Effect of graphenene nanoplatelets on microstructure and properties of cement mortar under simulated acid rain

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Abstract. The mortar loses strength under acid rain conditions, causing cracking, weight loss and damage to the structure. This paper studies the effects of graphenene nanoplatelets(GNP) mortar under simulated acid rain conditions. A control sample without GNP and the addition of GNP were ranging from 0.2% to 0.6% by weight of ordinary Portland cement were prepared. In different corrosion days, the mechanical properties of the GNP cement mortar were measured, scanning electron microscopy also applied. Results showed that the mechanical properties of cement mortar added with graphene are improved. Compared with the control sample, the compressive strength and flexural strength of specimens containing 0.2wt% GNP are increased by 10% and 8%, respectively. Adding GNP can improve the acid resistance and durability of cement mortar.

1. Introduction

Acid rain is a global environmental problem today. Cement-based materials under acid rain erosion C-S-H and other hydration products are prone to decomposition or expansion, resulting in a significant reduction or even loss of structural mechanical properties. In particular, steel bars in cement-based materials can easily lose protection and accelerate corrosion, resulting in a great attenuation of structural bearing capacity [1]. The Yangtze River and the region of Taiwan are the strongest caid rain precipitation in China [2-3]. One of the key scientific issues in the study of the durability of cement-based materials in acid rain environments is the using of which evaluation method to rationally quantify the degree of acid rain erosion. Xie et al. [4] simulated the deterioration of cement concrete in acid rain condition. Neutralized depth, strength and chemical composition were measured. The results showed that Ca(OH)₂ in hardened cement paste was dissolved by H⁺ in acid rain. Sheng yuan et al. [5] showed that when pH value of immersion solution was 2.50, the erosion depth was maximum.

Nanotechnology is a new approach to a variety of knowledge and technology areas. In recent years, nanotechnology has formed a new perspective in concrete technology. Some studies found adding nanomaterials could improve the durability of concrete materials. As an emerging nanomaterial, graphene could also be added to concrete to improve the sustainability of the building due to its excellent properties. Hunain et al. [6] used molecular dynamics to simulate the interfacial strength of graphene sheets extracted from C-S-H gels, undisturbed graphene sheets and graphene sheets with hydroxyl, nitro and carboxyl functional groups alone. Mohammed[7] shows that graphene oxide(GO) has a better effect on the pore structure and can effectively improve the impermeability and corrosion resistance of cement-based composites. Lv et al [8] and Cao Mingli [9] incorporated modified graphene into cement and found that it promoted the formation of cement hydrated crystal products and template effect, thereby improving the strength and toughness of cement-based materials.
Abrishami et al. [10] used NH$_2$ as a surfactant for GO, and activated GO could better enhance the strength of cement-based composites compared to unactivated GO. Alkhateb et al. [11] studied the Young's modulus and shear modulus of graphene reinforced cement paste and show graphene with a mass fraction of 0.5% not only significantly improved the graphene-cement matrix composite early (7d) Mechanical properties, the Young's and shear modulus are also increased by about 6.4% and 21.01% compared with pure cement paste. Lu Shenghua et al [12] added GO with a mass fraction of 0.015% in cement mortar and found that the compressive strength and flexural strength of the composite increased by 27.9% and 64.6%. Horszczaruk E [13] found that the addition of GO in cement mortar can greatly improve the elastic modulus of cement-based materials. However, it has limit study to research the effect of GNP on the performance of cement mortar under acid rain.

This paper studied the effect of GNP on mortar performance under simulated acid rain. Cement mortar mixtures containing 0%, 0.2%, 0.4% and 6% GNP, which the weight loss, compressive strength and flexural strength were conducted. Moreover, the influence of GNP on the microstructure with SME was characterized.

2. Experimental program

2.1 Material and Specimen preparation

P.O 32.5 R (Ordinary Portland Cement according to Chinese standards) cement was obtained from Weihai Shanshui Cement Co., Ltd. (Weihai, China) for the preparation of cement samples. The chemical composition and technical indicators are shown in Table 1 and Table 2, respectively. Fine aggregate: sand is China ISO standard sand (Xiamen Ai Siou standard sand), composed of coarse sand, medium sand and fine sand. Naphthalene water reducing agent (Water reduction rate of 18% to 20%). GNP is the graphene conductive and thermal conductive paste produced by Weihai Weili High Carbon Materials C. Ltd. The physical method is further used to further strip the GNP microchips in the liquid phase, and after centrifugation, high-quality and high-purity GNP is obtained, and the thickness is 3 to 5 mm, which is lighter and thinner. The content of the limited component in the product is determined by preliminary experiments to be 20%.

Table 1. Chemical composition of P.O 32.5R cement.

| Composition   | CaO  | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | SO$_3$ | MgO   | Loss on ignition |
|---------------|------|---------|-------------|-------------|--------|-------|-----------------|
| Content (%)   | 59.7 | 21.6    | 4.38        | 2.76        | 1.29   | 1.88  | 5.39            |

Table 2. The technical indicators of P.O 32.5R cement.

| Flexural strength/MPa | Compressive strength /MPa | Setting time/min |
|-----------------------|---------------------------|------------------|
| 3d 28d                | 3d 28d                    | Initial setting  |
| 3.5 6.5               | 17.0 43.5                | Final setting    |
|                       |                           | 210              |
|                       |                           | 280              |

2.2 Preparation of cement mortar test specimens

This experiment according to the preparation process of test method for strength of cement mortar. (National Standards of the People’s Republic of China. Method of testing cements-Determination of strength: GB/T17671—1999[14]). The mass percent of cement and the water to cement ration was kept 0.5, and the mass ratio of cement: sand: water reducing agent in this experiment's mixture is 1: 3: 0.01. Is designs a control mix and three groups of mixes with 0, 0.2, 0.4 and 0.6 wt% GNP, labeled as GC0, GC0.2, GC0.4 and GO0.6 respectively. Before mixing, dissolving the water reducing agent in water, stir the GNP into the glass rod until the solution is no longer turbid, pouring it into the cement mortar, and stirring them twice with water [15]. After all materials being mixed, fresh mortar was poured into the mold (40mm×40mm×160mm), each set containing three samples, which were compacted on a vibrating table with 60 vibrations per set. All specimens were demoulded after 24h of curing, and were placed in standard curing room (constant temperature 22°C, relative humidity 95%).
2.3 Methods
Accelerated test was adopt in this experiment. Wang et al. [16] pointed out that the sulfuric acid appear in most parts of China. In this study uses H$_2$SO$_4$ and HNO$_3$ (which molar ratio is 9:1) to simulate acid rain. The specimen was cultured for 28 days, and the timeliness of simulated corrosion was set for 3 days, 6 days, 9 days, 12 days, and 15 days. The pH of the simulated solution was adjusted with HNO$_3$ to keep pH1.0 every day.

3. Results and discussion

3.1 Visual observations
During the test, samples were picked out from the equipment periodically for visual inspection. The colour of the non-acid corrosion alternating test piece gradually becomes darker as the amount of GNP added increases, and the setting time is different. With corrosion time increases, the surface of the mortar specimen gradually changes. From the surface of the 9 days corrosion, specimens were observed small cracks and some porosity, and the samples at the corners have some loose. The control sample GC0 showed cracking but no damage was observed at GC0.2, GC0.4. The small holes in GC0.6 increased significantly. After 15 days, sample can observe damage including voids and flaking. The surface of GC0 changed from black gray to brownish yellow. White needle-like crystal spots formed on the bottom of the test piece covered the surface of the material. Serious cracks and brittle fracture occurred on the front side, and the corner part fell off. The surface of GC0.4 was dark, and the surface was uneven and have holes. The surface of GC0.6 is rough, and it is obvious that the sand has small cracks. GC0.2 has no obvious colour change, but small holes can be found at the bottom. In corrosion test, the acid penetrates into the pores of the mortar, causing a large amount of harmful ions to enter, destroying the composite materials.

Due to the addition of GNP, the product became densified, effectively improving the pore structure and weak interface transition zone inside the cement mortar [17]. Compared with the control sample during the acid treatment, the GNP sample showed less surface damage.

3.2 Mass
The mass was recorded using an electronic scale with an accuracy of 0.1g before and after the corrosion. For each set of masses is the average of three samples. The mass loss ratio is defined as

\[ D_n = \left(1 - \frac{m_n}{m_0}\right) \times 100\% \]

Where $D_n$ is the mass loss rate before the test in the corrosion period; $m_n$, the sample mass after the n days corrosion; $m_0$, the mass of the sample before the corrosion.

The relationship between the mass loss ratio and the corrosion time is shown in Figure 1. It shows that the mass of the four group of cement mortar specimens are all decreased with the increase of corrosion days. The swelling material produced by the reaction of cement and sulfate ions can increase the mass of the cement, but H$^+$ plays a major role in the early stage of the experiment [18]. The overall mass loss of GC0.2 and GC0.4 was less than that of other GC0 and GC0.6. As corrosion days increases, the difference between the different group became wider. The mass loss rate of GC0.6 in the early stage of corrosion is less than GC0, but the late loss trend increases and exceeds GC0, reaching a maximum at 15 days. This may be caused by the addition of graphene, which causes the fluidity of the cement mortar to decrease, the pores to increase, and the harmful ions to enter the inside of the test block. We note that the GC0.2 sample has the lowest mass loss rate throughout the test, and the fluctuations are small compared to the other three sets of group, which may be easier to blend in the cement mortar with 0.2% GNP with mortar and maintain a dense structure.

3.3 Compressive strength and Flexural strength
According to method of testing cements-determination of strength (GB17671-1999), the loading rate of the flexural and compressive strength was 50N/s and 2400N/s, respectively. Figure 2 shows the compressive strength of mortar with different GNP contents under different corrosion time. The
compressive strength of GC0.2 was the highest before and after acid corrosion. The GC0 was 5Mpa away from GC0.2 after 15 days, while the GC0.6 had the worst compressive capacity. Compared with GC0.2, GC0.4 and GC0.6 specimens have larger decrease in compressive strength with increasing corrosion days, which may be due to the uneven dispersion of GNP in the mixture, which reduces the structural density of cement mortar. Micro structural morphology confirms the evolution of internal morphology. From Figure 3, the difference in flexural strength variation is small, but the total test added to GNP is better than the GC0 group. As a two-dimensional thin-film nano-layered structure with extremely large specific surface area and super-flexibility, GNP still resists shearing force when the cement suffered seriously damaged. We can inferred that the addition of GNP enhances its flexural properties, but the loss ratio of flexural strength can improved about 2%.

In order to better study the deterioration trend of strength, Compressive strength loss ratio and flexural strength loss are defined as

\[ D_f = \left(1 - \frac{f_u}{f_0}\right) \times 100\% \]
\[ D_e = \left(1 - \frac{f_u}{f_0}\right) \times 100\% \]

Where \( D_f \) is the compressive strength loss ratio before the corrosion; \( f_0 \), the compressive strength after the corrosion; \( f_0 \), the compressive strength before the corrosion. \( D_e \) is flexural strength loss ratio before the corrosion; \( f_u \), flexural strength after the corrosion time; \( f_v \), flexural strength before the corrosion.

The relation between the compressive strength loss ratio and corrosion days is showed in Figure 4, and the flexural strength loss ratio and acid corrosion time is showed in Figure 5.

In the experiment, the compressive loss ratio and the flexural loss ratio of specimens increased with corrosion days. The compressive strength loss of the four sets of specimens were the same in the early stage. After 9 days of corrosion, the differences were obvious. After 12 days and 15 days of acid corrosion, \( D_f \) of GC0.2 were 22.9% and 24.3%, respectively, which were 4.1% and 4.2% higher than GC0 respectively. The \( D_e \) of GC0.4 was more obvious than the other three groups. Form it picture that \( D_e \) of GC0.2 change more stable comparing others and the loss reached 46.5%, which below 5% of GO0 in 15 days. It can be found that with corrosion days increase, the difference between G0 and GC0.2 will be even greater. The \( D_f \) of GC0 after 15 days of corrosion was the maximum in the four groups, and the GC0.6 reached the maximum. We can inferred that addition of GNP has a significant
effect on the cement mortar under acid rain. This may be that GNP regulates the cement hydration product, improves the pore structure and interfacial transition weak zone inside the cement mortar, improves the corrosion resistance and pressure resistance of the cement mortar. However, excessive GNP may cause more water absorption in the early hydration stage and lead to lower cement ratio, which explains that the corrosion loss rate of GC0.6 after 15 days of corrosion is greater than GC0.

4. Scanning Electron Microscopy
Figure 6. shows images of GNP with SEM, the shape of which is in the form of a sheet and a soft form, and the body shape is light and transparent.

Through the analysis of the microstructure of the GNP-containing mortar specimens, the morphological evolution of the specimens was observed by SEM in Figure 7. shows SEM micrographs of samples before corrosion. We can observe that GC0 has a large volume porosity and contains a large number of needle-like and rod-shaped cement hydration products, such as needle-shaped ettringite (Aft) crystals and square-plate Ca(OH)2 crystals (C-H crystals), hydrated calcium silicate gel (C-S-H) gel. After 15 days corrosion (Figure 8.), more surface micro cracks were observed in GC0, and the surface structure was loose and void. GC0.2 and GC0.4 behave more densely with finer particles and less voids due to the accumulation of C-S-H gels which allow the C-H-P crystals to develop better around. The addition of GNP improves the microstructure of the cement-based material and enhances the bond strength of the aggregate interface. Compared with the large amount of GC0.6, the GNP may be unevenly dispersed. In some areas, the filler forms a weak area and increases the acid ingress. The inside of specimens reduce the ability to resist corrosion. In this experiment, the product formation and distribution fusion effect of GC0.2 was the best.

5. Conclusion
In this paper, the following can be derived:

(1) The cement mortar test piece of GC0.2 is flatter than the surface of other types of test pieces, and the hole formation rate is low.

(2) With the increase of GNP, the mechanical properties of cement mortar increase first and then decrease. The GC0.2 mass loss rate is the smallest, which is 50% of GC0, and the compressive strength increases more than the flexural strength. The amount of compressive strength increased by up to 10%. The incorporation of GNP enhance the mechanical properties of cement mortar.

(3) The SEM image of the microstructure shows that the cement paste with proper amount of GNP is denser due to the filling structure, and the snow-like crystal formed fills the void with a large surface area, thereby reducing the porosity, improving the strength and toughness.
This experiment shows that GNP can effectively improve the mechanical properties and durability of mortar under the alternating dry and wet acid.

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