Reception carbon nanomodifiers in arc discharge plasma and their application for modifying of building materials

A P Semenov¹, N N Smirnyagina¹, L A Urkhanova², S V Kanakin³, S A Lkhasaranov², I A Semenova¹, B O Tsyrenov¹, D E Dasheev¹ and Z M Khaltarov¹

¹Institute of Physical Materials Science SB RAS, 670042, Ulan-Ude, Russia,
²East – Siberian state university of Technologies and Management, 670013, Ulan-Ude, Russia
³Geological Institute SB RAS, 670042, Ulan-Ude, Russia

E-mail smirnyagina09@mail.ru

Abstract. Carbon nanomaterials are perspective additives for modifying cement composites. In this work the influence of carbon nanomodifier (CNM) formed in plasma chemical reactor on phase composition, structure and properties of cement stone was investigated. Method of dispersion of nanoparticles has been used, which consists in sonication mixing water with carbon nanomodifier and super plasticizers (SP). Change in phase composition, structure and properties of modifying cement stone were investigated.

1. Introduction

Modification of cement by various nanomodifiers is promising because their introduction allows regulating the structure of the material directionally through the various effects [1].

Use of carbon nanostructures in the modification of the cement matrix is promising and has been investigated in many studies [2-5]. It is noted that they can be used not only as centers of crystallization, but also as objects, changing the direction and rate-controlling physical and mechanical processes in hardening systems. Due to their beneficial mechanical, electrical and chemical properties carbon nanotubes (CNTs) are an attractive candidate for reinforcement of composite materials.

The possibility of using fullerenes for modifying of cement systems studied to a lesser extent. In general researches are devoted to study the influence of fullerenes on the properties of mixing water [6].

Mechanism of additives containing fullerenes not disclosed enough full, so the aim of the research is to study the phase composition, structure and properties of ordinary Portland cement with the introduction of the carbon nanomodifier, which obtained in the [7].

2. Materials and methods

In current research were used Portland cement (OPC), LLC “Timlyuisky Cement Plant” (Republic of Buryatia, Russian Federation) CEM I 32.5N, superplasticizer SikaViscoCrete 5 neu®, superplasticizer C-3®. SikaViscoCrete 5 neu® - superplasticizing admixture on the basis of
polycarboxylates (Switzerland). Superplasticizer Polyplast C-3® (LLC "Poliplast-Uralsib", Russian Federation) is a synthetic compound based on polymeric naphthalene sulfonic acid.

The mechanical performance of modified cement stone was evaluated by compressive strength test. Samples of OPC 20*20*20 mm prepared with standard consistence, hardened under normal conditions at $t = 20 \pm 2 \, ^\circ C$ and a humidity of 100%, were tested by at the age of 7 and 28 days.

Synthesis of initial carbon nanomodifier carried out on the apparatus - a plasma-chemical reactor [7] (Figure 1). The basis of the system is based on the erosion of graphite electrodes in the arc discharge plasma [8]. The discharge is initiated at a pressure of $10^5$ Pa, by passing through the electrodes and current frequency 44 or 66 kHz. Erosion of rods occurs in closed sealed volume filled with helium.

![Figure 1](image_url) General view (plasma chemical reactor): 1 - camera for the synthesis 2-nitrogen trap, 3 - stocks, 4-block to meet the load, 5-carbon condensate storage device, 6-rack, 7-clips, 8-detent, 9-tap, 10 - the valve controlling the supply of cold water.

Apparatus contains a water-cooled chamber 1, in which there is synthesis of plasma.Towards the bottom and top of the chamber through the flanges mounted nitrogen traps 2. Within the camera body provided with an inspection windows for visual observation. Camera cover is removable. Towards the bottom of the camera connected removable stocks 3 with the system providing their movement as the combustion system of rods and to meet the load 4. Synthesized carbon condensate is collected from the chamber walls in the store 5. Camera is located on the rack 6. Electric power is carried out from voltage generator, with a rated capacity of 16 kW. Maximum current of erosion of graphite rods is 160 A. The average time of synthesis is 10 min.Carbon condensate containing 10-12 mass % fullerenes (80 % - $C_{60}$; 15 % - $C_{70}$ and oxides $C_{60}O$).

For uniform distribution of CNM in water is used ultrasonic machine having the following characteristics: operating frequency of 43-45 kHz, power 30 W.

Indicators of conductivity and pH of modified water were determined on the instruments - conduct meter «HM Digital Aquapro», pH-meter «Pen type pH-009».

X-ray diffraction analysis was carried out on a diffractometer Bruker Phaser D2 using Cu $K_{\alpha 1}$ radiation.

Microstructure of cement stone was studied by scanning electron microscope LEO-1430VP (Carl Zeiss, Germany) with energy dispersive microanalysis system INCA Energy 350 (Oxford Instruments, UK).
3. Results and discussion

Introduction of CNM changes rheological properties and setting time of cement paste (table 1).

| Indicators             | Unit | without additives | CNM 0.01% | CNM 0.001% |
|------------------------|------|-------------------|-----------|------------|
| Standard consistence   | %    | 25                | 26        | 25.5       |
| Initial setting        | min  | 145               | 160       | 150        |
| Final setting          | min  | 245               | 250       | 255        |
| Slump flow             | mm   | 135               | 140       | 135        |
| Slump flow through hours: | mm |             |           |            |
| 0,5                    |      | 135               | 140       | 135        |
| 1                      |      | 135               | 140       | 135        |
| 2                      |      | 130               | 140       | 135        |
| 3                      |      | 115               | 135       | 130        |
| 4                      |      | 110               | 135       | 130        |

It is found that in cement with CNM at various concentrations is lengthened setting time (initial set - up to 5%, final set - up to 22%). Simultaneously, slump flow of cement mortar is increased and retained through some hours, which is important, for example in long transportation of the concrete mix based on the modified cement. Obviously, the change of setting time and slump flow of cement pastes and mortars is associated with the change in the properties of mixing water.

Introduction of CNM contributes to creation around particles the hydration shells, which are oriented and contributed to changing the rheological properties of cement pastes and mortars.

The greatest effect of the introduction of carbon nanomaterials is achieved while providing their uniform distribution in the composite structure.

| Composition          | Compressive strength, Mpa after 7 daysofhardening | Compressive strength, Mpa after 28daysofhardening |
|----------------------|--------------------------------------------------|--------------------------------------------------|
| Control              | 40                                               | 61                                               |
| CNM 0.01%            | 38                                               | 67                                               |
| CNM 0.001%           | 44                                               | 82                                               |
| C-3® 0.7%            | 47                                               | 50                                               |
| C-3® 0.7% + CNM 0.01%| 42                                               | 67                                               |
| C-3® 0.7% + CNM 0.001%| 58                                           | 74                                               |
| SikaViscoCrete 5 neu®0.3% | 43                                           | 63                                               |
| SikaViscoCrete 5 neu® 0.3% + CNM 0.01% | 42                                           | 69                                               |
| SikaViscoCrete 5 neu® 0.3% + CNM 0.001% | 40                                           | 68                                               |

In work for the uniform distribution of the agglomerates in the mixing water CNM was used an ultrasonic method which is based on the use of cavitation. To increase the effect of distribution CNM in mixing water were introduced surfactants with different chemical compositions, which are traditionally used to modify Portland cement. We are determined the optimal time of water treatment with CNM.
Figure 2. X-ray diffraction patterns of cement samples after hydration: a) control; b) 0.001 mass % CNM; c) 0.001 mass % CNM with C-3®.
Introduction of CNM in the cement leads to a change in the physical and mechanical characteristics. Table 2 shows the strength characteristics of the cement to CNM at age 7 days and 28 days of hardening.

Analysis of the results showed that the introduction of carbon nanomodifier in an amount of 0.01 mass % increases strength by 25-35%. Introduction in an amount of 0.001 mass % jointly with C-3® increases strength by 20-25%.

Changing the properties with introduction of CNM associated with changes in the phase composition and structure of modified cement stone.

According to X-ray diffraction analysis, the original Portland cement includes traditional phase characteristic of OPC: calcium silicates Ca$_3$SiO$_5$ and Ca$_2$SiO$_4$, calcium aluminates Ca$_2$(FeAl$_{0.9}$Mg$_{0.1}$)O$_5$ and Ca$_3$Al$_2$O$_6$, and calcium sulfate CaSO$_4$.2H$_2$O (Figure 2). In hydrated cement decreased intensity of peaks of the original cement phases, appear peaks attributable to Ca(OH)$_2$ and calcium hydrosulfoaluminate in low-sulfate form Ca$_3$Al$_2$O$_6$(SO$_4$)$_4$14H$_2$O (d=0.4729 nm) with expressive

---

**Figure 3.** SEM patterns: a – hydrated OPC, 7 days; b – OPC+0.01% CNM, 3 days; c – OPC+0.01% CNM, 7 days.
intensity of peak (Figure 2 a). Introduction of CNM into the cement causes a change in the hydrated samples of distance from \(d = 0.4682\) nm to \(d = 0.4833\) nm (Figure 2 b).

Contents of aluminates \(\text{Ca}_2(\text{FeAl}_{0.9}\text{Mg}_{0.1})\text{O}_5\) and \(\text{Ca}_3\text{Al}_2\text{O}_6\) is reduced, which is testified to intensive hydration of these phases, especially in the presence of CNM. For example, for phase \(\text{Ca}_3\text{Al}_2\text{O}_6\) (PDF 00-006-0495 ICCD) a decrease in intensity of the reflection is \(a_{100} = 0.2700\) nm. Furthermore, the introduction of CNM into hydrated cement leads to change in samples of distance from \(d = 0.2561\) nm to \(d = 0.2604\) nm for this plane. This variation in the \(d_{hkl}\) distances can be explained in terms of the degree of crystalline of hydrated cement samples. So in the control sample cement a content of the amorphous phase reaches 46% and the addition of fullerenes leads to an increase in crystalline up to 63%, which indicates an increase the degree of hydration of PCs in the initial period of hardening.

Introduction of CNM changes not only phase composition of hydrated cement but also the microstructure of cement stone. Figure 3 shows the surface of hydrated cement structure with CNM hardened for 3, 7 and 28 days.

Introduction of CNM reduces porosity of cement stone due to formation of gelatinous hydration products filling interporous space. It should be noted that an increase in hardening time from 3 to 7 days leads to a substantial reduction in porosity of the hydrated stone and reducing crystallite size (Figure 3 b, c). All of this favorable effect on the changes in physical and mechanical properties of modified cement stone.

4. Conclusions
Comparison of superplasticizers of various natures suggests that both superplasticizers ensure a uniform distribution of CNM in the volume of mixing water. However, evaluating the physic-mechanical properties of the modified cement stone it can be say that the superplasticizer \(\text{C-3}\) is the most effective. Increasing of strength when it is used up to 25-35% compared with the control. Use of SikaViscoCreteneu ® is less effective (5-15%). This is due to the mechanism of action of this admixture, and enveloping and preventing interaction of the particles of CNM with cement grains. With the introduction of CNM in a cement matrix, there is a change of the phase composition, structure and physic-mechanical properties of the cement stone. This is due to the complex action of carbon nanomodifier. It changes structure of mixing water, creating around their directionally oriented particles of hydrated shells that lead to changes in the rheological characteristics of the cement paste. Furthermore, particles of carbon nanomodifier act as nucleation sites of hydration products of cement, which accelerates the hydration and hardening process of the cement, especially in the initial period of hardening. With introduction of CNM is reduced porosity of cement paste, which leads to high strength characteristics of modified cement.

Acknowledgements
This work was supported by the Russian Academy of Sciences (Artica, project №84).

References
[1] Artamonova O V, Sergutkina O R 2013 Bulletin the Voronezh State University of Architecture and Construction 13-23
[2] Lukutcova N P, Pykin A A, Karpikov E G 2011 Building Materials 9 66-67
[3] Konsta-Gdoutos M S, Metaxa Z S, Shah S P 2010 Cem. Concr. Res. 40 10 52-59
[4] Cwirzen A, Habermehl-Cwirzen K, PenttalaV 2008 Adv. Cem. Res. 20 (2) 65 -73
[5] Li G Y, Wang P M, Zhao X. 2005 Carbon 43 (6) 12 39-45
[6] Nasibulina L I, Anoshkin I V, Nasibulin A G, Cwirzen A, Penttala V, and KauppinenE I 2012 Journal of Nanomaterials 1-6
[7] ChurilovGN. Patent RU2320536 2007 BI number 20
[8] Churilov G N, Bulina N V, Fedorov A S 2007Fullerenes: synthesis and theory of formation(Novosibirsk: Publishing House of Russian Academy of Sciences) 227