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Effect of graphene oxide on the mechanical properties and the formation of layered double hydroxides (LDHs) in alkali-activated slag cement

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Highlights:
(1) Graphene Oxide (GO) caused a significant reduction in fluidity and a slight decrease in compressive strength of AAS mortars.
(2) The flexural strength of hardened mortars were improved by adding GO.
(3) Layered double hydroxides (LDHs) were observed and confirmed in GO-added AAS system.

Abstract

Due to its high aspect ratio and outstanding tensile strength, graphene oxide (GO) can dramatically reduce the brittleness of cement-based materials. In this paper, GO nanosheets were successfully synthesised using the modified Hummers’ method. Effects of the GO on the fluidity, mechanical properties of alkali-activated slag (AAS) mortars and the microstructure of the AAS pastes were studied.

It is found that addition of the GO caused a significant reduction in fluidity and a slight decrease in the compressive strength of the hardened mortars. However, the GO improved the flexural strengths by 20% with a dosage of 0.01 wt. % after 7 days. Large-scale layered double hydroxides (LDHs) were observed using SEM, the compositions of which were identified and EDS and XRD. A possible mechanism of the formation of LDHs in the GO-AAS system is proposed. Due to the Mg\textsuperscript{2+}/Al\textsuperscript{3+} decomposed from the slag and the Al(OH)\textsubscript{3} formed in the high pH condition in the GO-AAS system, the reaction pathway of LDHs
can be regarded as

\[ aMg^{2+} + Al(OH)_{4}^- + (2a - 2)OH^- + xH_2O + A^- \rightleftharpoons Mg_{a}Al(OH)_{2+2a} \cdot xH_2O(s), \]

This research provides a further understanding of the effect of graphene oxide which has a potential application of GO in AASC.

**Keywords:** GO nanosheets; Alkali-activated slag cement; Microstructure; LDHs; Reaction pathway
1. Introduction

Alkali-activated slag cement (AAS), which can be a clinker-free binder, provides an eco-friendly alternative to conventional Portland cement [1]. The use of granulated ground blast furnace slag (GGBFS) as the precursor provides a significant lower carbon dioxide emission as well as lower energy consumption than ordinary Portland cement (OPC) [2-5]. Furthermore, AAS has high compressive strength [1, 6], resistance to chemical attacks [1, 7] and better immobilization of heavy metals [8]. However, due to the higher drying shrinkage and brittleness [8-9], an easier tendency of cracking for AAS has been reported by previous reports [2-3, 9-10]. Different fibres have been introduced to improve its toughness [11-12].

The development of nano-materials, e.g. carbon nanofibres, carbon nanotubes and graphene, has offered an opportunity to improve the toughness of cement-based materials [13]. The combination of cement with a small amount of carbon material has an admirable impact on the mechanical behaviour of OPC and other inorganic cements [13-16]. Of all of the carbon-based materials, two-dimensional (2D) graphene oxide (GO) sheets with an ultra-high dispersibility and a superior aspect ratio compared to other nano-carbon materials show a suitable performance in a cement matrix [13, 17]. Previous studies [13-14, 18] have shown that the introduction of a small amount of GO (0.05 wt. %) can increase the compressive strength by approximately 30% and the flexural strength by approximately 50%. Moreover, the unique rough surface of GO with many functional groups (-OH, -COOH and -O-) has a seeding effect on the hydration kinetics in cement. Lv et al. [19] found that use of GO nanosheets could produce bar-like and flower-like crystals in OPC that are the hydration products in the system and regarded as the reason for the improvement in mechanical properties. In addition, calcium-type cross-linking has been found in OPC due to the presence of the carboxyl and hydroxyl groups of GO [20], which can minimise
the pore size and form strong interfacial adhesion to the cement matrix. Therefore, GO bridges the two main hydration products (CSH gel and Ca(OH)$_2$). The presence of GO in the AAS system can also form silica-type cross-linking in geopolymeric composites to enhance the mechanical properties of geopolymers [21]. Based on a similar type of products in AAS (C-A-S-H), the GO should have high performances in strongly linking hydration products. Moreover, some divalent ions (Mg$^{2+}$ and Ca$^{2+}$) could also enhance the influences of GO [22], as with the decomposition of GGBFS, some divalent ions could exist in the liquid phase.

In this research, graphene oxide was synthesised using the modified Hummers’ method. The fluidity, mechanical properties and hydration products of the AAS were investigated. Experimental results show that the incorporation of GO nanosheets improved the flexural strength of AAS significantly and had a noticeable impact on the formation of layered double hydroxides (LHDs) in AAS. The formation mechanism of LDHs in GO-supplemented AAS has been proposed based on this study.

2. Experimental Procedure

2.1 Preparation of graphene oxide

Graphene oxide was produced based on the modified Hummers’ method. Graphite powder (2 g) and NaNO$_3$ powder (1 g) were added into a 1000-ml round-bottom flask and then concentrated H$_2$SO$_4$ (100 ml) was slowly added into the flask in an ice bath. After 4 hours, KMnO$_4$ (6.0 g) was slowly added and stirred into the flask for 20 minutes in an ice bath. The flask was then moved out of the ice bath, and the sample was continuously stirred at room temperature for a further 24 hours. Then, the resulting mixture was mixed with deionized water (200 ml) to obtain a dispersion by stirring at 0 °C for 20 min, followed by a slow addition of H$_2$O$_2$ (10 ml) using a pipette gun to dissolve the MnO$_2$ produced from the oxidation reaction between graphite and KMnO$_4$. Sodium nitrate,
concentrated sulfuric acid, potassium permanganate oxidises double bond into hydroxyl and carboxyl groups and struts piece layer. The role of the hydrogen peroxide is to restore the excess of potassium permanganate. The obtained dispersible mixture was filtered through a Buchner funnel, and then HCl aqueous solution (20 ml) was transferred to the flask using a pipette gun to react with the SO\textsubscript{4}\textsuperscript{2-}. The products were then stirred with running ultrapure water for 4 days to remove some of those metal ions and residual acid. Finally, the prepared graphene oxide solution was purified by centrifugation four times, and then the solution was sucked with a vacuum suction filtration device to stop the repetition of the filtration process until the pH reached a neutral value. The obtained neutral graphene oxide particles were used in this investigation.

### 2.2 Preparation of AAS pastes and mortars

The starting material used in this investigation is a GGBFS from Chongqing Iron and Steel Company. The basicity coefficient \( M_0 = \frac{w_{CaO+w_{MgO}}}{w_{SiO_2+w_{Al_2O_3}}} \) and activity coefficient \( M_a = \frac{w_{Al_2O_3}}{w_{SiO_2}} \) are 1.03 and 0.45, respectively. Its specific gravity and Blaine fineness are 2.95 g/cm\textsuperscript{3} and 435 m\textsuperscript{2}/kg, respectively. A commercial sodium silicate solution, composed of 29.3% SiO\textsubscript{2}, 12.07% Na\textsubscript{2}O and 51.4% H\textsubscript{2}O by mass, was used as the alkaline activator of the GGBFS. The XRD pattern (Fig. 1) of the anhydrous GGBFS shows that the main crystalline phase is akermanite (Ca\textsubscript{2}MgSi\textsubscript{2}O\textsubscript{7}, PDF# 074-0990), and there are also minor traces of calcite (CaCO\textsubscript{3}, PDF# 70-0095). The content of alkali was 5% by weight of GGBFS, and the modulus \( M_e=SiO_2/Na_2O \) of sodium silicate was changed from the initial 2.46 to the final 1.2 by using NaOH (AR). The GO content ranged from 0.01% to 0.05% by weight of the GGBFS.

The water to binder ratio of all the samples was 0.4, and the binder to sand ratio of all the mortars was 1:3. The fluidity and mechanical properties were tested with AAS mortars, while XRD and SEM-EDS analysis were carried out with AAS pastes.
2.3 Methods

2.3.1 Macroscopic properties

The fluidity was evaluated by jump table tests performed according to Chinese Standard: GB/T 2419-2005. The fresh mortar was filled into a truncated conical model with inner diameters of 70 mm (upper end) and 100 mm (bottom) with a height of 60 mm. Then, the mould was removed and the table was started vibration with a frequency of 60 r/min. After 25 seconds, the diameter of the mortar expansion was measured as the fluidity.

The mechanical properties of all the specimens were measured as per Chinese standard GB/T 17671-1999 at 3 days, 7 days and 28 days. The specimens were cured in a standard condition (Temperature = 20±1 ℃, relative humidity ≥ 95%).

2.3.2 Microstructural characterisation

The oxygen functional groups of the GO were identified using Fourier transform infrared (FTIR) spectrometry (Nicolet iS5, Thermo Scientific). The hydration products of AAS were recorded by powder X-ray diffraction (XRD, PIGAKV D/max 1200, Cu Kα).

Scanning electron microscopy (SEM) was performed using a TESCAN VEGA 3 LMH instrument with a 20 kV accelerating voltage [23]. The selected samples were vacuum-dried at 50℃ for 48 hours and then coated with gold. An energy dispersive spectroscopy (EDS, Oxford Instrument) detector was used to determine chemical compositions.

3. Results and Discussion

3.1 Characterisation of graphene oxide

The SEM image of the GO is shown in Fig. 2. As indicated, ultrathin and well-dispersed GO nanosheets were successfully prepared. Fig. 3 gives the XRD spectrum of the GO. A typical single strong
peak appeared at approximately 10° [24], which indicates that the oxygen functional groups have penetrated onto the surface of graphene. An average thickness of 0.328 nm (single sheet) was also calculated from the XRD pattern according to the Scherrer equation with a constant (K) equal to 0.89 [24].

The FTIR spectrum of the GO is displayed in Fig. 4. The vibrations of the characteristic oxygen functional groups can be detected through FTIR analysis [25]. The adsorption peaks of the GO in Fig. 4 are as follows: 3416.62 cm\(^{-1}\) is the vibration of hydroxyl (\(-\text{OH}\)); 1720.72 cm\(^{-1}\) is attributed to carboxyl (\(-\text{COOH}\)); the absorption peaks between 950 cm\(^{-1}\) and 1275 cm\(^{-1}\) are corresponding to the stretching of carbonyls (C-O-), which include C-OH (1200 cm\(^{-1}\) - 950 cm\(^{-1}\)), C-O-CO (1275 cm\(^{-1}\) - 1150 cm\(^{-1}\)) and C-O-C (1270 cm\(^{-1}\) - 1050 cm\(^{-1}\)); and 1201.15 cm\(^{-1}\) and 980.52 cm\(^{-1}\) are the peaks of the \(-\text{SO}_3\text{H}\) groups on the surface of the GO nanosheets. These similar functional groups were also detected in other studies [17, 19, 23-24].

The above results show the characteristics of the synthetic GO nanosheets used in this research. The functional groups and the zeta potential of GO can aid in its dispersion into the alkaline solution [26-27]. Due to its special structure and surface properties, GO might be more suitable for use in the AAS system.

### 3.2 Fluidity and mechanical properties of AAS mortars

The fluidity of AAS mortars containing different solid dosages of GO (0.01%/0.03%/0.05% by weight of slag) is summarised in Table 2. The plain AAS mortar with a water to binder ratio of 0.4 had a fluidity of approximately 215 mm. However, with a dosage of GO of 0.05%, the fluidity of the mortars was reduced to approximately 155 mm, 27.91% lower than that of the reference AAS mortar. The results show a notable reduction trend in the fluidity of the AAS mortar with the increasing GO dosage, which is consistent with previous research on the phenomenon of nanomaterial-added cement specimens [13,
28-29]. A possible reason is that the large surface area of the hydrophilic GO could absorb more water in the system, so that there might be less free water that is related to the rheological behaviour of the mortar [13, 18].

The compressive and flexural strengths of the AAS mortars with GO at 3 days, 7 days and 28 days are also given in Table 2. It can be found that the flexural strengths of all of the GO-added specimens increased, and the optimal content was approximately 0.01 wt. %. The increase rate of the flexural strength at a dosage of 0.01 wt. % was approximately 20% after 7 days. However, this is inconsistent with the optimal content of GO in the OPC system, which is approximately 0.03% - 0.04%, as reported in previous studies [14, 19, 28]. Interestingly, the data of the compressive strengths of all the specimens with the addition of GO showed a slight decreasing tendency, except for GM-1 at 28 days, quite different from the trend for OPC [13-14, 18-19, 28]. The compressive and flexural strengths are determined by the synergetic effect of the GO itself and the microstructures that are formed in its presence [14].

3.3 Microstructural investigations

SEM images of AAS pastes with additions of different amounts of GO at 28 days are shown in Fig. 5. Without the GO, the typical rocklike hydration products mainly consist of C-(A)-S-H gel together with the remaining slag particles (lighter and angular part of Fig. 5a), which is similar to previous findings [30-35]. At a GO dosage of 0.01 wt. %, hydration products of a rhombohedral symmetry formed, as shown in Fig. 5b-c, which is similar to the morphology of synthetic layered double hydroxides (LDHs) discovered by previous studies [36-37]. LDHs, which often appear as hydrotalcite or other variants in AAS, are well known as one of the main hydration products when magnesium is present [30-33]. This has been investigated using XRD, SEM-EDS and MAS NMR methods on AAS pastes. Furthermore, no obvious crystal structure of LDHs was found in the previous studies [30-31, 33], except using the micro-
reactor approach [35], which was carried out using FIB/SEM. When the GO dosage was 0.03 wt. % and 0.05 wt. %, flower-like parallely grouped crystals were found in hardened AAS pastes. The crystal druse grew larger (see Fig. 5d-e), mainly due to the greater content of GO nanosheets.

The chemical composition of the crystals in the GO-added AAS pastes was subsequently determined by SEM-EDS analysis (see Fig. 6). The chemical analysis results show that calcium, silicon, aluminium and magnesium were the main elements in the rhombohedral symmetry, which is similar to the hydrotalcite-like LDH products in AAS pastes reported by Mobasher et al [30].

Fig. 7 illustrates the XRD analysis of AAS pastes with various contents of GO after 28 days curing at 20 °C. A main wide and disperse peak at 29˚ was identified as the main hydration product C-(A)-S-H gel in the AAS pastes, as was widely reported and verified in recent studies [12, 30-35]. A relatively lower-intensity peak at approximately 11˚ 2θ was also found in all of the samples, which can be attributed to the formation of an LDH phase [30-31, 36-37].

In Section 3.2, the decrease in the compressive strength and increase in the flexural strength in GO-added AAS mortars may be mainly associated with the formation of LDH crystals. An LDH-type phase could also exist in the plain AAS pastes, but it generally occurs as a near micro-scale combination with C-S-H gel [30, 39-40]. The addition of GO increases the size of the LDHs and promotes the growth of crystals. The growth and existence of flake-like crystals could cause defects in the AAS paste matrix and further decrease the compressive strength. On the other hand, the flake-like crystals could enhance the bonding between the GO and the matrix and thereby may improve the flexural strength. More specifically, the GO with an extra high specific area provides a template in the AAS system so that the C-(A)-S-H gel can grow on the surface of the GO due to the cross-linking between the functional groups on the GO and the divalent ions in the gel [22]. Hence, significant reinforcement of the AAS
by the GO can be attributed to strong interfacial adhesion between the GO and C-(A)-S-H [41, 42].

3.4 Formation mechanism of LDHs in GO-added AAS pastes

LDHs, which are often synthesised through a chemical approach, have a general formula of \( M^{2+} \). \( M^{3+} \) (OH)\(_2\)A\(_x\) • nH\(_2\)O, where \( M^{2+} \) stands for Mg\(_{2+}\), Zn\(_{2+}\) etc., \( M^{3+} \) stands for Al\(_{3+}\), Fe\(_{3+}\) and so on, and \( A_x \) stands for 1/2(CO\(_3\)\(_2\)), Cl\(^-\) or OH\(^-\)\[37\]. In alkali-activated slags with a moderate MgO content, the LDHs are identified as Mg\(_6\)Al\(_2\)(CO\(_3\))\(_{16}\) • 4H\(_2\)O [31] or variants. In chemical engineering, the most commonly used method to synthesise LDHs on the surface of GO is to introduce divalent and trivalent cations from solution [43] and then form chemical cross-linking between the cations and the functional groups on the surface of the GO [41]. Due to a co-precipitation process, precipitation will occur, thereby leading to the in situ growth of the LDH phase [38]. Based on previous studies [37, 31], the formation mechanism for LDHs in AAS pastes has been proposed, and a simple sketch is shown in Fig. 8. First, in a condition of alkaline liquor, the slag is dissolved, and Mg\(_{2+}\) and Al\(_{3+}\) together with other ions such as Ca\(_{2+}\) and Na\(^+\) are released to the liquid phase. In GO-added AAS, the negative charge of the GO surfaces leads to a gathering of positive ions including Mg\(_{2+}\) and Al\(_{3+}\). In a high alkalinity environment, the Al\(_{3+}\) could easily form Al(OH)\(_4\)\(^-\). With the increasing concentrations of Mg\(_{2+}\) and Al(OH)\(_4\)\(^-\), the continuous reaction between ions generates the obvious LDHs. Therefore, the possible reaction pathways are proposed as follows in GO-added AAS:

In the high pH condition, \( Al^{3+} + 4OH^- \rightleftharpoons Al(OH)_4^- \)

\[ aMg^{2+} + Al(OH)_4^- + (2a - 2)OH^- + xH_2O + A^- \rightleftharpoons Mg_aAl(Oh)_{2+2a}A \cdot xH_2O(s) \]

where A\(^-\) stands for 1/2 CO\(_3\)\(_2\) or OH\(^-\).

It is believed that the A\(^-\) is more likely verified as OH\(^-\) and the possibility of the presence of CO\(_3\)\(_2\) is mainly due to the absorption of CO\(_2\) from the air.
4. Conclusions

GO nanosheets well-dispersed in an aqueous solution were successfully prepared using the modified Hummers’ method. The effects of the GO on the fluidity and microstructure of alkali-activated slag mortars and pastes were investigated. The following conclusions have been drawn based on results obtained:

(1) The fluidity of AAS mortars is significantly reduced with the increasing content of GO.

(2) The introduction of GO into AAS mortars increases the flexural strengths and decreases the compressive strength. The increase rate of the flexural strength can reach 20% after 7 days curing in standard conditions (20 °C, RH ≥ 95%). The optimal content of GO is 0.01% by weight of slag.

(3) Layered double hydroxides (LDHs) are formed in GO-added AAS pastes, which are responsible for the changes in mechanical properties. With the increasing dosage of GO, the crystal dimensions become larger, and a flower-like crystal druse is generated. A formation mechanism is proposed based on this and previous studies. The main reaction pathway is regarded as

\[
\text{aMg}^{2+} + \text{Al(OH)}_4^- + (2a - 2)\text{OH}^- + x\text{H}_2\text{O} + A^- \rightleftharpoons \text{Mg}_a\text{Al}((\text{OH})_2 + 2aA \cdot x\text{H}_2\text{O}(s)
\]

where A\(^-\) is most likely OH\(^-\) or 1/2 CO\(_3\)\(^2-\).

The results suggest that GO could significantly affect the hydration process, influence the microstructure, and improve the mechanical properties of AAS. This study also suggests a potential application of GO in AAS materials. Further studies on durability, shrinkage behaviours and compatibility with other materials will provide a deeper understanding on this nano-carbon material.

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