Influence of Carbon Nanotubes on the Structure Formation of Cement Matrix

S Petrunin¹, ³, V Vaganov², V Reshetniak² and L Zakrevskaya²
¹Limited Liability Company “Macromer”, Vladimir, Russia
²Vladimir State University, Vladimir, Russia
E-mail: ser-petrue@yandex.ru

Abstract. The potential of application of CNTs as a reinforcing agent in cement composites is governed by their unique mechanical and electronic properties. The analysis of concrete strength changes under CNTs introduction shows non-uniformity and sometimes inconsistency of results. Due to the fact that CNTs influence the hydration kinetics, structure and phase composition of concrete, an idea concerning the importance of interaction between the surface of CNTs and hydrate ions formed by the dissolution of the clinker phases has been suggested. In this paper, the theoretical and experimental study of interaction between hydrate ions and CNTs surface is discussed. Reference nanotubes and nanotubes functionalized by carboxylic groups are used in this research. Phase composition was determined by X-Ray analysis according to the Rietveld method. It was found that the presence of oxygen-containing functional groups on CNTs surface leads to intensification of the hydration process and increase in concentration of C-S-H gel from 65.9% to 74.4%. Special attention is usually paid to interactions between Ca²⁺ ions and CNTs, because the hardening rate and structure of cement stone are determined by principle of Ca²⁺ localization in the solution. In this paper the possible binding mechanisms are discussed. Based on the experimental results, the hypothesis regarding the formation of cement composite structure for different CNTs surface functionalizations is considered. According to this hypothesis, the CNTs act as the centers of crystallization for hydration products contributing to the acceleration of hydration, increase of the concentration of C-S-H gel and strength improvement of CNTs based composites.

1. Introduction

Carbon nanotubes (CNTs) were considered as a promising filler for Portland cement composites by multiple authors [1-3]. Modification of concrete matrix by CNTs can increase the strength characteristics from 25% to 250%. The significant experimental scatter of mechanical properties may indicate high potential for technological optimization. Nevertheless, due to misunderstanding of the
strengthening mechanism, the problem is still unresolved. Properties of cement composites depend on surface chemistry of CNTs. Modification of cement system with functionalized CNTs contributes to a substantial increase in concrete strength compared with pure CNTs. Microstructural investigation demonstrated the existence of functionalized CNTs covered with hydration products, whereas hydration products on the surface of pure CNTs are absent. Functionalized CNTs can interact with hydration products of cement, leading to a decrease in porosity and, as a result, to an increase in composite strength. CNTs influence the hydration kinetics, structure and phase composition of concrete that is why an idea concerning the importance of interaction between the surface of CNTs and hydrate ions formed by the dissolution of the clinker phases has been suggested.

Special attention is usually paid to interactions between Ca$^{2+}$ ions and CNTs, because the hardening rate and structure of cement stone are determined by principle of Ca$^{2+}$ localization in the solution. As it is known [4], the interaction between Ca$^{2+}$ ions and aromatic hydrocarbons is usually realized by polarization mechanism. Due to its high dielectric constant, water makes such interactions much weaker, thus the influence of interaction on the ion distribution should not be strong [4, 5]. On the other hand, as multi-walled CNTs chemically and by the electron structure are much closer to graphene than to aromatic hydrocarbon [6, 7], the differences in the interaction mechanisms (between Ca$^{2+}$ ions and multi-walled CNTs and Ca$^{2+}$ ions and aromatic hydrocarbons) can be expected. That is the reason why the interaction between Ca$^{2+}$ ions and graphene surface is considered in the paper. The interaction was studied theoretically on the DFT GGA level using the plane wave method, which is realized in the Quantum Espresso program [8]. Calculations showed formation of the metallic type bonds between Ca$^{2+}$ ions and graphene sheet, with the binding energy 0.75 eV.

2. Experimental program

2.1. Materials
Portland cement CEM I 42.5B supplied by JSC “Mordovcement,” standard quartz sand with a fineness modulus of 1.5 and multi-walled carbon nanotubes produced by CVD technology at Vladimir State University (Russia) were used in this research. The CNTs’ concentration in the composite was 0.05% of the cement mass. Polycarboxylate (PCE) superplasticizer P-11 supplied by JSC “Macromer” was used to reduce the sedimentation and facilitate the dispersion of CNTs in water.

2.2. Preparation of concrete samples
All cement composites had the component ratio of 0.3:1:1 for water, cement, and sand, respectively. The CNTs were mixed with water and the polycarboxylate superplasticizer and sonicated at 20 kHz using the ultrasound processor (IL100-6/1-1) at maximal power (700 W) for 60 minutes. Cement and sand were added into a planetary mixer. Then the required amount of water with superplasticizer and carbon nanotubes was added into the mixer. The entire mixture was stirred for 7 minutes. After this procedure, the composite mixture was placed into the metal molds with dimensions of 40×40×160 mm and compacted by vibration. The composite specimens were demolded after 24 hours of initial hardening and were stored in lime water until the testing age.

2.3. CNTs functionalization
CNTs functionalization by oxygen groups was carried out to improve the hydrophilic properties and the interaction between the surface of CNTs and the material matrix. The functionalization was carried out as follows: CNTs were placed in a flask and backed up with the mix of concentrated HNO$_3$ and...
H$_2$SO$_4$ at a ratio of one-to-five. The mix was heated to 70°C at continuous hashing for 3 hours. During this process, the nickel catalyst particles left from the synthesis were oxidized with gas liberation. The solution was then cooled, diluted with distilled water and filtered. The filtered CNTs were washed out and dried. The assessment of functionalized groups occurring on the CNTs surface was made with the help of infrared spectroscopy.

Coagulation resistance of CNT dispersions depends on the character of charge distribution on nanotubes surface formed by the absorption of ions from the solution and the dissociation of the CNTs surface. Inoculating of oxygen-containing groups promotes the redistribution of surface charges and improves the hydrophilic properties of CNTs.

2.4. Research methods

The phase composition was defined on the Brucker D8 Advance diffractometer using the Rietveld method.

The supercell of the graphene with 50 carbon atoms (5x5 unit cells) was considered. In the cell one Ca$^{2+}$ ion was inserted (figure 1). To reduce the effect of the interaction between neighbour graphene sheets, the length of the orthogonal to the graphene sheet translation vector was applied equal to 4 nm. Calculations showed that the change of the cell energy due to increase of the vector length is not sufficient.

![Figure 1. The structure of the supercell of the Ca$^{2+}$-graphene complex.](image)

The calculation of the electron wave functions was performed using plane wave basis set and periodic boundary conditions on the cell boundaries. The Quantum Espresso program [8] and DFT method were used. The PBESol exchange-correlation functional [9], and relativistic Hartwigsen-Goedecker-Hutter pseudopotentials [10] were applied. The 9x9 Monkhorst-Pack k-point grid [11] was used.
3. Results and discussion

3.1. The X-ray analysis of hydrates
The changes of C-S-H due to the introduction of CNTs are identified. The resulting changes in phase composition of composites are demonstrated in table 1. The increase in the amorphous phase corresponds to the increase of cement hydration, promoting acceleration of hydration and an increase in the strength of a material.

| Minerals   | Reference | CNTs | Functionalized CNTs |
|------------|-----------|------|---------------------|
| C₃S        | 8.9 %     | 8.1 %| 6.5 %               |
| C₂S        | 4.4 %     | 4.1 %| 3.7 %               |
| C₄AF       | 3.2 %     | 2.8 %| 2.6 %               |
| Ca(OH)₂    | 9.2 %     | 7.3 %| 7.7 %               |
| CaCO₃      | 6.7 %     | 5.6 %| 4.9 %               |
| Ettringite  | 0.3 %     | 0.3 %| 0.2 %               |
| C-S-H      | 65.9 %    | 71.9 %| 74.4 %             |

The amorphous phase in the reference specimen is 65.9%. The increase of the amorphous phase to 74.4% was recorded for the composite with the functionalized CNTs. The character of the amorphous phase development corresponds to a tendency of compressive change at the age of 1 day. The composite with functionalized CNTs contains the greatest volume of C-S-H gel and possesses higher strength, whereas composites modified by pure CNTs have lower C-S-H gel concentration and weaker strength characteristics.

3.2. DFT calculation
The relaxation shows that there is a local energy minimum corresponding to the structure with Ca²⁺ position on the symmetry axis of the hexagon formed by the carbon atoms. The distances between Ca²⁺ ion and 6 closes neighbour C atoms are equal to 0.259 nm. The Löwdin population analysis shows charge transfer between Ca²⁺ ion and C atoms: the charge of the Ca ion due to the interaction became equal to +1.33e. Due to the interaction, the 3d orbital of the Ca ion becomes partially occupied and overlaps with the π-orbital of the graphene, which is formed by the 2p orbitals of the neighbour C atoms. The occupancy of the 3d orbital of the Ca ion is equal to 0.4. The hybridization of the electronic shells leads to the binding between Ca ion and graphene sheet by the exchange mechanism.

The map of the charge density distribution in the Ca²⁺ - graphene complex is shown in figure 2. The positive values of the charge density corresponds to the electron density and the negative values – to the hole density. In figure 2a the electron density map in the orthogonal to graphene sheet plane is shown (the light bar at the bottom of the figure corresponds to the carbon atoms of the graphene sheet, the bright spot in the centre – Ca ion). In figure 2b the charge density in the same plane is represented. The charge density was calculated by the subtraction of the electron density of the separate fragments (Ca²⁺ and graphene) from the electron density of the complex. In figure 2c the charge density map in the plane, parallel to the graphene sheet and equidistant to the both Ca ion and graphene plane is shown. It is seen that there is charge transfer between the Ca ion and C atoms, there is hybridisation of the electron shells, and that the formed bonds are nonlocal.
The charge density distribution in the orthogonal (a, b) and the parallel (c) planes. 

- a – electron density for all electrons, considered in the calculations;
- b, c – charge density: the residual of the electron density of the complex and the separate fragments (Ca$^{2+}$ and graphene).

Due to charge transfer, the C atoms became positively charged, and there is Coulomb repulsion between Ca ion and graphene sheet, which is competing with the metallic binding. Due to the transportability of the electrons in the graphene, the charge distribution in the sheet is uniform. It should be noted that the effect may lead to the dependence of the binding energy on the Ca ions concentration.

To calculate the binding energy between Ca ion and graphene, the potential energy scan was performed. The distance between the Ca and graphene plane was changed in the range from 0.19 nm to 0.51 nm. The calculations showed the nonmonotonic character of potential curve, which is shown in figure 3. There is a local maximum of the energy, which corresponds to the distance between Ca and graphene 0.35 nm. The energy in the point of the local maximum was set to be zero. The maximum appears due to the charge redistribution between fragments and the competing between Coulomb repulsion and metallic binding. Further increase of the distance decreases electron shells hybridisation and leads to the formation of the Ca$^{+}$ ion and charged graphene sheet.

As contrasted with the Coulomb interaction, which is vastly going down due to solvation with the solvent with high dielectric constant, the metallic bond is less susceptible to the solvation and may impact structure formation in the concrete significantly.
3.3. **Hypothesis related to composite structure formation**

In the process of cement hydration, the OH-, Ca$^{2+}$, CaOH- and H$_2$SiO$_4$$^{2-}$ ions are deposited on the surface of the cement grains and form a layer consisting of C-S-H gel with embedded Ca(OH)$_2$ crystals. With time, the thickness of this layer increases and its ionic permeability decreases. The formation of C-S-H gel and Ca(OH)$_2$ takes place when Ca$^{2+}$ concentration exceeds the saturation limit by factor of 1.5–2.

The intensification of hydration in the system with CNTs is due to an additional sorption of Ca$^{2+}$ ions on the surface of the CNTs. In this case, the hydration is accelerated, since the formation of C-S-H and Ca(OH)$_2$ crystals occurs in the zones supersaturated by Ca$^{2+}$ ions. The fragmentary formation of hydration products on the CNTs surfaces contributes to the improvement of ion exchange between the solid and liquid phases and results in acceleration of new phase formation. The presence of oxygen-containing groups on the surfaces of the CNTs leads to a more active sorption of Ca$^{2+}$ ions and higher rates of hardening when functionalized CNTs are used. According to this hypothesis, the CNTs act as the centers of crystallization for hydration products contributing to the acceleration of hydration, increase of the concentration of C-S-H gel and strength improvement of CNTs based composites.

4. **Conclusions**

Quantum chemical modeling showed formation of the metallic type bonds between Ca$^{2+}$ ions and graphene sheet, with the binding energy 0.75 eV. The metallic bond is less susceptible to the solvation and may impact structure formation in the concrete significantly. The presence of oxygen-containing functional groups on CNTs surface leads to intensification of the hydration process and increase in concentration of C-S-H gel from 65.9% to 74.4%. Based on the experimental results, the hypothesis of formation of cement composite structure for CNTs is described. According to this hypothesis, the CNTs act as the centers of crystallization for hydration products contributing to the acceleration of hydration, increase of the concentration of C-S-H gel and strength improvement of CNTs based composites.

5. **References**

[1] Sanchez F and Sobolev K 2010 Nanotechnology in concrete – a review Construction and Building Materials 24 2060–71
[2] Konsta-Gdoutos M S, Metaxa Z S and Shah S P 2010 Multi-scale mechanical and fracture characteristics and early-age strain capacity of high performance carbon nanotube/cement nanocomposites Cement and Concrete Composite 32 110–115
[3] Li G Y, Wang P M and Zhao X 2005 Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes Carbon 43 1239–45
[4] Harder S 2010 Chem. Rev. – 2010 – 110, No 7 p 3852
[5] Ma J C and Dougherty D A 1997 Chem. Rev. – 1997 – 97, No 5 p 1303
[6] Bhupesh Ch 2009 Synthesis and Electron Transport in Known Chirality Single Wall Carbon Nanotubes Ph. D. Thesis, Columbia university
[7] Nizam R, Rizvi S M A and Azam A 2011 Int. J. of Science and Technology 4 153
[8] Giannozzi P, Baroni S et al 2009 J. Phys. Condens. Matter. 39 395502
[9] Perdew J P, Ruzsinszky A, Csonka G I et al 2008 Phys. Rev. Lett. 100 136406-1:4
[10] Hartwigsen C, Goedecker S and Hutter J 1998 Phys. Rev. B. 58 3641
[11] Monkhorst H J and Pack J D 1976 Phys. Rev. B. 13 5188