

An investigation into the colloidal stability of graphene oxide nano-layers in alite paste



S. Ghazizadeh^{a,*}, P. Duffour^a, N.T. Skipper^b, M. Billing^b, Y. Bai^a

^a Department of Civil, Environmental & Geomatic Engineering, University College London, London WC1E 6BT, United Kingdom

^b London Centre for Nanotechnology, Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom

ARTICLE INFO

Keywords:

Colloidal stability
Graphene oxide
Alite
Portland cement

ABSTRACT

Recent studies have reported that graphene oxide (GO) is capable of enhancing the mechanical properties of hardened Portland cement (PC) pastes. The mechanisms proposed so far to explain this strengthening generally assume that GO is well dispersed in the pore solution of PC paste, serving as a reinforcing agent or nucleation-growth site during hydration. This paper investigates (i) the effect of GO on the hydration of alite, the main constituent of PC cement, using isothermal calorimetry and boundary nucleation-growth modelling, and (ii) the factors controlling the colloidal stability of GO in alite paste environment. Results indicate that GO accelerates the hydration of alite only marginally, and that GO is susceptible to aggregation in alite paste. This instability is due to (i) a pH-dependent interaction between GO and calcium cations in the pore solution of alite paste, and (ii) a significant reduction of GO functional groups at high pH.

1. Introduction

Graphene oxide (GO) is composed of a distorted graphene monolayer where a fraction of carbon atoms have been functionalised by various oxygen-containing chemical groups such as carbonyl and carboxyl [1]. In recent years, the use of GO as a potential strength-enhancing additive in Portland cement (PC) paste has been the focus of much research [2–13]. Previous studies have found that GO improves the compressive strength of PC paste, however the reported results are somewhat erratic and difficult to interpret in detail. For instance, Lv et al. [11] found that adding GO to PC paste with an GO:PC mass ratio of 0.02% yields a maximum increase of 60% in the compressive strength, whereas the same authors in a recent article [12] required a higher optimal GO:PC ratio of 0.06% to achieve the same level of strength improvement. Many factors might explain these discrepancies (e.g. the size and oxidation level of the GO layers [10,14]), but the mechanism by which the presence of GO leads to the strength improvements in PC pastes has remained controversial.

Two mechanisms have so far been put forward to describe the role of GO in enhancing the mechanical properties of PC paste: (i) as a derivative of graphene, the GO layers possess a high in-plane tensile strength and therefore could act as a nano-size reinforcing agent in the PC matrix, thereby delaying the formation of cracks [2-9,15,16]; (ii) the GO layers could serve as nucleation-growth sites during the hydration of PC, stimulating a higher degree of hydration [10-14,17].

With respect to the reinforcing mechanism, studies postulated that the functional groups of GO play a pivotal role in providing strong interfacial bonding between the GO nano-layers and C-S-H [2,5,16]. In a detailed molecular dynamics simulation study, Sanchez and Zhang [16] showed that a sufficient number of oxygen-containing functional groups should exist on the GO surface to achieve a strong interfacial bonding between GO and C-S-H (modelled as 9 Å tobermorite structure). They suggest that the nature of the interaction between GO and C-S-H is electrostatic, and that Ca²⁺ ions in the pore solution of paste could act as a bridge between the polarised oxygen atoms of GO and C-S-H [16]. Regarding the role of GO as extra growth sites, some studies suggest that GO accelerates the hydration of PC, resulting in an increased early-age compressive strength [13,17]. Others report that GO induces the formation of a new micro-structure with a highly regular flower-like pattern [10,11]. According to the latter, the GO layers may not act directly as a reinforcing agent, but rather stimulate a micro-structural pattern that gives the PC-GO paste enhanced mechanical properties.

Whether GO directly reinforces the PC matrix or increases nucleation, the mechanisms proposed to date are underpinned by a number of assumptions. First, the individual GO layers must remain well-dispersed in PC paste so that a homogeneous reinforcement and/or nucleation-growth is achieved. While it is established that due to the presence of oxygen-based functional groups, GO forms a stable aqueous colloid [18,19], the stability of its dispersion in a PC paste environment

* Corresponding author.

E-mail address: s.ghazizadeh@ucl.ac.uk (S. Ghazizadeh).

is so far unknown. Second, the source of interfacial bonding, *i.e.* the GO functional groups, must remain chemically stable during the hydration of PC, otherwise the reinforcing role would not be effective. Using Fourier Transform Infrared Spectroscopy (FT-IR) on solid PC-GO paste, Lin et al. [17] reported that the hydration of PC has no detrimental effect on the functional groups of GO. However, the FT-IR of PC-GO could have been easily misinterpreted due to the overlapping of various stretching vibrations associated with the hydration products and GO.

To avoid the complexities involved in the hydration of PC, we herein focus on the hydration of alite, the main constituent of Portland cement. First, the overall effect of GO on the alite hydration is investigated by conducting a series of isothermal calorimetry measurements. The calorimetry patterns show that GO accelerates the alite hydration, but the extent of observed acceleration is quite low. A theoretical boundary nucleation-growth (BNG) model was used to analyse the calorimetric data. According to the BNG analysis, the acceleration observed in the hydration of alite-GO system may stem from a combination of extra surface for the nucleation of hydration precipitates provided by GO; higher nucleation density on the GO surface compared to that of alite; higher rate of precipitation in alite-GO paste compared to alite paste. However, the BNG results indicate that both the amount of extra surface as well as the higher nucleation density added by GO is only a small fraction of what GO could potentially provide. This, together with direct microscopic observation pointed to a clear aggregation of GO in the pore solution of alite paste. This led us to investigate the underlying mechanisms controlling the interaction of GO with various calcium-containing aqueous electrolytes using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), FT-IR, thermogravimetric analyses (TG), and X-ray diffraction (XRD).

2. Materials and methods

2.1. Synthesis and characterisation of materials

Alite was synthesised by sintering pelleted powders of 3:1 stoichiometric mixture of high-purity CaCO_3 and SiO_2 (≥ 99 wt%, Sigma Aldrich) which were doped with 1.1 wt% MgO and 0.7 wt% Al_2O_3 (≥ 99 wt%, Sigma Aldrich) according to the procedure explained by Wesselsky and Jensen [20]. The pre-mixed powders were wet-homogenised in a mixer, and then dried and calcined for 5 h at 1000°C . The de-carbonated mix was pressed into pellets and subsequently heated at 1500°C for a period of 8 h in a muffle furnace. Thereafter, the pellets were removed from the furnace and quenched immediately in the air. Once cooled, the resultant material was ground using a ball-mill grinder (PM 100, Retsch). The pelleting-sintering-grinding procedure was repeated three times in order to produce a high-purity alite powder, and finally particles passed through a $80\ \mu\text{m}$ sieve were selected for this study. The final particle size distribution of alite used in this study was measured by a particle characterisation tool (Morphologi G3, Malvern Instruments) and is presented in Fig. 1a. The measured Brunauer-Emmett-Teller (BET) surface area of alite was $0.572\ \text{m}^2/\text{g}$. The crystal structure and composition of the final product was characterised using an X-ray diffractometer (PANalytical X'Pert Pro). The X-ray diffraction (XRD) pattern was recorded over 2θ ranging from 10° to 70° with the following experimental conditions: the X-ray tube was operated at 40 kV with 40 mA, fixed divergence slit with slit size 1° , and step size of 0.033° with 2 s per step. The alite powder used throughout this study was synthesised within one process and therefore there is no batch-variation in the final product. Rietveld refinement was used to quantitatively analyse the measured XRD pattern, as presented in Fig. 1b, indicating a slight trace of free lime.

Graphene oxide was synthesised using the procedure given in Marcano et al. [21]. Graphite flakes (+100 mesh, Sigma Aldrich) were oxidised using 3 g of graphite added to 360 mL of concentrated H_2SO_4 (≥ 95 wt%, Fischer Chemicals) and 40 mL of concentrated H_3PO_4 (\geq

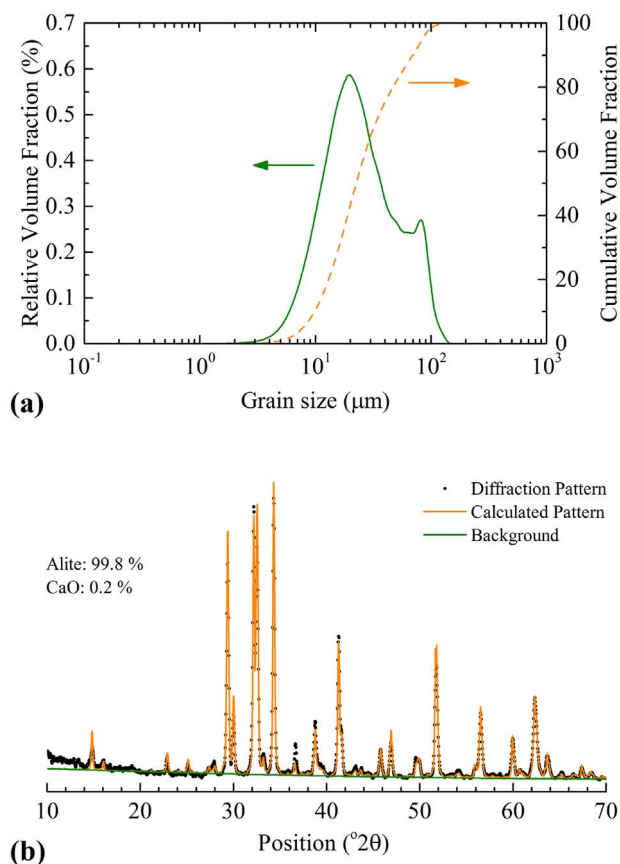


Fig. 1. (a) Particle size distribution of alite used to study the hydration kinetics, and (b) X-ray powder diffraction pattern of synthesised alite along with the Rietveld refinement fitting pattern, suggesting a slight trace of CaO in the sample.

95 wt%, Fischer Chemicals) in a 1 litre bottle equipped with a magnetic stirrer bar. This suspension was cooled to below 5°C using an ice bath. Once cooled, 18 g of KMnO_4 ($\geq 99.0\%$, Fluke Biochemika) were added, leading to an exothermic reaction. The mixture was left to stir in the ice bath for a further 30 min. Following this, the mixture was kept at 25°C and left to stir for 96 h. Once the desired oxidation time had elapsed, the bottle was cooled in an ice bath again and the reaction mixture was slowly diluted with 400 mL of distilled water over a period of 15 min. H_2O_2 solution (≥ 30 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 rpm for 1 h and were sequentially washed with deionised water, HCl (~ 3.5 wt%) and acetone until the supernatant was free of SO_4^{2-} (tested using BaCl_2). The residual solid was dried for three days under vacuum at room temperature. The resulting dried solid is graphite oxide, *i.e.* stacks of GO layers only partially exfoliated.

The BET surface area of the synthesised graphite oxide was measured to be $220\ \text{m}^2/\text{g}$. Note that this value is not related to the GO single layers, and it only corresponds to the surface area of partially exfoliated GO layers in graphite oxide form. This is because the nitrogen used in the BET test cannot easily penetrate within graphite oxide, and therefore it cannot be adsorbed on all GO layers [22]. Since there is still no reliable experimental method to accurately measure the surface area of GO single layers (S_{GO}) [22,23], we estimate S_{GO} theoretically and use it later to discuss the experimental results. S_{GO} was calculated assuming that GO is composed of carbon hexagons with a minimum C–C bond length of $a = 0.142\ \text{nm}$ [1] so that each hexagon has an area of $0.10477\ \text{nm}^2$ (including both sides). The mass of each atom (in gram) equals to its molar mass divided by Avogadro's constant, $N_{Av} = 6.022 \times 10^{23}$. The number of carbon atoms and hexagons per unit area (μm^{-2}) of a single layer was estimated to be approximately

Download English Version:

<https://daneshyari.com/en/article/5437136>

Download Persian Version:

<https://daneshyari.com/article/5437136>

[Daneshyari.com](https://daneshyari.com)