Structuring in Cement Systems with Introduction of Graphene Nano-Additives

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Abstract. At present, one of the most promising areas in the field of concrete research is the study of the effect of nano-additives for the production of highly effective concretes. Many authors have already obtained primary results which testify to the very effective role of nano-additives based on carbon in modifying concrete. In this paper, the influence of a nano-additive of graphene on the phase composition and microstructure of the cement stone was studied. It has been found that, when a nano-additive of graphene is introduced, low-basic calcium hydrosilicates are mainly formed. This leads to an increase in the compressive strength of concrete. The results of the study of the microstructure of cement stone with nano-additive graphene showed that the high compressive strength of concrete modified with nano-additive graphene is explained by the cement stone dense structure. Thus, it was found that the nano-additive of graphene contributes to the formation of a dense structure of cement stone, composed mainly of low-basic calcium hydrosilicates, and due to this, the physical and mechanical characteristics of concrete and its resistance to frost and other forms of aggression.

1. Introduction

The new generation of additives used in cement systems and having a size of 1-100 nm - the so-called nano-additives - are becoming increasingly widespread [1-3].

At the same time, nanofilms of graphene oxide are attracting increasing attention of researchers [4-6].

Graphene is a monolayer of carbon atoms. Obtaining this material from graphite is a laborious process due to the strong bond between the atoms [7-9]. Many researchers use the Hammers method, which consists in intercalating, that is, introducing, substances, most often acids, into layers of graphite to weaken the bond between them, and consecutive washing out of embedded substances [10-11]. However, it is not always possible to remove the embedded substances and many functional groups of oxygen remain on the surface of the graphene plates, for example -OH, -COOH and -SO₃H and others, which further increase the attraction of the formed primary crystals upon hydration with C₃S, C₂S and C₃A, forming points of growth of hydration products [12-14].

Another important step in the production of concrete, modified by a nano-additive, is the process of dispersing nano-particles in a cement matrix. Most often, this problem is solved by ultrasonic treatment and processing of nano-particles by additives based on polycarboxylate esters [15-17].
Many teams of scientists managed to obtain basic knowledge about the mechanism of action of nano-additives obtained from graphite [18-20]. Due to the high specific surface area of nano-particles (about 2500 m²/g, against 3000 cm²/g for cement) they are additional centers of crystallization of precipitated particles from the solution during hydration of cement.

Previously, the results of a study of concrete modified with nano-additive graphene in an amount of 0.005-0.025% of the mass of cement (Table 1).

| Composition number | Content of nano-graphene, % by weight of cement | Compressive strength, MPa | Number of cycles in the test |
|-------------------|-----------------------------------------------|---------------------------|------------------------------|
| 0                 | 0,000                                         | 29,4                      | 51                           |
| 1                 | 0,005                                         | 30,5                      | 78                           |
| 2                 | 0,010                                         | 34,3                      | 104                          |
| 3                 | 0,015                                         | 30,9                      | 82                           |
| 4                 | 0,020                                         | 30,2                      | 76                           |
| 5                 | 0,025                                         | 31,0                      | 80                           |

This article presents the results of a study of the phase composition and microstructure of a cement stone without a nano-additive of graphene and a nano-additive of graphene in the amount of 0,010 %.

2. Experimental

2.1. Materials

For the production of cement stone the following was used:

- portland cement CEM I - 42,5N GOST 31108-2016, GOST 30515-2013 produced by LLC "Dyckerhoff Korkino Cement", Korkino (Russia);
- metacaolin of MWCL produced by OOO "Plast-Rifei", Zhuravliny Log (Russia);
- highly effective powder hyperplasticizer based on polycarboxylate ether PANTARHIT® PC160 Plv (FM);
- nano-additive of graphene was obtained from raw materials purchased by OOO KhimPEK;
- tap water.

Figure 1 shows photographs of the nano-additive graphene used in this work at different magnifications.

Figure 1. Nano-additive of graphene at magnification: (a) x200 times; (b) x1000 times.
2.2. Sample production
For the study of cement stone, samples were prepared with cubes with an edge of 2 cm, after which they were conditioned for 28 days in a normal storage chamber at a temperature of 20 ± 3 °C and relative air humidity 95±5 %.

The cement consumption was 500 kg/m³, highly effective powdered hyperplasticizer PANTARHIT® PC160 Plv (FM) – 0,3 % from the mass of cement, metakaolin MKZhL - 14% of the mass of cement.

Nano-additive graphene was introduced in an amount from the mass of cement: 0% (composition No. 0), 0.010% (composition No. 2).

The water-cement ratio was 0.36 for all formulations.

2.3. Methods of research
The study of cement stone was carried out with the determination of X-ray diffraction analysis using the diffractometer "DRON-3M", modernized with the PDWin attachment.

Derivatographic and thermogravimetric analyzes were performed on the instrument-derivatograph of the LuxxSTA 409 system from Netsch.

The microstructure of the cement stone sections was studied with the help of a scanning electron microscope from Jeol Interactive Corporation, Japan JSM–700 1F.

3. Results

3.1. Derivatographic analysis
DTA was made for the cement stone of compositions No. 0 and No. 2 at the age of 28 days.

Figure 2 shows the derivatograms of compositions No. 0 and No. 2 at the age of 28 days of normal hardening.

Figure 2. Derivatograms of cement stone at the age of 28 days of normal hardening: a) composition No. 0; b) composition No. 2.

The thermogram of cement stone with nano-additive graphene clearly shows the appearance of an additional peak at a temperature of 203 °C, Corresponding to the initial stage of decomposition of a mixture of highly basic and low-basic calcium hydrosilicates.

At the temperature of approximately 480 °C There is decomposition of calcium hydroxide. The amount of calcium hydroxide decreases markedly from 8.22% to 3.29% at the age of 28 days with the addition of a nano-additive.
There was also a decrease in the number of highly basic hydrosilicates with the introduction of a nano-additive at the age of 28 days - the loss of chemically bound water at the temperature 710-730 °С decreased from 2.6 % to 1.7 %.

3.2. X-ray Phase Analysis
Figure 3 shows the radiographs of compositions No. 0 and No. 2.

![Figure 3. Roentgenograms of cement stone at the age of 28 days of normal hardening: a) composition No. 0; b) composition No. 2.](image)

X-RPA confirms the results obtained with DTA.
The presence of phases in a cement stone without a nano-additive (composition No. 0):

- Ca(OH)$_2$ with interplanar distance d/n= 0.491; 0.262; 0.192; 0.179; 0.168; 0.148; 0.144 nm;
- High basic C-S-H (II) phase and the low-basic C-S-H (I) phase d / n = 0.983 0.309; 0.303; 0.276 nm;
- high basic calcium aluminates C$_4$AH$_{13}$ d/n= 0.780; 0.165 nm, C$_4$AH$_{19}$ d/n= 0.253 nm and C$_3$AH$_6$ d/n= 0.204 nm.

In the cement stone with nano-additive (composition No. 2), phases:

- Ca(OH)$_2$ with interplanar distance d/n= 0.490; 0.263; 0.192; 0.181; 0.148 nm;
- high-basic C-S-H (II) phase and a low-basic C-S-H (I) phase d/n= 0.309; 0.304; 0.277 nm.

Thus, it can be seen that in the cement stone composition No. 2 of the highly basic calcium aluminates is practically not observed, the amount of the high-basic phase of C-S-H (II) and the low-basic phase of C-S-H (I) does not change.

Intensity of reflection Ca(OH)$_2$ very strongly varies with the presence of nano-additive graphene - decreases almost 2 times.

3.3. Microstructure
Figures 4-5 show photos of the microstructure of cement stone samples without nano-additive graphene and with it at different ages.

![Figure 4. Microstructure of cement stone with nano-additive of graphene in quantity 0% of the mass of cement with an increase in x3000 times the age: a) 7 days; b) 28 days.](image)
Figure 5. Microstructure of cement stone with nano-additive graphene in an amount of 0.010% of cement mass with an increase in x3000 times in age: a) 7 days; b) 28 days.

The photographs show that at the age of 7 days the structure of the cement stone with nano-additive and without it is loose, loose, fine-grained. However, at the age of 28 days, the cement stone with nano-additive has a compact, homogeneous microstructure, which is a plate. Unlike cement stone with nano-additive, the structure of the stone without additives from fine-grained (at the age of 7 days) becomes coarse and less uniform to 28 days.

4. Conclusion

Based on the research data X-ray phase, derivatographic and microstructural analysis, we can make the following generalizations on the effect of nano-additive graphene on the phase composition and microstructure of the cement stone:

- structure of cement stone without nano-additive graphene is represented mainly by high-basic hydrates;
- introduction of graphene leads to the formation of a large number of low-basic hydrate phases;
- microstructure of cement stone without additive in the initial periods of hardening fine-grained, eventually - enlarged;
- microstructure of cement stone with nano-additive in the initial periods of hardening is fine-grained;
- over time, crystals recrystallize in the plane with the formation of a lamellar structure.

In this paper, an attempt was made to explain the effect of the nano-additive on the phase composition and microstructure of the cement stone, and as a result, to explain the relationship between the improvement of the physical and mechanical properties of concrete when modified with a nano-additive.

It has been found that when a nano-additive of graphene is introduced, a large amount of low-basic calcium hydrosilicates is formed, which, thanks to the ability of the nano-additive to adsorb on its surface, promote the tight packing of hexagonal plates, making the microstructure of the cement stone dense and strong, more resistant to various types of aggression.

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