1                     | 98.6                           |
| CNT0.0015| 7.2                     | 100                            |
| CNT0.012 | 7.3                     | 104.1                          |

The best results were achieved with concrete with 0.012 % CNT addition. The increase in compressive strength compared to the reference samples was 11.9 % after 28 days.

Another observed characteristic was flexural bending strength. According to Chen and Chung, it has been found that flexural bending strength in samples using short carbon fibers can increase up to 85 %. In our experiments, the flexural strength of CNT0.0015 concrete has increased by 15.4 % and CNT0.012 has increased by 17.3 %.

After determining the tensile splitting strength after 28 days, there was an increase of 3 % for the CNT0.0015 mixture and 15.2 % for the CNT0.012 mixture. It is not possible to trace any CNT dose dependence on the strength characteristics of the monitored concrete from the results obtained in the tensile splitting strength test. It is, however, indisputable that the CNT test samples achieved the best results from the monitored sample set during the tensile splitting strength test, after 7 days by 3.2 % and after 28 days by 15.2 % compared to the reference samples.

Next test was to determine the concrete surface layer tensile strength, which determines the magnitude of the force applied perpendicularly to the observed sample at the time of the failure. The tensile strength test of the surface layers after 7 days showed increase only in the CNT0.012 recipe, 5.3 %. However, strengths after 28 days showed significant changes. Recipe CNT0.0015 showed an increase of 15.4 % compared to the reference samples. Recipe CNT0.012 showed an even larger increase of 26.9 %. Also interesting is the tensile strength of concrete surface layers in samples CNT0.0015, when a virtually 10 times smaller dose of CNT achieved an increase in strength by about 15 % compared to the reference samples.

Frost resistance is the ability of water-saturated concrete to withstand the effects of alternate defrosting and freezing. The test samples were stored for 25 days in a humid environment and then for 3 days in water. Subsequently, they were tested on 100 freezing cycles. For reference concrete, a decrease in strength was recorded after freezing, however, it met the condition that the flexural bending strength after freezing must be higher than 75 % of the strength of the non-frozen concrete. Consequently, the test reference concrete without the addition of CNT can be marked as frost-resistant. With recipes containing carbon nanotubes, it was possible to observe the positive influence of CNT in the area that is critical to the durability of all concrete structures in our climatic conditions. The frozen samples gained on the strengths compared to the non-frozen samples. This can be explained by the fact that the microstructure of cement stone is so dense that the effect of the alternating frost didn’t manifest yet. Based on the results of the tests, it can be argued that carbon nanotubes improve the resistance of concrete to freezing.

5. Conclusion
The experiment was focused on the observation of different doses of CNT 0.0015 and 0.012% of cement weight on the observed characteristics of concrete – compressive strength of concrete, flexural strength, tensile splitting strength, surface layer strength of concrete and frost resistance of concrete. Observation of strength characteristics was performed at age 7 and 28 days. Frost resistance was determined after 100 cycles. The carbon nanotubes from Yurui (Shanghai) Chemical Co., Ltd. were used for the experiment. The best results were found in concrete with an addition of 0.012 % CNT of cement weight, representing a dose of 43.2 g per 1 m$^3$ of concrete. The results obtained with a dose of 0.0015 % CNT of cement weight (i.e. 5.4 g per 1 m$^3$ of concrete) were also positive. Changes in properties of concrete with the addition of CNT were observed also in the case of frost resistance of concrete (8 % increase in the coefficient of frost resistance of concrete with the addition of 0.012 %
CNT of cement weight). Specifically, the increase of resistance and durability of concrete with the addition of nanoparticles is an interesting area which we should focus more attention to and direct more research that way. Increasing the tensile strength of surface layers and frost resistance shows an increased resistance and durability of the concrete with the CNT addition. Follow-up experiments are therefore aimed at monitoring the resistance of concrete to abrasive action, both by mechanical influences and in particular by flowing fluids, clean water or water with solid particles.

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References
[1] Harris P J F, 2009 Carbon Nanotube Science: Synthesis, Properties And Applications (Cambridge: Centre for Advanced Microscopy, University of Reading, Cambridge University Press) p 179
[2] Ham H T, Choi Y S and Chung I J 2005 J. Colloid Interf. Sci. 286 216–223
[3] Raki L, Beaudoin J J, Alizadeh R, Makar J M and Sato T 2010 Material 3 918-942
[4] Aqel A, Kholoud M M, Ammar Reda A A and Al-Warthan A 2012 Arab. J. Chem. 5 1-23
[5] Kolisko J, Hunka P, Rydval M and Kostelecka M 2013 Proc. Int. Conf. on Central Europe towards Sustainable Building (Prague) (Prague: GRADA PUBLISHING) pp 385-388
[6] Novakova I and Bodnarova L 2017 Mater. Sci. Forum 908 164-170
[7] Stehlík M, Hermankova V and Vitek L 2015 J. Civ. Eng. Manag. 21 177-184
[8] Holcapek O, Kotatková K and Reiterman P 2018 Advances in Civil Engineering 2018 1-10
[9] Foldyna J, Foldyna V and Zelenak M 2016 Procedia Engineer. 149 94-99
[10] Jarolim T, Labaj M, Hela R, Michnova K 2016 Adv. Mater. Sci. Eng. 2016 1-6
[11] EN 1008: 2002 Mixing water for concrete
[12] EN 12350 – 2: 2009 Testing fresh concrete - Part 2: Slump-test
[13] EN 12390 – 3: 2009 Testing hardened concrete - Part 3: Compressive strength of test specimens
[14] EN 12390 – 5: 2009 Testing hardened concrete - Part 5: Flexural strength of test specimens
[15] EN 12390 – 6: 2009 Testing hardened concrete - Part 6: Tensile splitting strength of test specimens
[16] CSN 731318: 1987 Z1: 1994, Z2: 2003 Determination of tensile strength of concrete
[17] CSN 731322: 1968 Z1: 2003 Determination of frost resistance of concrete