Modification of the structure and Properties of Fine-Grained Concrete with Carbon Black Dispersion

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Abstract. The study shows that adding carbon black (soot) in the form of an aqueous dispersion into the composition of fine-grained concrete leads to an increase in bending and compressive strength of the samples: at a soot concentration of 0.005% by weight of cement, respectively, to 37.63 and 15.99%, at a concentration of 0.02% up to 26.39 and 26.39% due to compaction of the structure of the cement matrix. An intensification of cement hydration processes has been noted, confirmed by the results of IR-spectral, differential-thermal analyses and studies of the cement matrix microstructure in the composition of fine-grained concrete. On the surface of new formations in the composition of modified soot dispersion, the formation of needle-like crystals has been observed. On their surfaces, structures of spherulites formed with sizes ranging from 100 to 200 nm, which are typical for calcium hydro-sulfonic aluminates of 3CaO·Al₂O₃·3CaSO₄·32H₂O type. The formation of spherulites is observed in the pores of the cement matrix, which contributes to additional compaction of the structure of fine-grained concrete.

1. Introduction

To modify the structure and properties of building composites of hydration hardening, carbon nanomaterials are used: fullerenes, single- and multi-walled nanotubes (MWCNTs). Along with fullerenes and MWCNTs, two-dimensional structures based on graphene, graphite plates of one atomic layer thick, are being actively used to improve physical and mechanical parameters of cement composite materials. The studies in which research data are presented show an improvement in the strength indicators, an increase in the density of the structure of cement matrices in the composition of concrete and mortars [1].

Studies in [2-5] focus on the use of graphene oxide for the modification of cement matrices, which significantly affect the change in the structure and properties of cement composites when graphene oxide
is added to the compositions. Adding graphene oxide is said to contribute to a significant increase in the strength properties of cement composites (bending and compressive strength), which is caused by creating favourable conditions for the formation of the set cement microstructure [6–8].

At the same time, there is no technology for mass production of graphene in quantity suitable for industrial use; therefore, their cost turns out to be higher than the cost of the existing carbon nanotubes. Graphene oxide, which is produced in sufficient volumes for possible use in the production of cement composites, is limited in use due to their complex technology and unsafe production associated with the use of strong oxidizing agents.

There are some studies on modifying cement matrices in concretes with isostatic graphite after dispersing it into an ultrafine product of nanoplates [9, 10]. In comparison with synthesized carbon nanotubes, they have the mechanical and physical characteristics required for modifying the structure at a relatively low cost but show evident hydrophobic properties and require surface functionalization with surfactants [11].

Thus, it becomes necessary to search for such forms of carbon for mass use in the construction industry, which, having dispersion at the nanometre level and, consequently, increased chemical activity, would not increase the cost of cement concrete and mortars more than the well-known chemical additives designed for the directional change of certain parameters of building composites.

The studies conducted by a group of authors [12] showed that adding ultradispersed carbon black into a concrete mixture provides a dense packing of the cement matrix grains, improves interfacial contacts between the matrix and fillers, and increases the strength of the modified concrete. Thus, comparing the production technology and the cost of soot, the authors suggest using carbon black dispersions.

2. Materials and methods of research
Carbon black (commonly named as "soot") is a product with desired properties, obtained as a result of controlled pyrolysis or thermal-oxidative decomposition of liquid or gaseous hydrocarbons. According to the particle structure, it occupies an intermediate position between amorphous coal and crystalline graphite. The interplanar distance between graphite-like layers is 0.35 - 0.365 nm (in comparison with 0.335 nm in graphite).

The particle size (13-120 nm) determines the “dispersion ability” of carbon black. The main physical and chemical indicator characterizing the dispersion ability is the specific surface area of soot. Its particles during the production process unite into aggregates, which stick together in less durable flake formations.

Soot is used for the production of industrial paints, pigments, and tinting pastes. For example, for universal tinting paste CS.BK black concentrated, “Palizh” TM, manufactured by “Novyy Dom” LTD, pigment soot with a particle size of 30 nm and a specific surface area of 65-100m2/g was used. The pigment content in the paste is 34%.

The experimental part of the study used the above described dispersed soot concentrate in an aqueous surfactant solution, presented in the form of a tinting paste. The dispersion analysis of this additive, performed on a SALD-7500nano laser analyzer, at the age of 3 years, is shown in Figure 1b.
Based on the data presented, it can be concluded that the average particle size is 0.140 μm.

3. Research results and discussion

To study the effect of the age of dispersion, samples of fine-grained concrete beams were produced according to GOST 30744-2001 “Cements. Test methods with polyfractional sand”, carbon black dispersion in the amount of 0.005 and 0.02% by weight of cement being used. After 24 hours of hardening in a humid environment, the samples were subjected to thermal and humidifying treatment in a steam chamber with the mode (3:6:2 h) at a temperature of 85 °C. The results of the physical and mechanical tests of the samples modified with carbon black dispersion are presented in Table 1.

The results of physical and mechanical parameters of fine-grained concrete modified with soot dispersion (Table 1).

| Sample after HWT | W/C | C, % of C | Ultimate strength, MPa: (check/experimental) | \(R_{\text{prod}}\) | \(R_{\text{soot}}\) |
|------------------|-----|-----------|---------------------------------------------|---------|-----------|
| 3 days           | 0.4 | 0.005     | 2,601/3,31                                 | 22,105/23,43 |
|                  |     | 0.02      | 2,601/2.8                                  | 22,105/25,38 |
| 28 days          |     | 0.005     | -                                           | 27,7/27,63  |
|                  |     | 0.02      | -                                           | 27,7/32,24  |

Analyzing the data, it should be noted that on the third day after the heat and wet treatment the strength indicators for bending and compression increased by 7.65% and by 14.82% respectively at a carbon black concentration of 0.02% and by 37.26% and 15.99% at a concentration of 0.005% by weight of cement. Strength indicators at the age of 28 days increased by 26.39% under compression with a soot concentration of 0.02% by weight of cement.

To study the processes occurring when soot dispersion is added into the mixture, the microstructure of the modified samples was studied. The results are shown in Figure 2.
Figure 2. The microstructure of fine-grained concrete at 20,000-fold magnification: a) the check sample, b, c) the samples modified with soot of 0.02% concentration

As it can be seen from the presented images, the structure of the sample modified with a freshly prepared dispersion of carbon black with a concentration of 0.02% has a more dense structure (Figure 2b) in comparison with the check sample (Figure 2a) with the presence of a significant amount of calcium hydroxide (long lamellar structures) along with calcium hydrosilicates of acicular (Figure 2b) and scaly structure with deformed plates (Figure 2c), typical for calcium hydrosilicates of the tobermorite group [13].

Thus, the microstructure correlates well with the mechanical test data given in Table. 1. The increase in mechanical properties is confirmed by the sealing effect of the cement matrix as a result of adding soot dispersion with nanometer-sized particles.

Figure 3. Microstructure of fine-grained concrete modified with soot with a concentration of 0.005% on the surface of the filler: a) at 5,000-fold magnification: b) a fragment of the microstructure at 20,000-fold magnification, c) new formations in the pores of the cement matrix at 50,000-fold magnification

The study of the microstructure of the cement matrix modified with 0.005% technical soot showed good adhesion to the surface of the fine aggregate and its interaction with new formations in the cement matrix (Figure 3a).
On the surface of calcium hydrosilicates, the formation of needle-like crystals was observed (Figure 3b), on which new formations in the form of spherulites with sizes ranging from 100 to 200 nm (Figure 3c) appeared, clearly seen with magnification of up to 50,000 fold. According to V.S. Gorshkov [13], such new formations are typical for calcium hydrosulfoaluminates of $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O}$ type. Their formation is observed in the pores of the cement matrix, which contributes to additional compaction of the structure of fine-grained concrete.

![Figure 4. X-ray microanalysis of new formations in the cement matrix a) the analyzed fragment, b) the spectrum of X-ray microanalysis](image)

In order to identify and determine the composition of spherulites in the pore structure of the cement matrix, an X-ray microanalysis of the observed new formations was conducted. It has been established that atoms of calcium Ca, oxygen O, silicon Si, aluminum Al, sulfur S, which are components of calcium hydrosulfonyluminate, dominate in the composition of nanometer-sized spherulites (Figure 4).

In order to study the composition of new formations, a simultaneous thermal analysis of the modified samples was conducted on a TGA/DSC1 Star system derivatograph, the results of which are shown in Figure 3. On the spectra of the check and modified samples (Figure 5), there are endothermic effects in the temperature range of 177-184 °C (removal of crystalline water), 512-521 °C (dehydration of calcium hydroxide in the composition of the cement matrix), 817-820 °C (dehydration of calcium hydrosilicates), and a weak exothermic effect at a temperature of 920 °C, associated with the formation of wollastonite. In this case, a more intense endothermic effect is observed during the dehydration of calcium hydroxide and a large mass loss of the sample at this temperature in the modified soot sample, which confirms the intensification of Portland cement hydration. The modified sample behaves in a similar way in the temperature range of 817-820 °C, which confirms the change in its microstructure accompanied with appearance of new formations of different structures.

Thus, the results of DTA confirmed the formation of a larger volume of calcium hydroxide in the composition of the cement matrix modified with soot and the results of the analysis of the microstructure in combination with X-ray microanalysis, which showed the formation of crystalline hydrates with an increased water content in the crystal lattice of the components of the cement matrix.
Figure 5. Differential scanning calorimetry of fine-grained concrete: 1 - calorimetry of the check sample; 2 - calorimetry of the sample modified with soot dispersion with a concentration of 0.02%.

To confirm the data obtained in the differential-thermal analysis of fine-grained concrete, IR-spectral analysis of the check and modified cement matrix sample with a soot content of 0.02% was conducted.

Figure 6. IR spectra of the check sample and the sample modified with soot dispersion: 1 - the spectrum of the check sample, 2 - the spectrum of the sample modified with soot dispersion with a concentration of 0.02%.
IR spectral analysis of the cement matrix performed on an IRAffinity-1 IR spectrometer showed a significant difference in the spectra of the samples modified with soot dispersion (Figure 6).

The spectrum of the test sample shows the intensity of the absorption line in the region of 3408.22 cm\(^{-1}\), corresponding to the OH\(^{-}\) group and the absorption line in the region of 1419.61 cm\(^{-1}\), corresponding to the carbonation of calcium hydroxide. The increase in the intensity of the absorption lines with values of 1419.61 and 1465.9 cm\(^{-1}\), corresponding to the CO\(^2\)- group, confirms the increase in the content of free calcium hydroxide due to the intensification of the hydration processes of Portland cement, which is also confirmed by a more intense endothermic effect at a temperature of 521 °C and increased water losses on the TG line. In addition, there is a shift of the absorption lines corresponding to calcium hydroxysilicates from 1089.78 to 1116, 78 cm\(^{-1}\) and the appearance of an evident “shoulder” with an absorption line of 1012.63 cm\(^{-1}\), which suggests a change in the basicity of calcium hydroxysilicates, which, in their turn, are responsible for increasing the strength of the cement matrix.

4. Conclusion
Thus, comparing the data obtained, we can speak about the structuring of fine-grained concrete by soot dispersion, leading to a change in the morphology of new formations along with compaction of the structure of the cement matrix. The intensification of Portland cement hydration processes was stated along with the formation of large volumes of calcium hydroxide, confirmed by differential thermal analysis and microstructure research. IR spectral analysis showed a change in the composition of calcium hydroxysilicates with the formation of new formations of lower basicity, ultrafine soot being added. At the same time the mechanical parameters of fine-grained concrete improve by 26.39%, being modified with technical soot dispersion in the amount of 0.02% by weight of Portland cement.

The study was performed within the State task by order of the Ministry of Education and Science of Russia (project 16.7823.2017/7.8)

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