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The influence of multi-walled carbon nanotubes additive on properties of non-autoclaved and autoclaved aerated concretes

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HIGHLIGHTS

- Multiwall carbon nanotubes (MWCNTs) act as nuclei during hardening of non-autoclaved and autoclaved aerated concretes.
- MWCNTs influence the hydration process and structure formation of these concretes.
- This leads to an increased crystallinity of hardened binding material.
- The higher is a crystallinity the better are characteristics of concretes.
- The influence of MWCNTs on characteristics of AAC is more significant than on the characteristics of NAC.

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ABSTRACT

The influence of multi-walled carbon nanotubes (MWCNTs) additive on characteristics of non-autoclaved aerated concrete (NAC) and autoclaved aerated concrete (AAC) was investigated. It was established that MWCNTs used as additive in NAC and in AAC production process acts as nucleators of crystallization influencing the hydration process and structure formation leading to increase in crystallinity of hardened binding material, as well as to increase in flexural and compressive strength of concretes and decrease in shrinkage during heating. The influence of MWCNTs on characteristics of AAC is more significant than on the characteristics of NAC. Investigation results allow to premise that NAC and as well AAC containing MWCNTs additive should be more stable during exploitation than those concretes without this additive.

1. Introduction

One of the methods recently applied to improve the technical characteristics of concrete is the use of additives consisting of nanodispersive particles. Previously we investigated the influence of the nanodispersed additives, such as amorphous nanodispersive SiO_2 (ANS) [1] as well as nanodispersive carbon nanoparticles obtained by dry- or wet milling of carbon fibre (CF) [2], on structure formation and technical properties of the aerated autoclaved concrete (AAC) and estimated the positive effect of these additives. Replacement of 1.0% of the milled sand in the forming mixture of AAC by ANS [1], which is not only nanodispersed, but also puzzolanic additive, resulted in formation of structure with considerably increased crystallinity and considerably increased compressive and flexural strengths as well as decreased shrinkage at temperature of 700 °C. Upon addition 0.1% (by mass of binder) of crushed carbon fibre (CF) [2] the cristallinity as well as the compressive strength of AAC increased considerably and decreased its thermal deformation. Basing on our works [1,2] and on other numerous works which state the positive influence of nanosized particles of additives, such as Fe_2O_3, ZrO_2, TiO_2, nanoalumina, and nanoSiO_2, on mechanical characteristics of the concretes, we draw the conclusion that nanoparticles of additives, used in our works [1,2], serve as nuclei of crystallization during hardening of AAC binding material and, consequently, improve the mechanical characteristics and thermal stability of AAC. These results show that the

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formation of targeted nanostructure is an effective way to improve AAC quality by using additives which act as nuclei of crystallization in the hardening process of AAC binding material. These findings comply with statements described in [3,4] to say that nucleation at early age of cement paste is very important for formation of structure.

During the last decade, the great interest was expressed in use of the carbon nanotubes (single-walled SWCNTs and multi-walled MWCNTs) as nanoreinforcements in cement based materials. The effect of SWCNTs on cement hydration and reinforcement is widely described in work [5] which reviews the investigations on use of nanotubes to improve the characteristics of concrete. The attention is drawn to work [6] where was shown that SWCNTs do act to nucleate cement hydration reactions and accelerate the hydration process. It is noticed in [5] that most works to date has been done on MWCNTs which are less expensive and more readily available than SWCNTs.

One can find papers where the positive influence of carbon nanotubes (CNTs) on the strength of concrete is described. In work [7] estimated that addition of CNTs in 0.05% by mass, manufactured using the technology of low-temperature synthesis of carbon nanotubes [8], caused the increase up to 70% the compressive strength of foam non-autoclaved concrete based on Portland cement. This work stated that CNTs additive leads to formation of continuous, non-holed, pore walls.

The review [9] cited the above mentioned work [7] and numerous other works on use of MWCNTs additive to improve the quality of cement-based concrete. In works [10–12] is noted that MWCNTs additive acts as reinforcement agent of concrete and increases its flexural and compressive strength by influencing the formation of porous structure in concrete. This statement agrees with observations on the subject in work [7].

The analysis of works performed in the field of use of CNTs additive to improve the characteristics of concrete shows that the positive action of this additive highly depends not only on nature of additive, length of its fibre, amount added, but also on previous treatment of fibre surface, on quality of CNTs dispersion in the forming mixture what is largely conditioned by properties of surfactant used, by w/c ratio and by blending mode. Therefore, the results, received using CNTs of different characteristics and different technologies for preparation of forming mixtures containing CNTs additive, vary considerably. For example, one can compare the results presented in work [13] where the influence exerted on reinforcement of concrete by MWCNTs additive (0.01 wt%), which was treated hydrothermally by mixture (1:1) of 69% nitric acid and 98% sulfuric acid, and by additive of non-treated MWCNTs was investigated. The increase in flexural and compressive strength was 5.4% and 8.4%, respectively, with the additive of treated MWCNTs and 20.7% and 15% with aqueous dispersion of non-treated MWCNTs additive. It was concluded in this work that the reason of strength increase difference lies in inconsistency of treated MWCNTs with binding material. Meanwhile the work [14] showed that the compressive and flexural strengths of concrete containing 0.5% by weight of cement additive of carbon nanofibres, treated in solution of nitric and sulfuric acids, are higher than these values obtained with untreated nanofibres. In works [15,16] it is stressed that to the aim of providing the sufficient transfer of load between the cement matrix and CNTs, the functionalization of their surface has to be performed. The functionalization should secure a chemical bond with cement paste. The chemical bond between carboxylated nanotubes with carboxyl groups on their surface and cement hydration products $Ca(OH)_2$ and C–S–H was estimated by FT-IR method [10] and it was concluded that the chemical bonding leads to an increase in flexural and compressive strengths.

The analysis of the above described investigations related to the improvement of the technical characteristics of cement concrete by means of nanotechnology, i.e. addition of CNTs to forming mixture, as well as of the inventions [17,18] done in the field, proves the effectiveness of the method. The investigations on application of nanotechnology for production of porous concrete are not numerous. We could not find any information about the possibility of using CNTs in manufacturing of AAC. Therefore, this work continues our previous works [1,2] in the field of use of nanotechnology in production of porous concrete, dealing with usage of MWCTs as an additive to improve the characteristics of NAC and AAC.

2. Materials and methods of testing

2.1. Materials

The raw materials used for preparation of forming mixtures of non-autoclaved and autoclaved aerated concretes named as NAC and AAC, accordingly, are described in Table 1.

Milled lime CL 90-Q (according to standard [19]) with CaO in 89.24% and reactivity expressed by time t_u, 3 min, and temperature T_u, 61.3 °C. Portland cement CEM I 42.5 R (according to standard [20]) of the following mineral composition (in %): C_3S 58.54; C_2S 15.29; C_3A 10.40; C_4AF 10.17. Milled quartz sand (according to standard [21]) with fineness of 2766 cm^2/g. Such fineness was obtained by milling in ball mill (capacity of 10 L, speed 100 rpm, porcelain balls of 20.0 mm diameter). In forming mixtures, as a gas-generating agent, aluminium paste DEG 4508/70 (specific surface 18.000 cm^2/g, content of pure aluminium 70%) was used. Before addition to the forming mixture, aluminium paste was dispersed for 1 min in 35 ml of water (taken from total amount of calculated water necessary for forming mixture) using glass cylinder of 70 ml capacity and ultrasonic disperser UZDN-2T (frequency of 22 kHz, power of 480 W).

Multi-walled carbon nanotubes (MWCNTs) were used as nanodispersive additives (filament length 0.1–10 μm, diameter 15–20 nm). The masterbatch named as Graphistrength CW2-45 prepared by company ARKEMA (France) was used as a source of MWCNTs. Graphistrength CW2-45 contains MWCNTs with purity >90% at concentration of 45% by weight of mixture, perfectly dispersed in carboxymethylcellulose at content of 55% by weight of mixture. Graphistrength CW2-45 is provided in form of pellets. The water suspension of Graphistrength CW2-45, freshly prepared before moulding of samples, was added to forming mixture of concrete. Preparation of Graphistrength CW2-45 water suspension went in accordance with the description presented by the company ARKEMA. The weighed amount of Graphistrength CW2-45 pallets, containing the necessary amount of MWCNTs, according to Tables 2 and 3, was immersed in 50 ml of hot (70–90 °C) distilled water for 15 min under mixing. After that carbon nanotubes were dispersed by ultrasound for 3 min, using the ultrasonic disperser UZDN-2T (frequency of 22 kHz, power of 480 W) in glass cylinder of 70 mL capacity. Thus obtained MWCNTs suspension (colloidal solution according to [22]) not exceeds 1–2% of MWCNTs concentration and contains carboxymethylcellulose, i.e. surfactant, as, according to [23], is required the nanofibres not to agglomerate. Using SEM of 1 nm resolution we established that in the suspension, prepared in this way, the MWCNTs were dispersed without agglomeration.

2.2. Preparation of forming mixtures and concrete samples

The components used for preparation of forming mixtures, with exception of Graphistrength CW2-45, were weighed by electronic balance EG 4200 2NM (capacity of 4.2 kg, precision 0.01 g). Graphistrength CW2-45 was weighed by electronic balance BP301S (capacity of 303 g, precision 0.2 mg)

The compositions of NAC forming mixtures were selected basing on methodical requirements described in [24]. The water/solids ratio was 0.51; content of aluminium paste in all the samples was the same (1.3 g) and amounted to 0.25% by weight of solids dry mass; binder/sand ratio 1:1. The content of MWCNTs additive was calculated as a percentage by weight of dry mass of binder (Portland cement) and ranged from 0 (control sample KN) up to 0.06% (sample 5N). The compositions of NAC forming mixtures are presented in Table 2.

The compositions of AAC forming mixtures were selected basing on methodical requirements [24]. The water/solids ratio was 0.55; content of aluminium paste in all the samples was the same (1.0 g) and amounted to 0.20% by weight of solids dry mass; binder/sand ratio – 1:2. The content of MWCNTs additive was calculated as a percentage by weight of dry mass of binder (lime + Portland cement) and ranged from 0 (control sample KA) up to 0.02% (sample 4A).The compositions of AAC forming mixtures are presented in Table 3.

All publications related to use of CNTs for improvement of properties of concrete underline the necessity of homogeneity of CNTs dispersion in concrete forming mixture. CNTs, due to their low mass and strong van der Waal's attraction to each other, can be dispersed in water when coated with adsorbed surfactant [21]. But even if the nanoparticles are well dispersed in the water, the problem known as geometry dependent clustering occurs [25]. The simulations done in work [26]