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Effect of graphene nano-sheets on the chloride penetration and microstructure of the cement based composite

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HIGHLIGHTS

- GNS suspensions were prepared with the help of CO890 and ultrasonic.
- GNS improve the microstructure of cement paste.
- GNS addition in cement paste decrease chloride penetration significantly.
- The mechanism of GNS in GNS/CC has been put forward.

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ABSTRACT

In this work, the effects of the non covalent surface modification method on the dispersion of graphene nano-sheets (GNS) in water and chloride diffusion of the cement paste incorporating these dispersions were investigated. Results showed that stable and homogeneous suspensions of graphene nano-sheets were prepared using polyoxyethylene (40) nonylphenylether (CO890) as a dispersant. In this research, water to cement ration is kept 0.30, the addition of GNS is ranging from 0.02% to 0.15% by weight of cement. It is found that introduction small quantities of GNS as little as 0.02% can decrease the chloride penetration depth and coefficient by as much as ~37% and ~42%, respectively. This improvement could be attributed to the enhanced degree of cement hydration, filling effect, barrier effect and crack-arresting effect of GNS in cement matrix. This work provides a new way to further understand the improvement of GNS in cement composites.

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1. Introduction

Cement-based composites are the most widely used construction material because of their abundant raw materials, low cost, high environmental adaptation and well document properties for design and construction [1]. They are favored in many fields including pavement, building and bridge. Cement-based composites used in pavement and bridge often exposed to a harsh environment because of the exposure in air or salt water or freezing and thawing [2]. The durability of cement-based composites is a key to the service life of concrete structure in hash environment, which has received more attention from researchers [3]. The durability properties of cement-based material include many aspects such as permeability, carbonization, abrasion resistance and frost resistance [4].

Permeability is defined as one of the most important factors influencing the deterioration of cement-based composites [5]. A low permeability reduces the ingress of external media (such as liquids, gases and various aggressive ions) in cement-based composites and thus is beneficial. Cement-based composites are a kind of heterogeneous and porous material. It is known that the pore structure and its distribution are the most important properties of cement-based composites and strongly affect its durability and mechanical properties [6]. So, the development and change of pores structure will affect the durability of cement-based material. Many studies showed that permeability of cement-based material rely mostly on pores of different sizes and shapes [7,8].

Many studies proved that the addition of PP fibers, mineral admixture and nano-materials decreases the permeability of cement-based material [9–11]. In recent years, nano-materials have been applied in civil engineering because of their small size, high specific surface and activity [12]. Graphene nano-sheets (GNS) are a kind of novel two-dimensional carbon nano-material by sp^2 hybridized orbit [13]. The excellent properties of GNS show

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Table 1
Chemical composition of P·O 42.5R cement.

Composition	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	Na_2O	Loss on ignition
Content (%)	61.13	21.45	5.24	2.8	2.5	2.08	0.77	3.5

Table 2
The physical properties of GNS.

Products	Density/g/cm^3	Purity/%	Electrical Conductivity/s/m		Tensile modulus/GPa	Special Surface Area/ m^2·g^{-1}
			Parallel	Perpendicular		
XGnP-M25	2.2	> 99.5	10^7	10^2	1000	120–150

Table 3
The chemical element of GNS analysis of GNS measured by XPS.

Chemical Element in GNS	C (%)	O (%)
GNS	94.83	5.16
Decorated GNS	93.22	6.78

great applications potential in many areas, such as electronics, optics, magnetic, biology, catalysis, sensors, energy storage and composites [14–16]. There are several reports about the reinforcing effects of GNS on cement composites. Pan et al. [17] demonstrated that the introduction of graphene oxide (GO) in cement paste increased the compressive strength and flexural strength by 15–33% and 41–59%. Lu et al. [18] indicated that 0.05 wt% GO in the magnesium potassium phosphate cement paste could also improve its mechanical properties. The durability of cement-based composites could be improved by GNS addition as well. Mohammed et al. [19] reported that the incorporation of GO can significantly improve the resistance to chloride ion and sorptivity of cement mortar. Du et al. [20] showed that the addition of 1.5% GNS into concrete reduced the water penetration depth, chloride diffusion, and migration coefficients by 80%, 80%, 37%, respectively. And Tong et al. [21] found that the use of GNS and GOs in mortar specimen could improve the frost resistance and the influence varied with the sizes of GNS and GOS.

In this study, homogeneous suspensions of GNS were obtained by the polyoxyethylene (40) nonylphenylether (Igepal, CO890) decoration. The surfactant CO890 is white solid polymer with average molecular-weight of 1982. It is water soluble and there are hydrophilic group (—OH) and hydrophobic group (—CH_3) on the surface of it. The thickness and lateral size distribution of GNS in aqueous solution were study. The chloride diffusion of cement-based composites doped with GNS was investigated. And the influence of GNS on the micro-structure of cement-based composites was also characterized. In the end, the mechanism of GNS in cement based was put up and analyzed.

2. Materials

P.O 42.5 R (Ordinary Portland Cement according to Chinese standards) cement was obtained from Dalian Onoda Co., Ltd. (Dalian, China) for the preparation of cement specimens, whose chemical composition is shown in Table 1. GNS were provided by XG science, Inc. (Lansing, MI, USA), and the physical properties and their chemical elements are presented in Tables 2 and 3, respectively. CO890 as a dispersant was purchased from Sigma-Aldrich, Co. (St. Louis, MO, USA) and the properties of it are shown in Table 4. The super-plasticizer (SP) was provided by Dalian Mingyuanquan Group Co., Ltd. (Dalian China). In order to eliminate bubbles caused by CO890 during the process of ultrasonic, the defoamer tributyl phosphate (TBP) is needed, which was supplied by Tianjin Chemical Reagent Plant (Tianjin, China).

3. Experiments

3.1. Preparation of GNS/CC

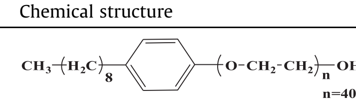
According to our previous research, GNS were dispersed in aqueous solution by applying ultrasonic energy with the chosen surfactant (CO890) and the optimum proportion of CO890 to GNS is 5:1 [22]. The homogenous GNS suspension was gained after ultrasonic processing (FS-600N, 360W) for 30 min. The prepared GNS suspension was used to GNS/CC preparing.

In this study, five batches of cement paste mixtures were prepared, which including a reference cement paste and four batches of mixes with 0.02, 0.05, 0.10 and 0.15 wt% GNS. The dosage of GNS was the mass percent of cement and the water to cement ration was kept 0.3. The mix proportions of these samples are shown in Table 5. The mixing procedure is illustrated in Fig. 1. After being mixed, the fresh cement paste was poured into the stainless mold (∅100 mm × 100 mm) and compacted on a vibration table. There are three specimens in each batch. Finally, the surface of these specimens were covered with a plastic sheet and cured in a standard box (RH ≥ 90%, T: 20 ± 2 °C). After 24 ± 2 h standard curing, all specimens were demoulded and cured in standard water until testing.

3.2. Test methods

Chloride diffusions of GNS/CC were measured by rapid chloride migration coefficient method (RCM) according to Chinese Standard [23]. RCM-NTB (Beijing NELD, China) was supplied to test the depth of chloride migration in cement paste, as is shown in

Table 4
Properties of CO890.

Products	Average molecular-weigh	Appearance	Chemical structure
CO890	1982	White solid	

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