Plasmochemical synthesis fullerenes \( \text{C}_{60} \) and \( \text{C}_{70} \) at atmospheric pressure and the effect of fullerenes on hydration of Portland cement

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Abstract. The paper presents the results of modification cement composites by carbon nano modifier which contains fullerenes \( \text{C}_{60} \) and \( \text{C}_{70} \). Carbon nanomodifier obtained in high-frequency arc discharge at atmospheric pressure. There are fullerenes \( \text{C}_{60} \) and \( \text{C}_{70} \), carbon nanotubes in composition of carbon nanomodifier. Carbon nanomodifier improves physical and mechanical properties with small amounts of additives. Cement hydration, and phase composition change with the use of carbon nanomodifier that allows obtaining a composite with improved properties.

1. Introduction

Fullerene is an allotrope of carbon. These are closed spherical or spheroidal molecules consisting of carbon atoms. All fullerenes have twelve pentagons and a different number of hexagons, which determines the shape of the molecule.

There are many methods for the synthesis of fullerenes. One of the most promising methods is the synthesis of fullerenes in arc discharge plasma. This method allows to obtain 10–15 wt. % of fullerenes in carbon soot. The composition and amount of fullerenes in a carbon condensate is determined by the method of synthesis and the conditions under which the synthesis of carbon condensate occurs. In our work, we studied the effects of synthesis parameters on the yield and content of fullerenes in carbon soot.

Fullerenes have unique properties; they find their application in various fields ranging from materials science to medicine. In our work, we will show how fullerenes are used as carbon nanomodifiers (CNM) of building materials. The use of carbon nanomodifiers allows you to improve the physico-mechanical properties building materials by 10–30% with small amounts of additives (0.01–0.1 wt. %)

2. Experimental

A carbon nanomodifier was produced in a plasmochemical reactor [2, 3]. 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. Content of carbon soot and hydration of cement stone was investigated by x-ray phase analysis (diffractometer Bruker Phaser D2 using Cu Kα1 radiation).

Thermodynamic calculations are carried out in the TERRA program [6]. 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 composition of the resulting additive can be adjusted by changing parameters of the arc discharge (table 1). The use of the arc discharge at a current frequency of 44 kHz is the most productive. Performance with these parameters is 16 mg-min⁻¹. For the synthesis of the additives, graphite rods were used for spectral analysis with a minimum amount of impurities.

| Type of current          | Current (А) | Amorphous carbon (%) | Fullerene yield (%) |
|--------------------------|-------------|----------------------|---------------------|
| Direct current           | 60–200      | 27–73                | 1.3–0.2             |
| Alternating current 50 (Hz) | 100–200    | 61–86                | 0.6–0.9             |
| Alternating current 44 (kHz) | 140–225    | 63–90                | 4.6–10.1            |

The effect of working gas pressure on composition of carbon condensate was investigated. With increasing helium pressure, an increase in the content of higher fullerenes C₇₀ is observed. The use of plasma-chemical synthesis at atmospheric pressure and elevated pressure allows obtaining carbon condensate of different composition.

Figure 1. The dependence of the yield and composition of fullerenes from the pressure.

In our investigation, carbon soot is used as a carbon nanomodifier of building materials. The strength of cement stone is investigated in the work. [5] The article shows that the addition of CNM increases the strength of cement stone by 10–30%. The carbon nanomodifier affects the phase composition and hydration of the cement stone, which allows improving the properties of the final composite. A thermodynamic method was chosen to investigate the hydration of Portland cement. The thermodynamic method examines systems based on only one reference information on the thermochemical and thermodynamic properties of individual substances. The initial composition of the
system: Portland cement (mineral composition, table 2), water (H₂O), carbon nanomodifier (carbon C, fullerene C₆₀, fullerene C₇₀).

| Mineral            | Quantity (%) |
|--------------------|--------------|
| 3CaO·SiO₂          | 65           |
| 2CaO·SiO₂          | 13           |
| 3CaO·Al₂O₃         | 6            |
| 4CaO·Al₂O₃·Fe₂O₃   | 13           |
| MgO                | 1.06         |
| SO₃                | 2.57         |

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. Thermodynamic calculations were made the yield of phases Portlandite Ca(OH)₂ and calcium monosulfoaluminate 3CaO·Al₂O₃·CaSO₄·12H₂O [4], depending on quantity of CNM (figures 2 and 3).

The yield of phase Ca(OH)₂ increases, but calcium monosulfoaluminate yield decreases, with increase quantity of CNM. At the same time, the optimal quantity is minimum amount of the CNM additive, which is consistent with experimental results of investigation effect of the CNM on the strength of cement stone [5]. The effect of UNM has an extreme character and better effect when adding CNM in an amount of 10⁻²–10⁻³ wt. % [5].

Figure 2. Calculated phase yield Ca(OH)₂ from content of CNM in system «cement – H₂O-CNM».

Figure 3. The dependence of the yield and composition of fullerenes from the pressure.
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. 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 determine the yield of the phases of portlandite Ca(OH)$_2$ and calcium monosulfoalluminate 3CaO-Al$_2$O$_3$-CaSO$_4$-12H$_2$O from temperature and quantity of additives. 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.

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