Fullerene synthesis and modification of building materials with fullerenes $C_{60}$ and $C_{70}$

N N Smirnyagina¹, B O Tsyrenov¹ and L A Urkhanova²

¹Institute of Physical Materials Science SB RAS, 670047, Ulan-Ude, Russia

²East Siberia State University of Technology and Management, 670013, Ulan-Ude Russia

E-mail: bulatzsk@gmail.com

Abstract. The article presents the results of the study of plasma chemical synthesis fullerenes using composite electrodes and the results of thermodynamic modeling Portland cement hydration. Boron was used as the additive. Boron acts as a catalyst and increases the yield of higher fullerenes $C_{70}$ in plasma chemical synthesis. The carbon soot was used as a carbon nanomodifier. Carbon nanomodifier contains fullerenes $C_{60}$ and $C_{70}$. Thermodynamic calculations make it possible to evaluate the contribution of the carbon nanomodifier to the hydration process of Portland cement. Using thermodynamic calculations, changes in the phase composition and general properties of the system (complete enthalpy, entropy) were determined when introducing a carbon nanomodifier.

1. Introduction

Fullerene is an allotropic form of carbon, a molecular compound that is a convex closed polyhedra composed of three-coordinated carbon atoms. The most stable fullerene is $C_{60}$, the spherical hollow structure of which consists of 20 hexagons and 12 pentagons [1]. There are also higher fullerenes containing more than 60 atoms. ($C_{70}$, $C_{76}$, etc.). The most productive method for producing fullerenes is plasma chemical synthesis. This method makes it possible to obtain carbon condensate, which contains up to 10-15% of $C_{60}$ and $C_{70}$ fullerenes. The first method for obtaining fullerenes in macroscopic amounts was proposed by W. Krätschmer [2]. The method is based on evaporating graphite electrodes in an inert medium under reduced gas pressure. To date, fullerenes obtained by a plasma chemical method are obtained by this method or improved in various ways. Fullerenes have unique physical, chemical and optical properties and can be used in various fields of science and technology. Taking into account the prospects for the use of fullerenes, studies of the synthesis of fullerenes in the plasma chemical method are relevant.

Fullerenes $C_{60}$ and $C_{70}$ are included in the carbon nanomodifier (CNM), which can be used to modify building materials. CNM, containing carbon and carbon allotropic forms (fullerenes, nanotubes, fulleroid particles), make it possible to improve the properties of a cement composite at small amounts - 0.001 wt% - 0.1 wt%. The composites obtained have improved strength characteristics and increased frost resistance. The use of carbon nanomodifiers in the future will reduce the consumption of cement in the production of concrete of various classes. One of the explanations for the effect of using carbon nanomodifiers is the effect of nanomodifiers on the kinetics of cement stone hydration, changes in the phase composition, and changes in the heat release of the
cement paste during hydration. The change in thermophysical properties can be determined experimentally (for example, by the calorimetric method) and theoretically, by the method of thermodynamic modeling.

Thermodynamic modeling is a universal research method that is widely used in the creation of new composite materials and in the development of new efficient, resource- and energy-saving synthesis methods. The main task of thermodynamic modeling is to determine the phase and chemical composition of the system and the values of the thermodynamic properties of the system. The obtained data make it possible to evaluate the possibility of processes from the point of view of thermodynamics [3-5].

2. Experimental part

The synthesis of carbon nanomodifier was carried out in a plasma-chemical reactor (Figure 1) [7,8]. The graphite electrodes evaporate in a high-frequency electric arc, forming carbon vapor, which condenses on the walls of the water-cooled chamber. The arc frequency is 44 kHz.

![Figure 1. General view of the installation (plasma chemical reactor): 1 - camera for synthesis, 2 - nitrogen trap, 3 - rods, 4 - block matching with the load, 5 drive of the carbon condensation, 6 - stand, 7 - clamps 8 - blank, 9 - valve, 10 - valve control cold water supply.](image)

The study of carbon condensate was carried out using X-ray phase analysis. Thermodynamic modelling was carried out in the TERRA software package [6].

TERRA software package contains:

*TERRA.* The maximum number of chemical elements that can make up the system under study is 50; the number of condensed phases considered in a single calculation is limited to 200, and the number of components of the gas phase formed in equilibrium (the number of individual substances) can reach 800. When performing calculations for heterogeneous systems, it is possible to use a model of single-component immiscible phases and models of condensed solutions.

*INFO.* The INFO helper program is designed to serve the TERRA database. The INFO database contains the thermodynamic data of substances for calculating chemical and thermodynamic equilibrium of arbitrary multicomponent systems.

For thermodynamic calculations hydration of Portland cement in the database of the TERRA software complex (INFO program) were added:
- fullerences $C_{60}$ and $C_{70}$ [9],
- fullerene $C_{60}$ hydrides [10],
- thermodynamic properties of substances involved in the hydration process (more than 50 compounds, calcium hydrosilicates, hydroaluminates, etc.) [11-13].
In our research, we used Portland cement (PC) “Timlyuui Cement Plant” (Republic of Buryatia, Russian Federation). The initial chemical composition of Portland cement is shown in Table 1. Thermodynamic calculations were carried out in the range of 273-573 K, the amount of CNM was 0.001 wt%, 0.01 wt%, 0.1 wt%, and the amount of water was 30%.

Table 1. Initial composition of Portland cement (PC).

| Oxides   | Content wt % |
|----------|--------------|
| SiO₂     | 21.5         |
| Al₂O₃    | 4.92         |
| CaO      | 65.4         |
| Fe₂O₃    | 4.27         |
| MgO      | 1.06         |
| K₂O      | 0.2          |
| SO₃      | 2.57         |

3. Results and discussion
When studying the synthesis of fullerenes, we used composite graphite electrodes containing various additives (Figure 2). The synthesis of fullerenes was carried out in a high-frequency arc, between graphite electrodes, into the holes of which an additive in the form of a powder was pressed. B, Si, Ni (CO)n, Ni₃B were chosen as additives. The yield of higher C₇₀ fullerenes increases depending on the type of additive. The pressure in the water-cooled chamber is 0.1 MPa.

![Figure 2. The composition of carbon condensate from the type of additive in graphite rods.](image)

The most effective increase in the yield of higher fullerenes is observed when using electrodes when using electrodes with boron and silicon additives (Figure 2). The results of the study of carbon condensate at different amounts of boron and at an increased pressure of the buffer gas are shown in Table 2. With an increase in gas pressure and use of boron as an additive, an increase in the yield of
C\textsubscript{70} fullerenes is observed, while the content of the crystalline phase does not change (Table 2). Boron participates in the synthesis process as a catalyst and enhances the production of C\textsubscript{70} fullerenes.

**Table 2.** Composition of carbon condensate with different content of additional substance, pressure 0,4 MPa.

| Type of rode | X-ray diffraction analysis results |  |
|--------------|-----------------------------------|--|
|              | B                   | Crystalline phase | Nanotubes | Graphite 3R | C\textsubscript{60} | C\textsubscript{70} |
| Graphite electrode with boron amorphous, 2 wt % | 12 % | 19 % | 18 % | 7 % | 12 % | 52 % |
| Graphite electrode with boron amorphous, 4 wt % | - | 19 % | - | - | 20 % | 77 % |
| Graphite electrode with boron amorphous, 7 wt % | - | 20 % | 4 % | - | 18 % | 78 % |

*results returned a number to integer values, «-» - phase is absent or its content < 2 %

The obtained carbon condensate can be used as a carbon nanomodifier. Cement stone strength increases by 30% with the addition of CNM in a minimum amount of 0.01-0.001 wt%.

**Table 3.** Cement stone strength.

| Composition | Compressive strength, after 7 days of hardening | 28 days of hardening |
|-------------|-------------------------------------------------|----------------------|
| Control     | 40                                              | 61                   |
| CNM 0,01%   | 38                                              | 67                   |
| CNM 0,001%  | 44                                              | 82                   |

One explanation for the effect of using carbon nanomodifiers is the effect of nanomodifiers on the kinetics of cement stone hydration, changes in phase composition, and changes in the heat release of cement dough during hydration. Thermodynamic modelling in the TERRA software was used to study the effect of CNM on cement hydration. Thermodynamic calculations determined the general properties of the system (enthalpy, entropy, heat capacity) and changes in the phase composition of the system depending on temperature. Analysis of the dependence of properties at certain temperature ranges revealed sharp changes, which can be attributed to phase and chemical transformations associated with the formation of new or intermediate compounds. The increase in enthalpy and entropy when adding CNM to the cement-water system can be explained by the effect of CNM on the heat generation of cement paste. The study of exothermic reactions and thermal effects in the cement-water-CNM system makes it possible to evaluate the process of cement hydration in the presence of CNM.
Figure 3. Enthalpy in system Portland cement – water – carbon nanomodifier.

The degree of cement hydration can be determined in various ways by measuring the amount of Ca(OH)$_2$ in cement paste; heat generation during hydration; specific gravity of the dough; amounts of chemically bound water; amounts of non-hydrated cement (by X-ray analysis), as well as indirectly by the strength of cement stone [16]. Calculations performed in the program and experimental data [14,15] on the study of the properties of modified composites using a carbon nanomodifier make it possible to evaluate the efficiency of using fullerenes C$_{60}$ and C$_{70}$ as a modifying additive (Figure 4). According to thermodynamic calculations, when a carbon nanomodifier is added to the cement-water system, the yield of the Ca(OH)$_2$ phase changes depending on the amount of carbon nanomodifier in the system. The change in calcium hydroxide yield shows that the carbon nanomodifier acts as a retardant additive for setting cement paste. Setting is the transition of cement paste from a liquid state to a solid state. The effect of such additives is estimated by the amount of Ca(OH)$_2$ in the liquid phase of the hydrated cement. The net effect of the retarder additives is to increase the pH of the slurry phase [17].

Carbon nanomodifier affects the hydration and hydration kinetics of cement, depending on the amount of carbon nanomodifier. Modification of the cement stone contributes to the deepening of the hardening processes, starting from the first hours from the beginning of mixing. Modification of CNM leads to an increase in the duration of the induction period with a subsequent acceleration of strength gain. After the initial hardening period (7 days), the strength of the modified cement stone is formed at an increasing rate and by 28 days of hardening exceeds the strength of the control sample by 30%.
4. Conclusion

A study of the synthesis of fullerenes at atmospheric and elevated helium pressures using composite electrodes has been carried out. The use of additives increases the yield of higher C\textsubscript{70} fullerenes. Boron acts as a catalyst and increases the formation of higher fullerenes.

Thermodynamic calculations performed in the TERRA program made it possible to assess the effect of CNM on the hydration of Portland cement. The results of the calculations are successfully correlated with the experimental data and confirm the assumption that CNM has a positive effect on the strength of the cement stone due to various effects. Thermodynamic calculations made it possible to evaluate the contribution of CNM to the process of hydration of Portland cement and the effect of CNM on exothermic reactions in the cement-water system of UNM. Thermodynamic modeling can be successfully used to study the modification of cement composites with both carbon nanomodifiers and various additives that affect the properties of the final composite.

References

[1] David W I, Ibberson R M, Matthewman J C, Prassides K, Dennis T 1991 Crystal structure and bonding of ordered C\textsubscript{60}. Nature 353(6340) pp 147-149
[2] Krätschmer W, Lamb L D, Fostiropoulos K and Huffman D R 1990 Solid C\textsubscript{60}: a new form of carbon Nature 347(6291) pp 354-358
[3] Kulik D A, Wagner T, Dmytrieva S V, Kosakowski G, Hingerl F F, Chudnenko K V, and Berner U R 2013 GEM-Selektor geochemical modeling package: revised algorithm and GEMS3K numerical kernel for coupled simulation codes Computational Geosciences 17(1) pp 1-24
[4] Belov G V, Iorish V S, and Yungman V S 2000 Simulation of equilibrium states of thermodynamic systems using IVTANTERMO for Windows High Temperature 38(2) pp 191-196
[5] Trusov B G 2012 Code System for simulation of phase and chemical equilibriums at higher temperatures Engineering Journal: Science and Innovation 1
[6] Trusov B G 2002 Program system TERRA for simulation phase and thermal chemical
equilibrium. *Proc. XIV Intern. Symp. on Chemical Thermodynamics* pp 483-484

[7] Churilov G N 2000 Plasma synthesis of fullerenes (review) *Instruments and experimental techniques* **43**(1) pp 1-10

[8] Churilov G N, Korets A Y and Titarenko Y N 2016 Production of fullerenes and nanopipes in a carbon plasma jet at kilohertz frequencies *Journal of Technical Physics* **41** pp 102-103

[9] Diky V V and Kabo G J 2000 Thermodynamic properties of C_{60} and C_{70} fullerenes *Uspekhi Khimii* **69** (2) pp 107–117

[10] Karpushenkava L S and Kabo G Y 2008 The thermodynamic properties of fullerene hydrides C_{60}H_{2}. *Russian Journal of Physical Chemistry A* **82**(7) pp 1170-1174

[11] Lothenbach B, Kulik D A, Matschei T, Balonis M, Baquerizo L, Dilnesa B, Miron G D and Myers R J 2019 Cemdata18: A chemical thermodynamic database for hydrated Portland cements and alkali-activated materials. *Cement and Concrete Research* **115** pp 472-506

[12] Dilnesa B Z, Lothenbach B, Renaudin G, Wichser A, Kulik D 2014 Synthesis and characterization of hydrogarnet Ca_{3}(Al_{x}Fe_{1-x})_{2}(SiO_{4})_{y}(OH)_{4}(3-y) *Cement and Concrete Research* **59** pp 96-111

[13] Winnefeld F and Lothenbach B 2016 Phase equilibria in the system Ca_{4}Al_{6}O_{12}SO_{4}–Ca_{2}SiO_{4}–CaSO_{4}–H_{2}O referring to the hydration of calcium sulfoaluminate cements *RILEM Technical Letters* **1** pp 10-6

[14] Semenov A P, Smirnyagina N N, Urkhanova 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 Conference Series: Materials Science and Engineering* **168**(1) 012059

[15] Smirnyagina N N, Semenov A P, Tsyrenov B O, Dasheev D E, and Khaltarov Z M 2016 Plasma-chemical synthesis of carbon nanotubes and fullerenes to create frost-resistant composite building materials *International Congress on Energy Fluxes and Radiation Effects* pp 356-356

[16] Sobolev V I and Chernigovskaya T N 2020 Research into the dynamics of radio telescope foundations using laser vibration measuring equipment *Proceedings of Universities. Investment. Construction. Real estate* **10**(3) pp 420–427

[17] 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* **7**(106)

[18] Kozlova V K, Karpova Y V, and Volf, A V 2006 Evaluation effectiveness of additives that slow down the setting of cement dough *Polzunovskij vestnik* **2**