An Investigation into the Colloidal Stability of Graphene Oxide Nano-layers in Alite Paste

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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, (ii) a significant reduction of GO functional groups at high pH.

Keywords: Colloidal dispersion, Graphene oxide, Alite, Portland cement
1. Introduction

Graphene oxide (GO) is composed of a distorted graphene mono-layer 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 et al. [16] showed that a sufficient num-
ber 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 interac-
tion between GO and C-S-H is electrostatic, and that Ca\(^{2+}\) 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 dis-
persion in a PC paste environment 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
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$_2$ ($\geq$ 99 wt.% Sigma Aldrich) which were
doped with 1.1 wt.% MgO and 0.7 wt.% Al$_2$O$_3$ ($\geq$ 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 hours at 1000°C. The de-carbonated mix was pressed into pellets and subsequently heated at 1500°C for a period of 8 hours 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 µm 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 m$^2$/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 2$\theta$ 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 seconds 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$_2$SO$_4$ ($\geq$ 95 wt.%, Fischer Chemicals) and 40 mL of concentrated H$_3$PO$_4$ ($\geq$ 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 KMnO₄ (≥ 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 minutes. Following this, the mixture was kept at 25°C and left to stir for 96 hours. 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 minutes. H₂O₂ 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 hour and were sequentially washed with deionised water, HCl (~3.5 wt.%) and acetone until the supernatant was free of SO₄²⁻ (tested using BaCl₂). 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 m²/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 nm [1] so that each hexagon has an area of 0.10477 nm² (including both sides). The mass of each
atom (in gram) equals to its molar mass divided by Avogadro’s constant, \(N_A = 6.022 \times 10^{23}\). The number of carbon atoms and hexagons per unit area (\(\mu m^{-2}\)) of a single layer was estimated to be approximately \(1.94 \times 10^7\) and \(9.6 \times 10^6\), respectively. This leads to a surface area of around 2600 m²/g which is well-known for graphene [19]. Given that GO usually has a carbon-to-oxygen atomic ratio of 2-3 [1, 18], \(S_{GO}\) can be between 1500-1700 m²/g. This is in agreement with previous estimations [22].

GO layers were exfoliated in aqueous solutions by sonicating dry graphite oxide in deionised water using a sonication bath (Fisher Scientific, FB15050) for 1 hour. The quantity of graphite oxide used in sonication depended on the required concentration of GO in water. The thickness of GO layers exfoliated in water was measured using the tapping mode of an Atomic Force Microscope (Bruker Dimension 3100). The sample for AFM imaging was prepared by depositing an aqueous dispersion of GO (0.5 mg/ml) on a freshly cleaved Mica surface. Fig. 2a shows the AFM topographic image of GO nano-layers. The height profile measured from the topographic image, presented in Fig. 2b, indicates that the exfoliated GO has an approximate thickness of 1 nm. This is in agreement with previously reported data for the thickness of a GO mono-layer [1, 18, 19, 21]. The Mica surface was further studied every 5 \(\mu m \times 5 \mu m\) over an area of 50 \(\mu m \times 50 \mu m\), and the topographic images were analysed using an AFM software (NanoScope Analysis v1.40). Results shown in Fig. 2c indicates that the 1 nm thickness was dominant.

2.2. Iso-thermal calorimetry

The hydration of alite in the absence and presence of GO was investigated by conducting a series of isothermal calorimetry experiments. The primary
aim of this study was to investigate the extent to which GO alters the rate
and level of heat released from the hydration of alite. If GO serves as a
nucleation-growth site in the pore solution of alite paste, and accelerates
the formation of hydration precipitates, one would expect the rate and level
of heat evolution for the alite-GO hydration to increase noticeably compared
to that of plain alite paste.

The hydration kinetics of plain and GO-containing alite pastes were mea-
sured for the first 24-hours of hydration using an isothermal calorimeter
(TAM Air model, TA instruments). All samples were prepared using 3 g of
alite powder placed into a plastic vial and then mixed in-situ with the re-
quired amount of water (de-ionised) which either contained GO or not. Alite
powder was mixed with water using a polyethylene stirrer at 350 rpm for 30
seconds, following a standard mixing procedure based on ASTM C186-13.
Once mixed, the vial was immediately sealed tightly and placed into the
calorimeter set at 20 °C.

In the case of GO-containing samples, the required quantity of GO (depend-
ing on the GO:alite mass ratio) was first dispersed in 20 ml of de-ionised
water using sonication, and then depending on the water to alite mass ra-
tio, the desired amount of GO-containing solution was taken to prepare the
paste. Four water to alite mass ratios of 0.3, 0.4, 0.5 and 0.6 were selected
in this study to investigate the effect of GO on alite hydration more thor-
oughly. For the pastes containing GO, GO was added in the amount of 0.02,
0.04, 0.06, and 0.08%, with respect to the alite mass, and we followed the
same stirring procedure as with the plain paste (350 rpm for 30 seconds) to
mix the aqueous solutions containing GO with alite powder. The range of
GO mass ratios and the standard mixing procedure were chosen on the basis
of previous studies where significant strength improvements were reported.
To ensure the repeatability of the results and appreciate the degree of uncertainty of the measurements, calorimetry experiments were repeated three times, and each calorimetry curve was analysed using three parameters which characterise the main features in the trend of heat evolution. As shown in Fig. 3a, these are: (i) the peak value of the derivative of heat-flow during the acceleration period, denoted by \( (d^2 Q/dt^2)_\text{acc} \), (ii) the peak value of heat flow, \( (dQ/dt)_p \), (iii) the time at which the heat flow reaches the peak, \( t_p \).

2.3. Boundary nucleation and growth (BNG) modelling

A boundary nucleation and growth (BNG) model was adapted and implemented to mathematically describe the calorimetry patterns. The BNG theory employed in this study was based on the concept of time-dependent growth rate of precipitates, as described by Bullard et al. [24]. In this model, the kinetics of alite hydration depends on the precipitation of hydration products from the pore solution of paste which always remains undersaturated with respect to alite dissolution. The hydration precipitates are assumed to form as ellipsoidal particles on the surface of substrates (i.e. anhydrous alite and GO), and initially nucleate on a fixed number of sites, denoted by \( N_S \) [25].

The BNG model predicts the volume fraction of paste that is transformed into hydration products as a function of time. At any given time \( t \) (hours), this volume fraction (referred to as the real volume \( V_{\text{real}} \)) can be calculated from the extended volume \( V_{\text{ext}} \) using equation Eq. [1]

\[
V_{\text{real}}(t) = 1 - \exp\left(-V_{\text{ext}}(t)\right). \tag{1}
\]
The extended volume, $V_{\text{ext}}(t)$, can be computed at each time step using equations Eqs. 2-4:

$$V_{\text{ext}}(t) = 2 \cdot G_{\text{out}}(t) \cdot r_G \cdot O_B \cdot V \cdot \left(1 - \frac{F_D(x,t)}{x(t)}\right), \quad (2)$$

$$F_D(x,t) = \exp \left(-x^2 t^2\right) \int_0^{x \cdot t} \exp \left(y^2\right) \, dy, \quad (3)$$

$$x(t) = G_{\text{out}}(t) \sqrt{\pi N_S g}, \quad (4)$$

where $G_{\text{out}}(t)$ ($\mu$m/h) is the time-dependent outward growth rate of hydration product with respect to the surface of substrates, $r_G$ is the ratio of the growth rates into and out of the substrate (only applies to alite particles), $g$ is the degree of anisotropy of the growth rate defined as the ratio of parallel and outward growth rates. $O_B^V$ ($\mu$m$^{-1}$) is the total boundary area (specific surface area) of substrates per unit volume of paste, which can be calculated using equations Eq. 5 and Eq. 6:

$$O_B^V = \left[ S_{\text{alite}} + \gamma \cdot S_{\text{GO}} \right], \quad (5)$$

$$\gamma = \frac{m_{\text{GO}}}{m_{\text{alite}}}, \quad (6)$$

where $m_{\text{GO}}$ and $m_{\text{alite}}$ are the mass of GO and alite, respectively. $S_{\text{alite}}$ (m$^2$/g) is the specific surface area of alite as measured by the BET method, $V_w$ and $V_{\text{alite}}$ are the volume of water and alite (per gram of alite) in the paste, respectively. $N_S$ ($\mu$m$^{-2}$) is the total number of nuclei per unit area of the substrates, which can be calculated using Eq. 7:

$$N_S = \left[ \frac{N_{\text{alite}}^S \cdot S_{\text{alite}} + N_{\text{GO}}^S \cdot \gamma \cdot S_{\text{GO}}}{S_{\text{alite}} + \gamma \cdot S_{\text{GO}}} \right]. \quad (7)$$
where $N_{alite}^{S}$ and $N_{GO}^{S}$ are the number of active nucleation sites per unit surface area of alite and GO, respectively.

The volume fraction of alite consumed and transformed into hydration products ($V_{real}$) can be related to $\alpha$, the dimensionless degree of alite hydration, by a constant $B$, as described by equation Eq. 8;

$$\alpha = V_{real}.B,$$

(8)

$B$ (dimensionless) can be calculated for a specific water to alite mass ratio ($R_{wc}$) according to equation Eq. 9 [24]:

$$\frac{1}{B} = \left(\frac{\rho_{alite}/\rho_{H}}{1 + R_{wc}\rho_{alite}/\rho_{w}}\right)\left(\frac{c + 1/\rho_{alite} - 1/\rho_{w}}{1/\rho_{H} - 1/\rho_{w}}\right),$$

(9)

where, $\rho_{alite}$ is the density of alite (3150 kg/m$^3$), $\rho_{w}$ is the density of water (1000 kg/m$^3$), $\rho_{H}$ is the average density of hydration products (taken as 2230 kg/m$^3$), $R_{wc}$ is the water to alite mass ratio, and $c = -7.04 \times 10^5$ m$^3$/kg is a constant parameter related to the chemical shrinkage per kilogram of alite when its hydration is complete [24]. Using the rate of change in the degree of hydration, the rate of heat flow for the reaction of alite with water can be calculated using Eq. 10:

$$\frac{dQ}{dt} = \frac{d\alpha}{dt}.H_{alite},$$

(10)

where $H_{alite}$ is the enthalpy of alite hydration and is fixed to 517 J/g [26].

A number of assumptions were made in the implementation of the BNG model in this study: (a) the hydration products grow outward and parallel to the surface of alite, and the $g$ ratio is considered to be 0.5 [25], (b) the BNG model is only used here to investigate the acceleration period (see Fig. 3a) when the formation of hydration products is only allowed outwards of the substrates into the aqueous phase, and therefore the $r_G$ factor is
assumed to be 0.5 [25], (c) the number of active growth sites on the alite surface ($N_{\text{alite}}^S$) is assumed to be 12 $\mu m^{-2}$ [27].

To simulate the calorimetric patterns of plain alite (with no GO) hydration, the only unknown variable that needs to be calculated at each time $t$, is the rate of growth $G_{\text{out}}$. An iteration process was used to determine $G_{\text{out}}$ at each time step such that the value of $dQ/dt$ calculated from the model matches that measured by isothermal calorimeter. Fig. 3 shows the fitted calorimetry curve of alite hydration for a paste with water to alite mass ratio of 0.5, up to 12 hours of hydration. This water to alite ratio is used as an illustrative example. In Fig. 3, the rate at which the hydration product grows on the surface of alite particles is presented as a function of hydration degree ($\alpha$) and time. The generally descending pattern of growth rate is consistent with the simulations in [24], and the values of $G_{\text{out}}$ are within the same order of magnitude as those reported in previous studies [24, 27–29].

In the case of plain alite paste, $O_B^V$ and $N_S$ parameters are known and can be simply calculated using Eq. 5 and Eq. 7 with $\gamma = 0$. For instance, $O_B^V = 0.6235 \mu m^{-1}$ and $N_S = 12 \mu m^{-2}$ for a plain paste with water-to-alite ratio of 0.6. However, these variables cannot be directly estimated for alite-GO pastes as the nucleation kinetics of hydration precipitates on the GO surface is as yet not well understood.

Simulating the hydration of alite-GO pastes involves three unknowns: $O_B^V$, $N_S$ and $G_{\text{out}}(t)$. Our goal is to estimate the possible $O_B^V$ and $N_S$ values consistent with the acceleration observed in the alite-GO calorimetry data. To do this, we first define a lower and an upper bound for $G_{\text{out}}(t)$, beyond which the rate of growth is meaningless for alite-GO systems. $G_{\text{low}}(t)$ and $G_{\text{up}}(t)$ denote the lower and upper bounds (resp.) of $G_{\text{out}}(t)$ for the alite-GO system, and are defined as:
- $G_{\text{low}}(t)$ is the $G_{\text{out}}(t)$ calculated from fitting Eq. [10] to the calorimetry curve of plain alite paste (having the same $R_{\text{wc}}$ as alite-GO) using $O_{V}^B$ and $N_S$ of plain alite. Any $G_{\text{out}}(t)$ computed for alite-GO should lie above this level since alite-GO always hydrates faster than plain paste (as shown in the results).

- $G_{\text{up}}(t)$ is the $G_{\text{out}}(t)$ computed from fitting the alite-GO calorimetric data but using the $O_{V}^B$ and $N_S$ values of plain paste. According to the BNG formulation, the acceleration in alite-GO hydration can be associated to three factors: (i) extra solid surface for nucleation ($O_{V}^B$), (ii) higher nucleation sites ($N_S$), (iii) higher growth rate of hydration products ($G_{\text{out}}(t)$). In essence, $G_{\text{up}}(t)$ neglects the first two factors and considers the alite surface to be the only place available for the nucleation. Therefore, $G_{\text{up}}(t)$ ignores the contribution of GO as a nucleation surface and any acceleration observed in the calorimetric data is solely attributed to the rate of growth ($G_{\text{out}}$). By increasing $O_{V}^B$ and $N_S$ for alite-GO system (i.e. GO starts to act as a surface in the model) the $G_{\text{out}}(t)$ resulting from the BNG fitting reduces and so is bound to be lower than $G_{\text{up}}(t)$.

Once $G_{\text{low}}(t)$ and $G_{\text{up}}(t)$ are defined, $O_{V}^B$ and $N_S$ are incremented systematically from their plain values considering all possible pairings. For each pair, $G_{\text{out}}(t)$ is computed. Only those $[N_S,O_{V}^B]$ combinations such that $G_{\text{low}}(t) < G_{\text{out}}(t) < G_{\text{up}}(t)$ are deemed consistent with the hydration data. The ranges of $N_S$ and $O_{V}^B$ obtained from this process are then used in Eqs. [5] to calculate $S_{GO}$ and $N_{S}^{GO}$. In this way, the BNG calculation allows us to consider all possibilities and determine the extent to which GO adds extra surface and nucleation sites in alite paste.
2.4. Characterisation of GO chemical structure and its aqueous solution

The chemical structure of GO was characterised by recording the X-ray photoelectron spectra (XPS) of solid graphite oxide sample over a spot size of 400 µm and dwell time of 50 ms, using a photoelectron spectrometer (K- Alpha XPS, ThermoFisher Scientific) with a monochromated Al Kα source. C1s spectra were recorded 10 times with a resolution of 0.1 eV. In addition, Fourier Transform Infrared spectroscopy (FT-IR) was conducted on the graphite oxide sample using a FT-IR spectrometer (Bruker, Tensor II). The spectra were recorded with 256 scans at 4 cm\(^{-1}\) resolution. The specific aim of this characterisation was to identify the functional groups existing in the chemical structure of GO, and to relate their presence to the colloidal stability of GO in water. To explain this relationship, the pH and zeta-potential of aqueous solutions containing 0.6, 1.2, 2 and 2.4 mg/mL of GO were measured using a pH meter (Sevenmulti, Mettler Toledo) and zeta-potential analyser (Brookhaven, NanoBrook Omni). The measurement of pH was repeated 10 times over a period of 20 minutes for each sample, and the mean value along with the data distribution was reported. The maximum range of pH observed in this study was ±0.2.

2.5. Interaction of calcium electrolytes and alite pore solution with GO layers

In general, the aqueous pore solution of alite paste contains various ionic species produced from the dissolution reaction of alite particles in water, according to Eq. [11]:

\[ \text{C}_3\text{S} + 3\text{H}_2\text{O} \rightarrow 3\text{Ca}^{2+}{}_{(aq)} + 4\text{OH}^-{}_{(aq)} + \text{H}_2\text{SiO}_4{}^-{}_{2(aq)} \]  

The concentration of calcium in alite paste is much higher than any other divalent cations, such as Mg\(^{2+}\), and therefore, this study mainly focuses on
the interaction of Ca$^{2+}$ with GO. In addition to calcium cations, the pH of alite (and PC) paste is known to be highly alkaline.

The interaction of calcium and hydroxide ions with GO was characterised using a series of GO solutions, each containing a specific dosage of GO, and mixed with various solutions containing Ca$^{2+}$. Three sources of calcium-solution were considered: (i) saturated calcium hydroxide solution (CH) with [Ca$^{2+}$]=23.3 mmol/L, (ii) calcium chloride solution (CC) prepared such that it contains the same [Ca$^{2+}$] as that of CH, (iii) alite pore solution (PS).

The preparation of PS was carried out by mixing 200 ml of de-ionised water with 4 g of anhydrous alite powder to yield a dilute suspension with a water to solid mass ratio of 50. The alite suspension was stirred for 30 minutes in order to ensure that enough ionic species were available in the pore solution, and thereafter, the undissolved particulates were separated from the solution by centrifuging the suspension for 10 minutes at a speed of 3500 rpm. Then the supernatant was removed and passed through a 0.45 µm syringe filter, and the resulting solution was used as PS. Before any use, centrifugation and filtering were also carried out on the CH and CC solution to ensure the removal of undissolved particulates.

To help identify the mechanism behind the GO interaction with alite pore solution, the effect of various concentrations of GO (ranging from 0.33 mg/ml to 2.66 mg/ml) on the uptake of calcium was quantitatively analysed using ICP-AES. For this quantitative experiment, only the GO-CH and GO-CC solutions were studied since it was possible that the pore solution of alite suspension was saturated with respect to C-S-H and some precipitates could have formed during the sample preparation, affecting the ICP data. For the ICP study, samples were prepared by mixing 5 ml of GO aqueous colloid with 5 ml of either CC or CH solution, and then the solid was extracted
from the solution by centrifuging for 15 minutes at 3500 rpm speed. 5 ml of supernatant obtained from this process was acidified using 1% HNO₃ solution and selected for ICP-AES analysis. For each GO dosage, the whole preparation and ICP measurement were repeated three times to evaluate the variability in measured data, and the mean value as well as the variation were reported.

The effect of calcium solutions on the chemical structure of GO was also investigated. To do this, 40 ml of 0.6 mg/ml GO aqueous colloid was mixed separately with 40 ml of the CH, CC and PS solutions, and the GO solid was removed from the aqueous solution using centrifugation and dried for 18 hours in a freeze-dryer with no pre-freezing. The dried GO samples, referred to as GO-CC, GO-CH and GO-PS were characterised using FT-IR, XRD and TG. The XRD patterns were recorded over 5° to 50° with the step size of 0.022°. 8 mg of each dried GO solid was analysed in a TG instrument (Netzsch, TG 209 libra) at a heating rate of 2 °C/min from 30 to 400 °C under nitrogen atmosphere (20 ml min⁻¹). For this characterisation, the solid of GO was washed-centrifuged 5 times with de-ionised water before freeze-drying to remove the ionic species that could otherwise remain in the sample as a result of drying.

3. Results and Discussion

3.1. Effect of GO layers on the hydration of alite

Fig. 4 shows the rate of heat evolution for the reaction of alite with water in the absence and presence of GO nano-layers, measured for various water to alite mass ratios. In general, all the heat evolution curves follow the typical pattern of alite hydration, including a period of accelerating heat flow which
thereafter starts to decelerate. It can be observed that for all water to alite mass ratios (Figs. 4a-d), the alite pastes containing GO have a slightly altered hydration pattern compared to the plain samples. GO marginally increases both the rate of heat flow during the acceleration period as well as the peak of heat flow; however, the time required to reach the maximum heat flow remains almost unchanged for all samples, regardless of their water to solid mass ratios. It can also be seen that the higher the water to alite ratio in the paste (higher aqueous volume), the more pronounced the effect on the hydration pattern.

To compare the hydration trends observed in Fig. 4 more systematically, the heat evolution experiment was repeated three times, and each calorimetry curve was analysed using three parameters which characterise the main features in the trend of heat evolution, as described in Section 2.2. Figs. 5a-c show the trend of $(d^2Q/dt^2)_{acc}$, $(dQ/dt)_p$ and $t_p$ as a function of GO concentration. Figs. 5a and 5b confirm that the rate of acceleration period, $(d^2Q/dt^2)_{acc}$, as well as the peak rate, $(dQ/dt)_p$, increase slightly (and vary almost linearly) with the concentration of GO. Fig. 5c shows that the time of peak does not depend appreciably on the concentration of GO in alite paste.

The calorimetric results show that the presence of GO accelerates the hydration of alite. Since the rate of formation of hydration precipitates is a rate-controlling step during the acceleration period [30-33], the calorimetry findings are in line with the role of GO as a nucleation-growth site in cement paste. However, the extent of observed acceleration seems to be quite low and not as significant as expected from previous reports [2]. To further investigate this, we use the BNG model described in Section 2.3. Our BNG analysis aims to estimate the possible extra surface and nucleation
sites provided by GO in alite-GO hydration consistent with the acceleration observed in the calorimetry data. To do this, we first calculate \(G_{\text{low}}(t)\) and \(G_{\text{up}}(t)\) as defined in Section 2.3. Fig. 6a shows the patterns of \(G_{\text{low}}(t)\) and \(G_{\text{up}}(t)\) for alite paste containing 0.08%GO with \(R_{\text{wc}}=0.6\). This system is selected for illustration. \(G_{\text{up}}(t)\) describes the acceleration of alite-GO hydration solely in terms of the growth rate, and it neglects the contribution of GO as a nucleation surface. The presence of GO as a surface was included in the BNG model by increasing the \(N_S\) and \(O_{V}^{B}\) values. Figs. 6b-c show the dependence of \(G_{\text{out}}\) at times \(t=2\) hours and \(t=10\) hours as \(N_S\) and \(O_{V}^{B}\) values are increased. These times were only selected as illustrative examples. Figs. 6b-c confirm that \(G_{\text{out}}\) is a decreasing function of \(N_S\) and \(O_{V}^{B}\). Since the state of GO in alite paste is unknown, it is not possible to directly determine \(O_{V}^{B}\), \(N_S\) and \(G_{\text{out}}(t)\) for alite-GO pastes. However, we can find all possible ranges of these variables.

As described in Section 2.3, all \([N_S,O_{V}^{B}]\) combinations can be determined such that their corresponding \(G_{\text{out}}(t)\) falls between \(G_{\text{up}}(t)\) and \(G_{\text{low}}(t)\). For instance, Fig. 7 shows \(G_{\text{out}}\) at \(t=10\) hours resulting from the BNG fitting for various combinations of \([N_S,O_{V}^{B}]\). The acceptable values of \(G_{\text{out}}\) in Fig. 7 are those that lie above the orange plane surface \((G_{\text{low}})\) and remain below point A \((G_{\text{up}})\). Considering all acceptable points in Fig. 7, there are three kinds of possibilities for the GO as a nucleation surface in alite paste: (i) high \(N_S\) but low \(O_{V}^{B}\) (towards point B), (ii) low \(N_S\) but high \(O_{V}^{B}\) (towards point C), (iii) moderate \(N_S\) and moderate \(O_{V}^{B}\) (e.g. point D). The ranges of acceptable \(N_S\) and \(O_{V}^{B}\) such that \(G_{\text{low}}(t) < G_{\text{out}}(t) < G_{\text{up}}(t)\) are given in Table 1 for alite-0.08%GO pastes at various water-to-alite ratios.

Using the \(O_{V}^{B}\) value from Table 1, the possible maximum and minimum values of GO surface area \((S_{GO})\) involved in the alite-GO hydration was
calculated using Eq. 5 and Eq. 6. Taking the calculated $S_{GO}$ and the $N_S$ values given in Table I, the number of active nucleation sites per unit area of GO surface ($N_{S}^{GO}$) was calculated using Eq. 7, and the maximum and minimum values are also given in Table I. It can be seen from Table I that the BNG-calculated $S_{GO}$ values (maximum 230 m$^2$/g) are about one order of magnitude lower than the theoretical predication of $S_{GO}$ (1500-1700 m$^2$/g). The BNG calculated $N_{S}^{GO}$ values are 15-500 $\mu m^{-2}$. A theoretical value of $N_{S}^{GO}$ can be predicted using Eq. 12:

$$N_{S}^{GO} = \left[ \frac{N_{active}}{S_{GO}} \times N_{Av} \right] \times 10^{-15}, \quad (12)$$

where $N_{active}$ is the potential quantity of active sites per gram of GO (mmol/g) which is 5-8 mmol/g according to [33]. This leads to a theoretical $N_{S}^{GO}$ value between 1.99 – 2.75 $\times$ 10$^6$ for per unit area of GO single layer. The $N_{S}^{GO}$ estimated from BNG fitting is several orders of magnitude lower than what GO could potentially provide in the paste.

The BNG results indicate that the acceleration observed in the calorimetric patterns of alite-GO hydration involves a small fraction of GO surface area and active sites. This sheds some doubt on the effectiveness of GO as nucleation site in alite paste in contrast to previous reports [10–12, 14].

The micrographs of pastes hydrated for 24 hours with and without GO are shown in Fig. 8. It can be seen from Fig. 8b that in the alite-GO paste, there are in-homogeneously scattered dark-brown aggregates which represent the state of GO in the hydrated paste. From this, as well as the BNG analysis, we hypothesise that the aggregation of GO in alite paste could be at the origin of GO ineffectiveness as nucleation-growth sites. The remainder of the paper investigates this hypothesis by considering the chemical structure of GO and its interaction with various calcium electrolytes including the
pore solution of alite paste.

3.2. Characterisation of GO chemical structure

The chemical structure of GO is characterised using the FT-IR and C1s XPS patterns shown in Fig. 9. The chemical features of GO are described in some detail in this section as they will be shown to be key in explaining the interaction of GO with the pore solution of alite paste.

The FT-IR spectrum of GO shown in Fig. 9a, reveals five main vibration regions. Assigning a definite chemical group to each peak is not straightforward, and the peak identification proposed here is based on a wide survey of the GO literature. The spectrum features a broad region in the range of 2400-3700 cm$^{-1}$ which is associated with the stretching vibration of O-H ($v_{\text{OH}}$). The peak band in this region (band 5) has been attributed to the vibration of O-H existing as part of the GO structure as well as the adsorbed water molecules on the surface of GO [35, 36]. The peaks at $\sim$1225 cm$^{-1}$ (band 1) and 1354 cm$^{-1}$ (band 2) are related to the vibration of C-O and the bending vibration of C-OH, respectively [37]. The relatively strong band at 1692-1728 cm$^{-1}$ (band 4) is attributed to the stretching vibration of non-carboxyl carbonyl (C=O), which may exist in single structures such as ketones, or can be part of chemical structures such as carboxylic anhydrides [36]. Inset A shown in Fig. 9a highlights the presence of a small shoulder at 1585 cm$^{-1}$ which is the characteristic peak of de-protonated carboxyl (carboxylate) structure. The peak at 1619 cm$^{-1}$ (band 3) is commonly attributed to the stretching vibration of the carbon network (C=C) [10, 12, 21, 38]. However, the assignment of this band is not straightforward as it overlaps with that of water molecules undergoing O-H bending vibration ($\beta_{\text{OH}}$). Mermoux et al. [35] showed that the FT-IR spectrum of
strongly de-hydrated GO has no significant peak at 1619 cm$^{-1}$. This has been recently confirmed by Szabo et al. [37] and Dimiev et al. [34] using deuterated GO, suggesting that the 1619 cm$^{-1}$ peak cannot solely represent the carbon network, and the intensity of this peak may be altered in the presence of surface-bound water in GO.

Further to the FT-IR results, the XPS C1s spectrum of GO shown in Fig. 9b, indicates that the carbon atoms are in three chemical states. The first peak at 285 eV corresponds to a non-oxygenated carbon structure which can be present in both forms of C=C and C-C hybridised carbon. The peak at 286.6 eV is attributed to the carbon from C=O and C-O structures which can exist in GO within the carbonyl, hydroxyl and epoxide functional groups. The last peak at 288.5 eV indicates the presence of carboxylate (O-C=O) structures.

Two key features must be highlighted from the analysis of GO: first, a variety of oxygen-containing functional groups exist in the GO structure which have hydrophilic characteristics, second, the 1585 cm$^{-1}$ peak in FT-IR curve and the O-C=O peak in the XPS spectrum indicate that the GO structure contains carboxylate structures.

3.3. Factors controlling the colloidal stability of GO in water

GO forms well-dispersed colloids in water due to its functional groups [1,18]. The overall effect of these groups is to counteract Van der Waals forces between the GO layers which would otherwise make them agglomerate. In detail, this is achieved through several concurrent mechanisms:

- The GO layers are negatively charged in water. This is primarily due to the presence of carboxyl groups which can dissociate in water,
releasing protons (H\(_+_\)) as described by reaction Eq. 13:

\[
\text{C-OOH} + \text{H}_2\text{O} \rightarrow \text{C-OO}^- + \text{H}_3\text{O}^+ \quad (13)
\]

This reaction makes the aqueous solution acidic and also causes the GO layers to be negative as confirmed by the pH and zeta-potential measurements shown in Fig. 10. It can be seen that the pH is acidic (∼3), and the values of zeta-potential are highly negative for all GO solutions. Most agree that the carboxyl group contributes to the negative zeta-potential but other mechanisms still being debated could also play a role [34, 39, 40].

- The functional groups of GO are all hydrophilic causing water molecules to be strongly bonded to these groups. Evidence of surface-bound water has previously been reported by Buchsteiner et al. [41] and Cerveny et al. [42], but this has rarely been related to the stability of GO in water.

Using these mechanisms as basis for the stability of GO in water, the following sections describe how the pore solution of alite paste or other calcium-containing electrolytes interact with GO layers in aqueous environment.

3.4. Interaction of GO layers with calcium cations

Fig. 11a shows an aqueous colloid of GO with a solid concentration of 0.3 mg/ml prepared by mixing 5 ml of 0.6 mg/ml GO colloid with 5 ml pure de-ionised water. The GO colloid appears homogeneous with a brownish colour. To test the effect of various ionic species on the colloidal stability of GO, two separate 5 ml GO colloids (0.3 mg/ml) were mixed with 5 ml of saturated calcium hydroxide (Fig. 11b) and 5 ml of pore solution of
alite paste (Fig. 11d). The measured pH values of Ca(OH)$_2$ (CH) and alite pore solution (PS) prior to mixing with the GO solution were 12.1±0.18 and 11.6±0.2, respectively. It can be seen that the GO layers have coagulated in the GO-CH and GO-PS. To verify whether this agglomeration still occurs with a low-pH calcium electrolyte, a calcium chloride solution with pH=8±0.2 containing the same concentration of Ca$^{2+}$ as that of saturated CH ([Ca$^{2+}$]=23.3 mmol/L) was mixed with 5 ml GO colloid. This mix is shown in Fig. 11c. As can be seen, the colloidal stability of GO-CC is similar to the plain GO colloid, and is significantly different to that of GO in GO-CH and GO-PS. Note that the image in Fig. 11 was taken almost immediately after mixing the Ca-based solutions with the GO colloid, and although not clear from the picture, the GO-CC solution does in fact contains very small agglomerates and even precipitate a few hours after the mixing. From these observations, a pH-dependent interaction between GO and calcium-containing solutions clearly takes place which causes the GO layers to flocculate.

To analyse more thoroughly how GO interacts with the Ca-electrolytes, the concentration of calcium in various GO-Ca solutions was measured using ICP-AES, as explained in Section 2.5. Fig. 12a shows the concentration of calcium as a function of GO dosage in water. It appears that for the GO-CC mix, there is no appreciable change in the concentration of calcium. By contrast, the calcium content decreases noticeably in the GO-CH mix as the concentration of GO in the solutions increases. The ICP data suggest that a cationic interaction between Ca$^{2+}$ and GO only happens when the GO solution is exposed to a high pH environment. Since the pH of alite pore solution is similar to that of calcium hydroxide, it can be expected that the same Ca-interaction occurs between GO layers and alite pore solution.
As an attempt to correlate the calcium uptake with the concentration of carboxylate, the shaded area in Fig. 12a shows the range of quantity of carboxylate functional groups available in the GO-CH solutions. This range was obtained using three XPS C1s surveys conducted on the 400µm area of dried GO solid (shown in Fig. 12b). The concentration of carboxylate, denoted $\alpha_{O_2C}$ (mmol/ml) was calculated using equation Eq. 14:

$$\alpha_{O_2C} = \frac{A_{O_2C}}{A_T} \times \frac{M_{GO}}{M_{O_2C}},$$

(14)

where $A_{O_2C}$ is the area under the deconvoluted fitting curve corresponding to the O-C=O structure as shown in Fig. 9. $A_T$ is the total area under the XPS C1s spectrum, $M_{O_2C}^m$ is the molar mass of carboxylate group, and $M_{GO}$ is the mass of GO per unit volume of solution (mg/ml). It was found between 7 to 16.5% of the carbons of GO exist within a carboxylate structure. This implies for instance that $\alpha_{O_2C}$ could be in the range of $1.59-3.75 \times 10^{-3}$ mmol/ml for 1 mg/ml GO solution.

Fig. 12a shows that the concentration of calcium in the solutions follows that of the carboxylate groups suggesting that the carboxylate groups interact with calcium ions. At pH=3, the carboxyl groups have a low degree of dissociation and would not interact much with calcium. As the pH increases, the carboxyl groups become more de-protonated (carboxylated) and more susceptible to form a complex with the calcium cations. Therefore, a plausible mechanism that governs the calcium interaction with GO layers could be based on the complexation of calcium with de-protonated carboxyl (carboxylate) groups. Accordingly, the carboxyl groups which were an important source of negative charges between the GO layers can no longer act in this role, causing the GO layers to aggregate in GO-CH and GO-PS solutions shown in Fig. 11.
A number of studies have investigated the aggregation kinetics of GO in the presence of calcium chloride \[43–45\]. All pointed out that Ca\(^{2+}\) ions affect the colloidal stability of GO. Without measuring the uptake of calcium directly, they suggest that the mechanism controlling the aggregation of GO is related to the adsorption of calcium on the functional groups of GO. However, the ICP data in Fig. 12a shows that there is almost no uptake of calcium in the GO-CC solution, suggesting that the GO aggregation we observed in the GO-CC mix cannot simply be explained by the role of calcium and it is likely that the calcium interaction is not the main controlling mechanism for the colloidal instability of GO in GO-CC.

3.5. pH-dependent stability of GO chemical structure in Ca-based electrolytes

Fig. 13 shows the FTIR spectra of various GO samples extracted from the GO-CH, GO-CC and GO-PS solutions, prepared according to the methodology described in Sections 2.2.2. Comparing the plain GO sample with GO-CH and GO-PS, it can be seen that the main peak associated with the non-carboxyl carbonyl group has disappeared from the spectrum (1728 cm\(^{-1}\)). The 1223 cm\(^{-1}\) peak band which could be related to the epoxide group, or possibly other C-O structures, is also significantly lower. However, from the spectrum of GO-CC, it can be seen that these peak bands are still present in this sample, and there is a sharp amplification of 1619 cm\(^{-1}\) peak which was identified before (Fig. 9) as the bending vibration of water molecules. Note that the spectrum of GOPlain corresponds to the sample analysed after synthesis, whereas the other spectra were measured on dried samples extracted from an aqueous solution. It should be noted that although the major peaks still exist in the spectrum of GO-CC sample, the chemical structure of this sample is not left intact. It can be seen that
the C-O peak band (1223 cm\(^{-1}\)) is reduced for this sample.

The FT-IR spectra suggest that GO has been de-oxygenated in all Ca-containing mixes, and that the degree of structural alteration depends on the pH of the electrolytes used to prepare each mix. As the GO-CC sample has more hydrophilic functional groups, it contains more bound-water compared to GO-CH and GO-PC. This can be clearly seen from the 1619 cm\(^{-1}\) peak. This shows that as the hydrophilic functional groups are reduced, the intensity of water bending vibration is also decreased.

Since most of the non-carboxyl groups are removed at high pH, it is possible that the de-oxygenation mechanism of GO is controlled by reactions between the hydroxide ions and those groups, as also shown by Dimiev et. al. [34]. Considering the ICP data and the FT-IR pattern of GO-CC, it can be concluded that the adsorption of calcium is not the primary mechanism destabilising the dispersion of GO colloids in GO-CC mix, but that it is rather the loss of hydrophilic functional groups. The same mechanism along with the calcium-uptake could occur in the GO-PS and GO-CH mixes.

In discussing the ICP data shown in Figs. 12a and 12b, it was suggested somewhat tentatively that calcium mostly interacts with the carboxyl groups in GO-CH. This is further confirmed by the FT-IR spectrum of GO-CH showing a more pronounced peak associated with the carboxylate structure. This implies that the carboxylate group is the most stable structure in GO at high pH range and therefore the only one left to interact with calcium.

The X-ray diffraction patterns of various electrolyte-treated GO samples are shown in Fig. 14. The pattern of GO-plain shows no background and a single peak representing a distance of 7.78 Å between GO layers, created due to the surface functional groups in GO as well as water molecules (compared to graphite pattern). The XRD pattern of GO-CC shows that this sample
contains GO structures with various levels of oxidation as there is a clear change in XRD background level with respect to the intensity of the main peak. This background is broadband and indicates an irregular reduction of inter-layer spacing between the GO layers. This is made possible by the disappearance of some of the functional groups. The change in GO-CC structure is consistent with the de-oxygenation of this sample as found in the FT-IR.

Comparing the GO-CH and GO-PS with GO-CC and GO-plain, it can be seen that the extent of the spacing irregularity is significantly increased, implying that there should be even fewer functional groups present in GO-CH and GO-PS samples. From this observation, it can be concluded that the majority of remaining functional groups in GO structure are not placed between the graphitic layers (i.e. reduction of functional groups on the GO surface). This confirms the conclusions drawn from the FT-IR spectra according to which carboxylate is the most stable group in GO, which is known to exist at the edge of GO layers [1]. In the XRD pattern of GO-CH and GO-PS, there is a peak corresponding to calcium carbonate which cannot be found in the GO-CC sample. This is consistent with the uptake of calcium in the GO-CH and GO-PS samples, as found in the ICP data. It should also be noted that there is an increase of space between GO layers in GO-CC, GO-CH and GO-PS samples which one might interpret as an intercalation of calcium between the GO layers. However, this should not be seen as an evidence for the uptake calcium in these samples, and the ICP data are more informative in this respect. Overall, the XRD patterns confirm that there is a relationship between the pH of the electrolytes used and the extent of reduction in surface-functionality. The XRD of GO-CH and GO-PS samples indicates that the surface structure of GO is significantly damaged in these
mixes.

Figs. 15a and 15b show the TG and differential TG curves obtained for the plain-GO, GO-CH, GO-PS, GO-CC and GO-W samples. GO-W was acquired by centrifuging the GO solution in its stable colloidal form at a speed of 11000 rpm. The TG curve for the plain GO sample shows two regions of major mass-loss: one around 30-100 °C which is related to the loss of absorbed water on GO, and one between 100-200 °C corresponding to the decomposition of oxygen-containing functional groups [46]. Comparing the plain GO with the GO-CH sample, it can be seen that the level of mass-loss associated with the decomposition of functional groups is reduced significantly from 32.9% for plain GO to 12% for GO-CH. The thermal stability of GO-PS is also affected but less so with a mass-loss of 19.7% at 150-200 °C. In agreement with the FT-IR data, the GO-CC sample has been de-oxygenated, however the position of functional group decomposition peak has shifted to a higher temperature. An identical shift can be observed between plain GO and GO-W. In this case, the shift can only be attributed to the presence of water in GO-W sample. The XRD pattern of GO-W shown in Fig. 14 also suggests that the inter-layer distance of GO layers are increased in this sample compared to plain GO as a result of water-intercalation between the layers. From the identical position of GO-CC peak, it is reasonable to infer that the peak has shifted because of strongly bonded water molecules to the oxygen-based functional groups of GO. The higher mass-loss below 100 °C for the GO-CC and GO-W samples also confirms this. Comparing the position of the DTG peaks of GO-W and GO-CC with that of GO-CH and GO-PS suggests that latter two contain less bound water as there are fewer functional groups remaining in their GO structure.
The TG results confirm that (i) GO-CC contains more functional groups than GO-CH and GO-PS and (ii) the more functional groups present, the more water is still bonded on the GO surface. Therefore, one would clearly expect that the loss of hydrophilic functional groups plays a role in controlling the stability of GO dispersion in water. As GO loses its functional groups in exposure to high pH electrolytes (i.e. GO transforms to a hydrophobic material), it tends to form aggregates. This explains the observations made from Fig. 11: the GO-PS and GO-CH have lost most of their dispersing capacity and GO-CC occupies a somewhat intermediate position in terms of dispersion.

3.6. Mechanisms controlling the stability of GO dispersion in alite paste

According to the mechanisms discussed in Sections 3.4 and 3.5, the nanolayers of GO aggregate in the pore solution of alite paste. This aggregation occurs while mixing the GO suspension with alite particles, and starts from the very first seconds of hydration when the alite particles dissolve in water. Two mechanisms simultaneously cause the instability of GO dispersion in alite paste: (i) the carboxylated GO layers form complexation with calcium ions available in the pore solution of paste, (ii) due to the high alkalinity of the paste environment, GO reduces and loses its hydrophilicity.

In addition to the interaction of GO with the paste pore solution, it is worth mentioning that the negatively charged carboxylated GO layers may be electrostatically attracted to the surface of alite particles and/or form complexation with the Ca ions at the alite surface. This interaction is reported for carboxylate-based polyelectrolytes with cement particles, and is known to retard the cement hydration [47, 48]. The retardation occurs as the carboxylated groups adsorb onto the surface of cement particles and/or
complex with the calcium ions present at the surface, affecting the dissolution reaction. Since our calorimetry results show no sign of retardation (Fig. 4), the surface interaction mechanism does not seem to occur in the present study. However, it could play a role in other cement systems.

4. Conclusions

In this paper, the hydration of alite was first investigated in the presence of GO nano-layers using isothermal calorimetry. Results indicated that the presence of GO accelerates alite hydration. However, the observed acceleration was found to be quite low. A boundary nucleation-growth (BNG) model was used to better understand the role of GO as a nucleation-growth site. The BNG analysis showed that the amount of extra surface and nucleation sites added by GO was several orders of magnitude lower than what GO could potentially provide in alite paste. Direct microscopical observations pointed to the aggregation of GO in the paste. This led us to investigate the colloidal stability of GO in various calcium electrolytes including the pore solution of alite paste.

Results showed that GO aggregates when exposed to high-pH electrolytes containing calcium cations. The main mechanisms causing this instability are:

• Due to the high pH environment, the carboxyl group of GO nano-layers are de-protonated, forming complexation with calcium cations released from the dissolution of alite in water.

• The hydrophilic functional groups present on the GO surface are reduced, possibly as a result of a reaction between hydroxide ions and GO.
As the pore solution of alite paste is highly alkaline and rich in calcium ions, these two mechanisms simultaneously prevent the effective dispersion of individual GO layers in alite paste.

Overall, the findings of this study imply that the mechanisms commonly proposed in the literature to explain the role of GO in PC paste are probably invalid as the structure of GO prevents it from being well dispersed in high pH and calcium-rich environments. Considering that GO had little effect on the kinetics of hydration and that it was shown to agglomerate in alite paste, it is unlikely that the significant strength improvements previously reported in the literature resulted from GO single layers serving for the nucleation of hydration precipitates. Since GO reduces at high pH and loses the majority of its surface functional groups, the idea of interfacial bonding between GO and C-S-H suggested in previous studies needs to be revisited. If the aim is to achieve a good dispersion of GO in PC paste, further work should focus on functionalising graphene with different groups such that the mechanisms brought to light here are not encountered.

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Laboratory.

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Table 1: Range of $N_S$ and $O^B_V$ values involved in the hydration of alite-GO paste containing 0.08%GO, obtained from the BNG analysis. $S_{GO}$ and $N^S_{GO}$ values were calculated using Eq. 5, Eq. 6 and Eq. 7.
Figure 1: (a) Particle size distribution of alite used to study the hydration kinetics, (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.
Figure 2: AFM micrograph of GO: (a) tapping mode topographic image of GO deposited on a freshly cleaved mica surface, (b) height profile for the line-section shown in (a) confirming that the synthesised GO is in the form of mono-layer with an approximately 1 nm thickness, (c) height distribution of GO layers studied over 50µm×50µm, indicating that GO is dominantly in the form of single layer.
Figure 3: (a) Typical heat evolution curve of alite hydration along with the parameters extracted in order to quantitatively compare the hydration of plain and GO-containing alite pastes, (b) BNG fitting simulation to the calorimetric pattern obtained for the hydration of alite paste with water:alite mass ratio of 0.5, (c) time-dependent growth rate of hydration product ($G_{out}$) found as a result of BNG simulation for the calorimetric data shown in figure (b).
Figure 4: Rate of heat evolution ($dQ/dt$) for the reaction of alite with water in the presence of various concentrations of GO nano-layer. Rate is normalised by the mass of alite and is measured for four water to alite mass ratios: (a) 0.3, (b) 0.4, (c) 0.5, (d) 0.6.
Figure 5: Influence of GO concentration on three parameters characterising the heat evolution curves of alite hydration: (a) the rate of acceleration period \((d^2Q/dt^2)_{acc}\), (b) the value of heat rate at the peak \((dQ/dt)_p\), (c) the time at which the maximum rate peak occurs, \(t_p\). 

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Figure 6: (a) Growth rate of hydration precipitates ($G_{out}$) as a function of time, acquired by fitting the BNG equations to the calorimetry curve of plain alite (straight line) and alite-GO (dashed line) paste. These curves correspond to $G_{low}(t)$ and $G_{up}(t)$ as defined in Section 2.3. Both curves were calculated using $N_S = 12 \mu m^{-2}$ and $O^V = 0.6235 \mu m^{-1}$. The growth rate is only presented here for pastes with water to alite ratio of 0.6, and the alite-GO paste contains 0.08% GO. (b) and (c) show the dependence of $G_{out}$ at times $t=2h$ (circle) and $t=10h$ (dimond) as total $N_S$ (with $O^V = 0.6235 \mu m^{-1}$) and OBv (with $N_S = 12 \mu m^{-2}$) are varied in the fitting simulation of alite-GO calorimetry curve. Horizontal dashed lines in (b) and (c) show the lower- and upper bounds in (a) at times 2 and 10.
Figure 7: Growth rate of precipitates ($G_{out}$) at time $t=10$ hours as a function of $N_S$ and $O_V^B$ used in the BNG fitting (gray surface). The plane surface (orange) corresponds to $G_{low}(t)$, and point A shows the maximum allowed $G_{out}$; that is $G_{up}$. Points B and C are the maximum allowable $N_S$ and $O_V^B$, respectively. Any $G_{out}$ points located above the plane surface but below point A are deemed consistent with the calorimetry data, for instance point D.
Figure 8: Micrograph of GO aggregation in alite paste captured using a light microscope with magnification X8 (Discovery V8, ZEISS): (a) plain alite paste, (b) GO-alite paste. Image was captured for a sample hydrated for 24 hours with water to alite ratio of 0.5.
Figure 9: (a) FT-IR spectrum of GO, suggesting the vibration of C-O (band 1), C-OH (band 2), water molecules bound on the surface of GO (band 3 and 5), non-carboxyl C=O (band 4), O-H group (band 5). Inset A magnifies the FT-IR spectrum at the peak band 3, and it points out to the presence of a shoulder corresponding to the vibration of de-protonated carboxyl group (carboxylate); (b) C1s XPS spectrum of GO, which is de-convoluted into three chemical states, indicated as sp$^2$ and sp$^3$ hybridized carbon, carbonyl (C=O), alcohol and epoxide (C-O), and carboxyl (O-C=O) functional groups.
Figure 10: Zeta-potential of GO nano-layers measured in water (right axis) and pH of GO aqueous solution (left axis) as a function of GO dosage in water (mg/ml).
Figure 11: Coagulation of GO solution as a result of introducing Ca-electrolytes: (a) GO mixed with pure de-ionised water, (b) GO-CH prepared by mixing GO solution with saturated Ca(OH)$_2$ – in this mix there is [Ca$^{2+}$]=11.5 mmol/L available to interact with GO layers, (c) GO-CC is the mix of GO solution with CaCl$_2$ solution, also having [Ca$^{2+}$]=11.5 mmol/L, (d) Pore solution of alite paste extracted from a dilute aqueous suspension of alite powder (H$_2$O:alite= 50). Note that this image shows the condition of GO solutions almost immediately after the mixing with electrolytes, and small aggregates form in the GO-CC mix which are not visible in this image.
Figure 12: (a) Calcium concentration as a function of GO dosage in aqueous solution, indicating that Ca is removed by GO layers only in the case of GO-CH mix where GO layers are exposed to high alkaline environment (pH > 12). Assuming that each carboxyl group of GO is converted to carboxylate and is an active site to form complexation with calcium, the two dashed lines show the possible upper- and lower-boundary of carboxylate quantity that can remove Ca cations from the solution. (b) C1s XPS spectra (data is normalised and the background is removed) which were used to quantify the amount of carboxylate group in GO sample in order to calculate the dashed lines shown in (a).
Figure 13: FT-IR spectra of plain GO, GO-CH, GO-CC and GO-PS, indicating that the oxygen-based functional groups of GO were reduced in exposure to calcium-containing electrolytes. The extent of this reduction depends on the pH of the electrolytes mixed with the GO aqueous solution.
Figure 14: XRD patterns of graphite, plain GO, GO-W, GO-CH, GO-CC and GO-PS presented as a function of Q (Q equals to $2\pi/d$, where d is the distance between the graphene and GO layers in graphite and graphite oxide crystal structures, respectively). Note that the vertical dashed line with $d=5.711$ Å corresponds to the distance between GO layers in a completely dried GO sample.
Figure 15: TG patterns of plain GO, GO-CH, GO-CC, GO-PS and GO-W: (a) mass-loss as a function of heating temperature; (b) differential mass-loss of TG patterns shown in (a).