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## Understanding the behaviour of graphene oxide in Portland cement paste

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## ABSTRACT

This study reports on the effect of graphene oxide (GO) on the hydration of Portland cement (PC) and industrial clinker. GO accelerates PC hydration, whereas it temporarily retards that of clinker. This difference reflects a twofold behaviour of GO in cement pastes. Retardation is due to the interaction of GO with the surface of hydrating grains, while acceleration results from a seeding effect. Gypsum causes this difference. GO is shown to have little effect on the strength of hardened pastes, and this merely relates to the change of hydration degree, as opposed to reinforcing effect formerly assumed. Overall, GO is not particularly active as a nucleation surface, as it aggregates and behaves in a similar way to inert fillers (e.g. quartz). Polycarboxylate-ether copolymer could make GO an active seed in cement pastes, as it prevents GO from aggregating. Nevertheless, this was found to occur only in alite pastes but not PC pastes.

## 1. Introduction

Graphene oxide (GO) is composed of a single layer of mixed  $sp^2$  and  $sp^3$  hybridised carbon atoms, functionalised with various oxygen-derived groups such as carbonyl, hydroxyl and carboxyl [1]. A GO single layer has a thickness of about 0.7–1 nm and a lateral size ranging from hundreds of nanometers to tens or hundreds of micrometers [2]. Fig. 1 shows a schematic model of GO molecular structure. It is generally accepted that carboxyl sites are primarily located around the edges of GO layers whereas the other functional groups are within the carbon network [1,2]. These oxygen groups are hydrophilic, which allows GO to form stable colloids in water. As a derivative of graphene, GO possesses a high in-plane Young's modulus (210 to 470 GPa [3,4]) and high specific surface area (1500–1700  $m^2/g$  [5,6]). Due to these characteristics, it has often been stated that GO could be utilised as a reinforcing and/or nucleation-seeding additive in cement pastes whose matrix suffers from a low tensile strength [7,8]. Previous studies have claimed that adding GO to cement pastes or mortars improves the compressive, flexural and tensile strengths of these systems. The strength improvements were found to occur in systems made of Portland cement (PC) [7, 9–20], alkali activated slag [21] and magnesium phosphate [22]. The majority of these studies assumed that GO layers were well dispersed in the paste matrix. However, evidence has emerged that GO aggregates in the pore solution of alite [5] and PC pastes [23,24]. Therefore, it seems likely that the strength improvements reported for PC-GO systems resulted from the presence of GO aggregates and not of single layers [25, 26].

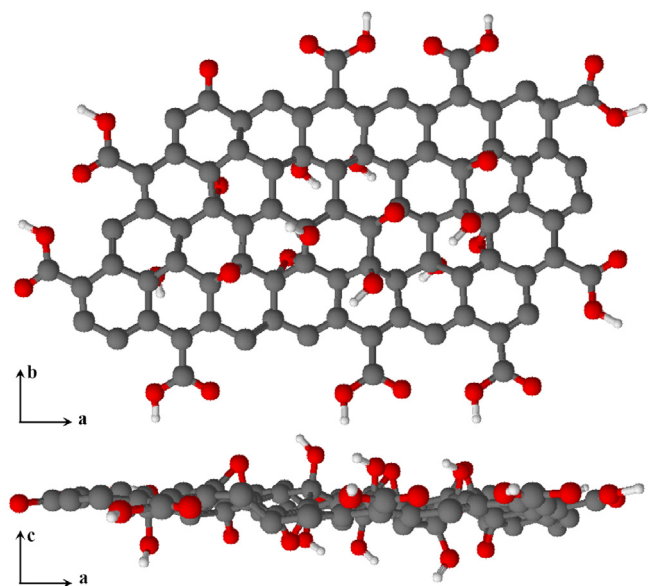
GO is susceptible of aggregation in PC pastes, as it reacts with divalent and trivalent cations as well as hydroxide ions present in the paste solution. The aggregation occurs while mixing the paste, and starts from the very beginning of hydration when cement particles dissolve in water. The high pH level in PC pastes ( $pH > 12$ ) causes hydrogen to dissociate from the GO carboxyl sites where calcium, the most abundant cation in PC paste, forms  $COO^-Ca^{2+}-OOC$  complexes [5]. Since calcium is a divalent cation, it tends to react with two carboxylated sites. As a result, it bridges the GO layers, causing their aggregation [5,28]. Other divalent or trivalent cations can act similarly [28,29].

In addition to the cationic effect, GO reacts with hydroxide ions in alkaline solutions and loses the majority of its oxygen-bearing groups. Reduction of GO was found to occur in aqueous electrolytes containing LiOH [29], NaOH, KOH [30,31] and  $Ca(OH)_2$  [5]. It appears that all GO functional groups are prone to reduction in alkaline solutions except carboxylate [31]. This phenomenon contributes to GO aggregation in alkaline solutions. GO remains dispersed in water because the oxygen groups on its basal plane increase the repulsive forces between the individual layers, overcoming the van der Waals attractions [28,29]. However, as the oxygen groups disappear in alkaline solutions, the overall force acting between the GO layers switches from repulsion to attraction, causing GO to aggregate. Therefore, high pH environments, such as that of PC pore solution, tend to cause GO to aggregate [5].

Despite some of the recent advances in understanding the role of GO in PC pastes, several issues remain open. The first issue concerns the interaction of GO with cement particles while mixing the paste. GO is

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**Fig. 1.** A simple schematic model of GO atomic structure, showing the presence of carboxyl sites at edges of the GO layer while other functional groups, such as hydroxyl, are located on the basal plane. Grey, red and white atoms represent carbon, oxygen, and hydrogen, respectively. The actual atomic structure of GO is complicated and the oxygen groups are randomly distributed within the carbon network [1]. Compared to graphene, the structure of GO is damaged as a result of oxidation, with holes up to  $5 \text{ nm}^2$  present in some cases [27]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

negatively charged in water (with zeta-potential lower than  $-30 \text{ mV}$ ) as it carboxylates. GO layers become even more negatively charged in alkaline solutions, as more carboxyl sites are deprotonated [32]. Wang et al. [33] suggested that carboxylated GO adsorbs onto the surface of PC particles in the paste. This mechanism is plausible because PC grains are known to possess a positive electrostatic charge in water [34], so in principle, GO layers could be attracted to PC surfaces. This is similar to how carboxylated molecules or copolymers behave in cement pastes, where they are well known to retard cement hydration. They do this because they adsorb on the surface of hydrating particles and hinder the dissolution of cement and/or precipitation of hydration products [34–37]. However, this may not be the case for GO as it has been shown to accelerate cement hydration [5,38]. Therefore, the charge characteristics of the surfaces alone seems insufficient to explain the interaction between GO and PC grains in water.

Secondly, the reason why GO strengthens PC pastes has remained unclear. Some suggest that GO serves for the nucleation of hydration precipitates, causing a higher degree of hydration [9,10,12,14,16]. Others propose that GO reinforces the paste matrix at the nano-scale [11,15,17,18,20,25,26]. A combination of these two mechanisms has also been suggested [7,11,15,19,38]. However, the reinforcing mechanism is often posited with no convincing evidence. Moreover, pastes containing GO hydrate faster than plain pastes, and this makes it difficult to decouple the effect of nucleation seeding from that of reinforcing.

Another issue relates to the methods proposed to prevent GO from aggregating in PC paste pore solution [23,24,39,40]. Evidence exists that polycarboxylate ether (PCE) copolymer prevents GO from aggregation in  $\text{Ca}(\text{OH})_2$  and  $\text{NaOH}$  electrolytes (molarities and PCE/GO ratios were unfortunately not specified) [23,24]. Lu et al. [39] demonstrated that PCE stabilises GO dispersion in dilute PC suspensions, with water-to-PC mass ratio of 15. From this observation, they claim that PCE disperses GO in PC pastes with water-to-PC ratio of 0.35, thereby strengthening the hardened matrix. Similar claims have also been reported elsewhere [23,24,39]. However, it is not obvious to

which extent the behaviour of GO in such dilute suspensions can be generalised to pastes with much lower water content.

Following from our previous study on the effect of GO on alite hydration [5], a series of isothermal calorimetry tests were used in this paper to investigate the effect of GO on the hydration of industrial clinker, either alone or in substitution with gypsum and limestone. These systems were chosen because they are of intermediate complexity between alite and PC. The heat evolution patterns of clinker hydration are then compared to those obtained for alite and PC hydration. Results show that GO acts very differently in clinker paste compared to alite and PC pastes, which sheds some new light on the behaviour of GO in cement pastes. We also report the compressive strengths of PC and clinker pastes at 7, 14, and 28 days of hydration as a function of total hydration heat. This allows any reinforcing effect to be isolated from that of nucleation-seeding. Finally, this study reports on the effectiveness of PCE copolymer in dispersing GO nano-layers in alite or PC pastes, with a view to test some of the claims found in the literature.

## 2. Materials and methods

### 2.1. Synthesis and characterisation of graphene oxide

Graphene oxide was synthesised following the procedure described in Ref. [5]. Three grams of graphite flakes ( $+100$  mesh, Sigma Aldrich) were added to  $360 \text{ mL}$  of concentrated  $\text{H}_2\text{SO}_4$  ( $\geq 95 \text{ wt } \%$ , Fischer Chemicals) and  $40 \text{ mL}$  of concentrated  $\text{H}_3\text{PO}_4$  ( $\geq 95 \text{ wt } \%$ , Fischer Chemicals). Following this,  $18 \text{ g}$  of  $\text{KMnO}_4$  ( $\geq 99.0\%$ , Fluke Biochemika) was gradually added into the acid-graphite mixture. This mixture was kept at  $25^\circ\text{C}$  and left to stir for  $96 \text{ h}$  using a magnetic stirrer. Thereafter, the mixture was cooled in an ice bath and was slowly diluted with  $400 \text{ mL}$  of distilled water.  $\text{H}_2\text{O}_2$  solution ( $\geq 30 \text{ wt } \%$ , Sigma Aldrich) was then added drop-wise to the reaction mixture until the solution became bright yellow and no further colour change was observed. The solids were collected by centrifugation at  $3500 \text{ rpm}$  for  $1 \text{ h}$  and were sequentially washed with deionised water,  $\text{HCl}$  ( $\sim 3.5 \text{ wt } \%$ ) and acetone (each conducted five times). The solid residue, which is graphite oxide, was dried for seven days under vacuum at room temperature.

Dried graphite oxide was characterised using an X-ray photoelectron spectrometer (K-Alpha XPS, ThermoFisher Scientific) with a monochromated  $\text{Al K}\alpha$  source ( $E = 1486.6 \text{ eV}$ ). The XPS spectra were recorded on dried graphite oxide flakes over a spot size of  $400 \mu\text{m}$  and dwell time of  $50 \text{ ms}$ . The flakes were prepared by depositing the acetone-washed graphite oxide on a filter paper and drying it for seven days in a desiccator. This helped produce flakes with analogous thicknesses for XPS analyses (always  $\sim 0.5 \text{ mm}$ ). XPS survey scans (Fig. 2a) were conducted three times with a resolution of  $1 \text{ eV}$ , and the  $\text{C1s}$  spectrum (Fig. 2b) was recorded 10 times with a resolution of  $0.1 \text{ eV}$ . This setup was chosen based on a number of preliminary trials. Data shown in Fig. 2 confirm that the synthesised graphite oxide is mainly composed of carbon and oxygen (and hydrogen) with no other elements present in the sample, and that the synthesis procedure employed in this study resulted in a highly oxidised GO with oxygen-to-carbon ratio of about 0.52. This was also consistent with the mass of the bulk graphite oxide after its synthesis;  $3 \text{ g}$  of graphite led to about  $5 \text{ g}$  of graphite oxide. The high oxidation level acquired in this study is in agreement with previous reports [41]. It is important to note that XPS surveys are often obtained on solid samples pressed onto a carbon substrate, but, as Fig. 2 shows, this gives an inaccurate elemental composition for graphite oxide as the carbon in the substrate could contribute to the XPS measurements. Indium was used on top of the carbon substrate in this study to avoid any background contribution from the substrate. Fig. 2b shows the  $\text{C1s}$  pattern of graphite oxide, which confirms three chemical states for carbon consistent with our previous study [5]. In detail, these states relate to  $\text{sp}^2$  and  $\text{sp}^3$  hybridised,  $\text{C}=\text{O}$  and  $\text{C}-\text{O}$ , and carboxyl-like structures.

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