Thermodynamic modeling effect of fullerenes C_{60} and C_{70} on phase composition and hydration of Portland cement

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Abstract. This paper presents thermodynamic calculations of the hydration of cement stone with carbon nanomodifier. Carbon nanomodifier was obtained at atmospheric pressure and elevated helium pressure in arc discharge. Cement stone with the use of carbon nano-modifier has improved physical and mechanical properties. Thermodynamic calculations showed that with the addition of carbon nanomodifiers, the phase composition and the kinetics of the hydration of cement stone change.

1. Introduction
Cement composite complex hydration system, which is still not well understood. At the same time, modern methods of modifying its structure repeatedly complicate the problem of research and interpretation of the results, while at the same time having a significant impact on the processes of hydration and hardening [1].

Carbon nanoparticles change the chemical equilibrium in the process of cement hydration as the solubility of the phases of hydrating cement changes. The thermodynamic equilibrium model is used to study complex multicomponent systems and is suitable for studying the hydration of cement composite. The advantage of the thermodynamic method is its universal character, which allows studying systems of arbitrary chemical composition on the basis of reference information only on thermochemical and thermodynamic properties of individual substances – components of equilibrium.

Carbon soot is used as a carbon nanomodifier (CNM) of building materials. The study of exothermic heterogeneous interactions and thermal effects in the system "cement - water - nanomodifier" allows estimating the influence of nanomodifier on the rate and depth of hydration of cement stone. In work [5] it is shown that at introduction carbon nanomodifier the temperature of hydration cement paste increases by means of the thermo-kinetic analysis. Taking into account the fact, that introduction CNM leads to considerable effect of improvement of the basic properties of cement and concrete, carbon nanomaterials, received plasma-chemical method, research of possibility of use is of interest for modifying of a cement stone. The study of the possibility of using a carbon nanomodifier is relevant because the introduction of a carbon nanomodifier leads to improvement the physical, mechanical and operational properties of the cement composite. The carbon nanomodifier obtained by plasma chemical method differs in composition depending on the conditions of production.
2. Models and Methods
A carbon nanomodifier was produced in a plasma chemical reactor. [1,2]. Installation diagram is shown in Figure 1. The installation uses the erosion of the electrodes in the high-frequency arc discharge. The discharge is initiated in the inert gas flow of helium when the current passes through the electrodes 44 kHz. Graphite electrodes are vaporized in a closed volume with filled helium at atmospheric and elevated pressures. Carbon soot was studied by x-ray phase analysis. Carbon soot contains parts by weight: 0.8 – C₆₀; 0.15 - C₇₀; the rest - higher fullerenes and oxides C₆₀O and C₇₀O.

Hydration of cement stone was investigated by x-ray phase analysis (diffractometer Bruker Phasor D2 using Cu Kα₁ radiation) and thermodynamic modeling.

Cement stone was obtained by hydration Portland cement. Mineral composition of Portland cement: 3CaO·SiO₂ – 65%; 2CaO·SiO₂ – 13%; 3CaO·Al₂O₃ – 6%; 4CaO·Al₂O₃·Fe₂O₃ - 13%; MgO – 1.06%; SO₃ – 1.94%.

Thermodynamic calculations are carried out in the TERRA program [3]. The TERRA program calculates the phase composition of the multicomponent systems for the model of single-component immiscible phases and for the model of condensed solutions.

3. Results and Discussion
The results of the study effect of carbon nanomodifier on the physical and mechanical properties of cement stone are shown in the article [6]. The addition of carbon nanomodifier in an amount of 0.01 % by weight of cement increases the strength by 10% and in the amount of 0.001 % increases the strength by 35 %. With the introduction of the carbon nanomodifier in the cement matrix there is a change in the phase composition, structure and physical and mechanical properties of the cement stone. Carbon nanomodifier changes the structure of the mixing water, creating around their directionally oriented particles of hydrated shell, which leads to the change of rheological characteristics of cement paste. Furthermore, the carbon particles serve as nanomodifier nucleation hydration products of cement, which accelerates the cement hydration and curing, especially in the initial period of hardening [6].

Change in phase composition, structure and properties of modifying cement stone were investigated. The effects of the CNM on the early hydration process of cement were studied using X-ray diffraction analysis and thermodynamic modeling. The CNM were found to accelerate the hydration reaction of the C₃S in the cement. In particular, the CNM appeared to act as nucleating sites for the hydration products, with the CNM becoming rapidly coated with C-S-H. The addition of CNM improves the strength characteristics of cement stone because it reduces the porosity of cement stone and building materials based on it.

![Figure 1](image_url). The change in enthalpy in the reaction mixture cement - 25 wt% water - 0.01 wt% C.
The degree of cement hydration can be determined in various ways by measuring: the amount of Ca(OH)$_2$, heat release during hydration; the amount of non-hydrated cement (using X-ray analysis), as well as indirect strength cement stone. X-ray structural analysis and thermodynamic modeling were carried out to assess the hydration of the cement composite with UNM. Thermodynamic calculations made it possible to determine the molar phase compositions, the pressure of gaseous components, thermodynamic properties at each temperature, including the total enthalpy $\Delta H$, the entropy $\Delta S$, and the equilibrium heat capacity $C_P$. The calculations were carried out in the temperature range 298-898 K at a pressure 0.1 MPa (Figure 1). Analysis of the dependence of $\Delta H$ (T) in certain temperature ranges revealed sharp changes in enthalpy, which can be attributed to the phase or chemical equilibrium transformations associated with the formation of new or intermediate compounds in the presence of carbon/fullerenes.

The change in enthalpy with the introduction of CNM indicates a more complete course of reactions. Calculations have been made of the yield of phases, the portlandite Ca(OH)$_2$ and calcium monosulfoaluminate [5] kind of 3CaO-Al$_2$O$_3$-CaSO$_4$-12H$_2$O from quantity of CNM. With an increase in the number of CNM, the yield of portlandite increases, but the yield of calcium monosulfoaluminate decreases (Figure 2,3). At the same time, the optimal amount corresponds to the minimum amount of the CNM additive, which is consistent with the experimental data on the study of the effect of the CNM on the strength of the cement stone. The effect of UNM has an extreme character and better effect when adding CNM in an amount of $10^{-2}$-$10^{-3}$ wt% [6].
Thermo-kinetic analysis [4] and thermodynamic modeling revealed a temperature increase of hydration with the introduction of CNM into the cement paste that shows the complete progress of the reactions. The dynamics of reduction of calcium silicate peaks characterizes the activation of the processes of hydration and binding of portlandite, which explains the increase in strength of the modified cement stone. The structure of the cement stone has a high density and uniformity in the introduction of CNM [6]. Improvement of physical and mechanical characteristics of the modified cement stone is associated with the improvement of the structure caused by the features of the hardening process and the quality of the resulting crystalline hydrates.

4. Conclusion
This article shows the results of a study of synthesis fullerenes and the modification of building materials by fullerenes. Optimization of synthesis fullerenes at atmospheric pressure is carried out. In the synthesis of fullerenes at atmospheric pressure, it is possible to obtain carbon condensate of different composition by changing the pressure of helium or by using additives in graphite electrodes [6].

The use of carbon soot increases the strength of the cement stone. Carbon nanomodifier changes the phase composition and kinetics of hydration of cement stone, which allows obtaining building materials with improved properties. Thermodynamic calculations allowed us to determine the yield of the phases of portlandite Ca(OH)₂ and calcium monosulfoaluminate 3CaO·Al₂O₃·CaSO₄·12H₂O from the amount of additive and temperature. Adding a CNM changes the phase composition, the phases yield, and the total heat dissipation of the system, which indicates the complete course of the reactions.

References
[1] Churilov G N, Korets A Y and Titarenko Y N 1996 Production of fullerenes and nanopipes in a carbon plasma jet at kilohertz frequencies J. of Technical Physics 41 (1) 102-3
[2] Churilov G N 2000 Plasma synthesis of fullerenes (review) Instruments and experimental techniques 43 (1) 1-10
[3] Trusov B G 2012 Code System for simulation of phase and chemical equilibriums at higher temperatures Engineering Journal: Science and Innovation 1 240-9
[4] Pukharenko Yu V, Ryzhov D I and Staroverov V D 2017 Peculiar properties of structural formation of Cement Composites in the Presence of Fueleroid Type Carbon Nanoparticles Proc. of Moscow State University of Civil Engineering (Moscow: Vestnik MGSU) 12, 7 (106) pp 718–23
[5] Winnefeld F and Lothenbach B 2016 Phase equilibria in the system Ca₄Al₆O₁₂SO₄–Ca₂SiO₄–CaSO₄–H₂O referring to the hydration of calcium sulfoaluminate cements RILEM Technical Letters 1 10-6
[6] Semenov A P, Smirnyagina N N, Urkanova L A, Kanakin S V, Lkhasaranov S A, Semenova I A, Dasheev D E, Tsyrenov B O and Khaltarov Z M 2017 Reception carbon nanomodifiers in arc discharge plasma and their application for modifying of building materials IOP Conf. Ser.: Materials Science and Engineering 168 (1) 012059