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Effects Of Graphene Oxide On The Early-Age Hydration Of SCM Modified Low-Carbon Cementitious Composites

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Abstract **-** While graphene oxide (GO) has been shown to significantly improve the early-age hydration and mechanical properties of clinker-based cementitious materials, additional supplementary cementitious materials (SCMs) such as ground granulated blast-furnace slag (GGBS) can slow the early age hydration rate, while the opposite can occur with addition of limestone fines (LF). These SCMs in combination with GO can cause interdependent interactions which could potentially offset their individual drawbacks, however the nature of the GO-, GGBS- and LF-cement interactions remains unclear. Towards understanding this, the present study investigates the effects of GO on the early-age hydration of GGBS and LF modified low-carbon cementitious composites. The heat of hydration rate, cumulative heat of hydration, and relative setting time of cement pastes incorporating GO (0.08% by weight of binder), GGBS (0-60% by weight of binder), and LF (0-20% by weight of binder) were evaluated using an isothermal calorimeter measurement method. The results show that GO can significantly reduce the dormant period of cement hydration, shift the hydration heat rate peaks upwards and earlier, and improve the overall hydration degree by accelerating the hydration process in cement. The combination of GO and supplemental cementitious materials offers a promising avenue for SCMs-modified binders with enhanced performance and reduced carbon footprint.

Keywords**:** Embodied carbon reduction, Ground Granulated Blast-furnace Slag, Isothermal calorimetry, Limestone fines, Nanomaterials

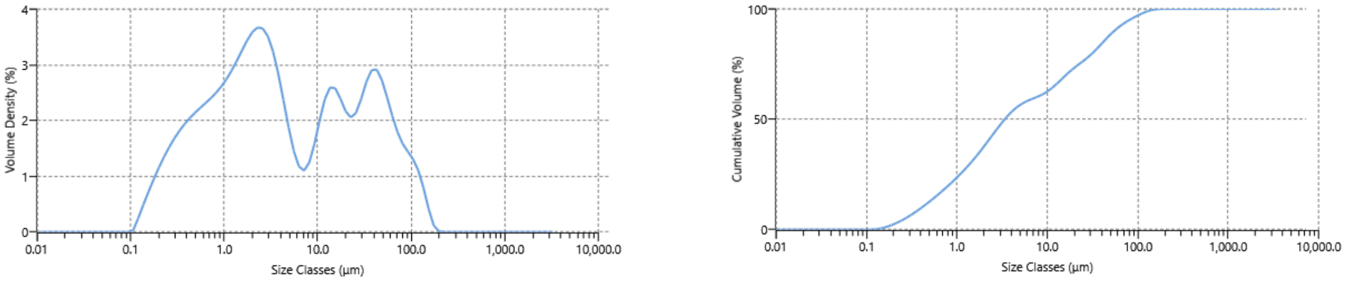
1. Introduction

Portland cement concrete is recognized as the most widely used construction material globally [1]. However, Ordinary Portland Cement production comes with significant environmental consequences and results in high CO_2 emissions, which is widely recognized as a major contributor to the overall carbon footprint of construction [2]. To address this pressing issue, supplementary cementitious materials have been incorporated to partially replace Portland cement. Among the commonly used SCMs, limestone fines and GGBS are particularly promising partial replacements for clinker due to their low carbon footprint, i.e., 0.03-0.06 kg of CO_2 per kilogram of limestone fines and 0.05-0.5 kg of CO_2 per kilogram of GGBS [3], compared to 0.8 kg of CO_2 per kilogram of clinker [4]. However, the addition of SCMs effects the performance of cementitious materials in various ways. For example, the dilution effect resulting from SCM additions, especially at large replacement ratios often causes reduction in the overall mechanical properties [5]; some SCMs influences the released heat of hydration which is critical to inducing thermal cracks [6]; and the early-age hydration rate and strength can also be affected depending on the type and content of the SCMs [7]. As a result, many researchers have focused on how to maintain the mechanical performance while achieving a reduction in the carbon footprint. With the discovery of graphene in 2004 [8], the application of nanomaterials in cement-based materials has received extensive attention [9]. Among them, graphene oxide, as a hydrophilic two-dimensional nanomaterial, has been shown in many studies to significantly improve the mechanical strength and durability of cementitious composites at low dosages [10]. When it comes to early-age hydration, SCMs and GO can play a synergetic effect and offset the individual shortcomings associated with each other, however the mechanism of GO-, GGBS- and LF-cement remains unclear. Calorimetry has been well established as a versatile method used to determine, via direct measurement, the heat flow or temperature of the exothermic hydration reaction in cementitious materials. Therefore, a series of isothermal calorimetry tests were conducted in this study to investigate the effect of GO on the early-age hydration of clinker-based cement, both alone and with substitutions of GGBS and LF.

2. Materials and Methodology

2.1. Materials

The materials used in this study include Portland Cement CEM I 52.5N provided by Titan Cement Ltd. in compliance with BDS EN 197-1 [11], GGBS with a density of 2.85 – 2.95 g/cm^3 provided by Ecocem Ltd. in compliance with Regulation (EC) No. 1907/2006 [12], Limestone fines (BETOCARB UF) provided by Omya with $CaCO_3$ content 98.5%, specific surface area (BET) 10 m2/g, and the d_{50} (mean) particle size 7.77 µm. Figure 1 presents the cumulative volume of the average particle size from 10 tests of the ultrafine limestone powder used in this study measured by a Malvern Mastersizer 3000. Commercially available graphene oxide pastes with 49.1% total solid ratio supplied by William Blythe Ltd. were used. The d_{50} platelet size of the GO measured by laser diffraction is 6.5 µm, and the d_{90} is 17.3 µm. A high range polycarboxylate superplasticizer was used to enhance the GO dispersion and increase the workability of the cement paste. The water-to-binder (w/b) ratio was 0.55, and the superplasticizer concentration was 0.3% by weight of binder for all tests for consistency.



(a) (b)

Fig. 1: The particle size of the ultrafine limestone powder (a) volume density (b) cumulative volume.

There are 15 different binder mixes tested in this study with the GGBS content of 0, 15, 30, 45, and 60% by weight of binder, and the LF content of 0, 10, and 20% by weight of binder, see Table 1 for details. The GO dosage tested in this study was 0.08% of the GO total solids by weight of binder and is referred to as G8, while control specimens without any GO are referred to as G0. As an example of the naming convention used in this study, sample M7G8 contains a binder of 75 wt% clinker, 15 wt% GGBS, 10 wt% LF with 0.08 wt% GO.

Table 1: List of binder mixes

	Clinker (wt%)	GGBS (wt%)	LF (wt%)
M1	100	0	0
M2	85	15	0
M3	70	30	0
M4	55	45	0
M5	40	60	0
M6	90	0	10
M7	75	15	10
M8	60	30	10
M9	45	45	10
M10	30	60	10
M11	80	0	20
M12	65	15	20
M13	50	30	20
M14	35	45	20
M15	20	60	20

2.2. Preparation of binder and GO suspension

The binder was prepared by dry hand-mixing the powder of clinker, GGBS (if any) and LF (if any) for 2 minutes until until it was uniformly mixed. The total binder weight for each specimen was 50 g. Aqueous GO suspensions were prepared prepared within an hour of calorimetry testing to prevent flocculation or sedimentation of GO particles. The GO suspensions suspensions were prepared using a Silverson high-shear mixer by the following steps: steps: a. addition of the GO paste into paste into water; b. high shear mixing of the GO-water suspension at 5000 rpm for 10 minutes; c. addition of superplasticizer into the GO-water suspension; d. high shear mixing of the GO-water-superplasticizer suspension at 5000 rpm for 1 minute. The suspension weight for each specimen was 27.5 g.

2.3. Isothermal calorimetry characterization techniques

The early-age hydration of the cement paste was measured by a high precision 4-channel isothermal calorimeter (I-Cal 4000 HPC Isothermal Calorimeter) supplied by Calmetrix. The isothermal calorimeter was calibrated, and all the channels were prepared to maintain a stable temperature of 20 °C. The binder particles (50 g) were hand-mixed with GO suspension (27.5 g) for 2 minutes in a plastic container using a small spoon. After this, the container was sealed by a lid with the mixing spoon in it, and then was placed in the channel of the calorimeter. The starting time of the mixing was recorded for each specimen, and the hydration data was recorded for 72 hrs at 20 °C.

3. Results and discussions

3.1. The effect of GO on pure cement hydration

By comparing the 0 wt% and 0.08 wt% GO samples (M1G0 and M1G8 in Figure 2), it can be seen that the addition of 0.08 wt% GO resulted in a 7% increase in the peak power of hydration, from 4.02 mW/g to 4.30 mW/g, with a 16% reduction in relative setting time.

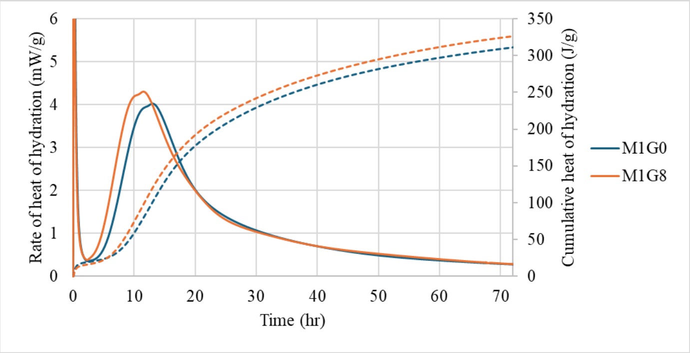


Fig. 2: Effect of GO on the hydration of pure cement paste (Solid line for the rate and dashed line for the cumulative heat)

The relative setting time was taken as the time it took to reach half the maximum of the main hydration peak in the heat flow curve [13]. This is consistent with results which have been reported in other studies [14][15] and is an anticipated result which demonstrates the impact of high surface area of the nanoparticles providing nucleation sites for cementitious hydration reactions [16]. Furthermore, in Figure 2, the observed dual-peak shape in the hydration heat flow curve, with larger intensities for both sub-peaks upon GO addition, indicates a more pronounced formation of C3S and C3A, which are associated with the first and second hydration phases, respectively. Moreover, the cumulative heat of hydration increased 7% from 202.24 J/g to 216.32 J/g at 24 hrs, and increased 5% from 311.12 J/g to 326.30 J/g at 72 hrs. This implies that adding a low concentration, i.e., 0.08 wt% of GO to cement paste accelerates the early-age hydration process forming C-S-H and CH, and hence reduces setting time and increases early-age strength significantly.

3.2. The effect of GO on GGBS-modified cement hydration

The effect of GO on GGBS-modified cement paste was investigated by adding 0.08 wt% GO to 0, 15, 30, 45, and 60 wt% GGBS-modified cement paste as shown in Figure 3.

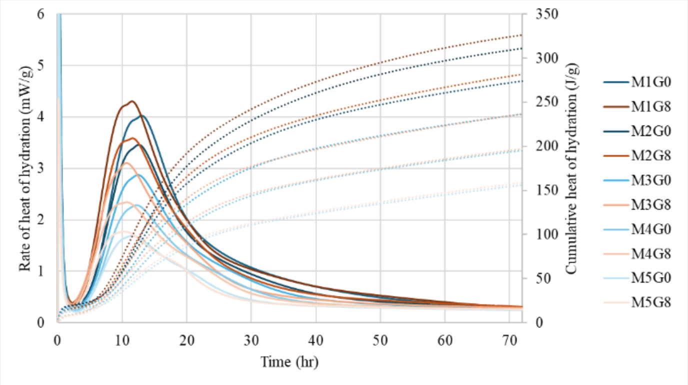


Fig. 3: Effect of GO on the hydration of GGBS-modified cement paste (Solid line for the rate and dashed line for the cumulative heat)

First, an overall observation of the isothermal calorimetry results without any GO is that the addition of GGBS caused a significant reduction in both peak rate of hydration and cumulative heat of hydration. For instance, at 72 hrs, the cumulative heat of hydration decreased 20%, 24%, 37% and 50% with 15 wt%, 30 wt%, 45 wt% and 60 wt% GGBS addition compared to pure cement paste. This is due to its two-stage hydration process, i.e., GGBS reacts with alkali hydroxide from Portland cement in the first stage and reacts with calcium hydroxide produced during the hydration of Portland cement in the later stage to induce the formation of secondary C-S-H [17]. This finding agrees with other studies. For example, Xu et al. [18] found that a 40 wt% GGBS replacement reduced the 3-day cumulative hydration heat by 32%, while 55 wt% GGBS resulted in a 44% reduction over the same period. However, the relative setting time was still reduced with the increase of GGBS replacement. This is consistent with observations from other authors and has been attributed to the effective increase in the w/c ratio caused by the replacement of cement with GGBS [19]. Moving forward from the effect of GGBS on cement paste to the effect of GO on GGBS-modified cement paste, by comparing the isothermal calorimetry test results of 0 wt% and 0.08 wt% GO samples in Figure 3, for all the tested GGBS concentrations, the addition of GO shifted the rate of hydration heat curves (the solid lines) upwards and earlier, which indicates an increase in the peak power and a decrease in setting time due to the acceleration of the early-age hydration process. This can also be seen through the upwards shift of the cumulative heat of hydration curves (the dashed lines), which implies an increase in overall hydration degree and thus an increase in the early-age mechanical strength. However, such positive effect of GO on the hydration process became less pronounced with the increase of GGBS dosages. For example, at 0 wt%, 15 wt%, 30 wt%, 45 wt% and 60 wt% GGBS concentrations, the rise caused by GO in 1-day cumulative heat of hydration was 7.0%, 4.5%, 3.6%, 3.4% and 2.9% accordingly.

3.3. The effect of GO on LF-modified cement hydration

The effect of GO on LF-modified cement paste was investigated by adding 0.08 wt% GO to 0, 10, and 20 wt% LF-modified cement paste, and the isothermal calorimetry test results are presented in Figure 4. When observing the results of specimens without any GO (the blue curves), it can be seen that the addition of ultrafine limestone powder shifted the rate of heat of hydration curves to the left, indicating a faster early-age hydration reaction, a reduction in setting time, and an increase in 3-day cumulative heat of hydration. There are two possible reasons to explain this, i.e., in terms of the chemical and physical properties: i) Limestone fines can participate in the hydration of cementitious systems with aluminate to produce hemi- and mono-carboaliminate phases [20][21][22]; ii) Limestone fines can also provide additional nucleation sites which accelerate the early reaction [23]. However, the accelerating impact of LF is highly dependent on its particle size and surface area [24], which influence the availability of nucleation sites and the extent of chemical reaction. Kadri et al. [25] found that finer mineral powders enhance hydration more significantly, with LF showing greater acceleration compared to other fillers like silica fume and alumina when particle size is similar. Therefore, it is difficult to compare the impact on the hydration degree caused by LF across different studies due to the variations adopted. In this study, a LF addition of 10 wt% and 20 wt% resulted in a 4.8% and a significant 11.3% increase compared to M1G0 in 3-day cumulative heat of hydration respectively.

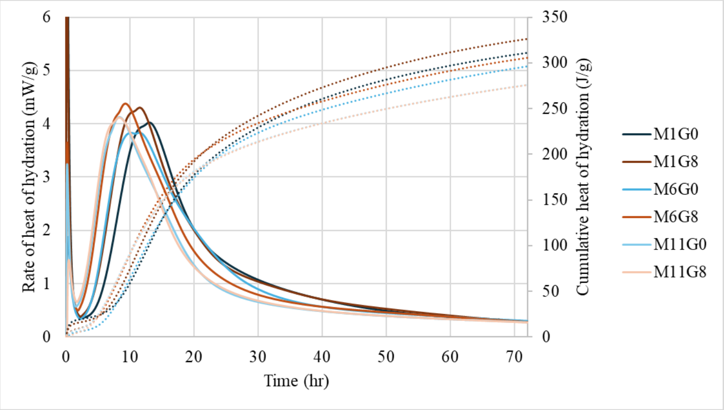
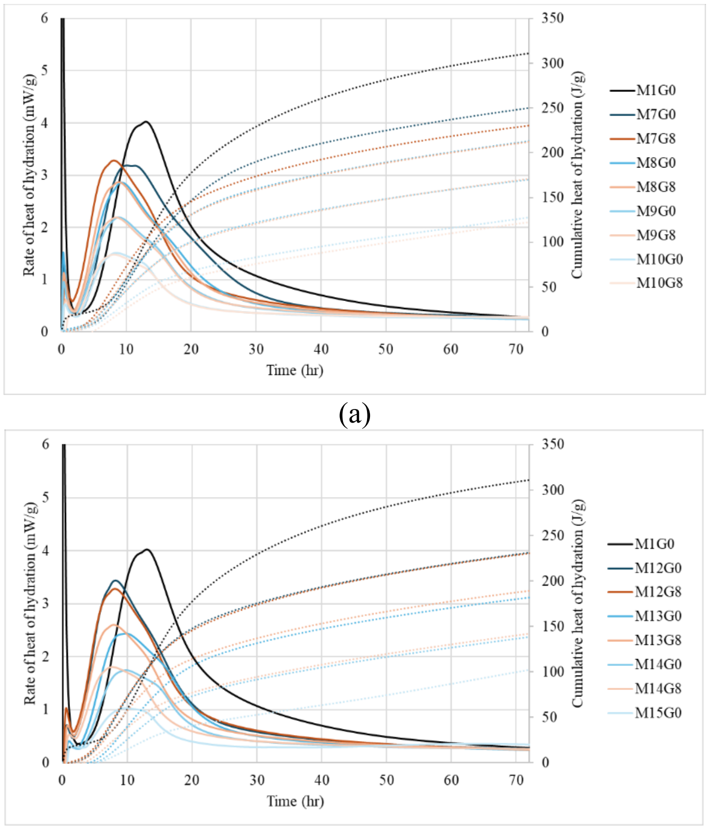


Fig. 4: Effect of GO on the hydration of LF-modified cement paste (Solid line for the rate and dashed line for the cumulative heat)

A further investigation of the test results with 0.08 wt% GO addition reveals a threshold of increase in hydration caused by the nucleation effect. Comparing specimens with GO (the orange curves) to those without GO (the blue curves) in Figure 4, for LF dosages of 10 wt%, the addition of 0.08 wt% GO caused an acceleration in early-age hydration, i.e., a 14% rise from 3.83 mW/g to 4.38 mW/g for the peak rate of hydration, and a 3% rise from 296 J/g to 306 J/g for the cumulative heat of hydration. However, for specimens with 20 wt% LF, the addition of GO hardly changed the hydration behaviour in the recorded 72 hours, implying a threshold of nucleation effect caused by the small particle sizes of both LF and GO.

3.4. The effect of GO on GGBS- and LF-modified cement hydration

To investigate the effect of GO on the early-age hydration of low-carbon cement paste with partial replacement of OPC with both GGBS and LF, isothermal calorimetry tests were conducted on M7-M10 and M12-M15 specimens with 0.08 wt% GO, the corresponding results are shown in Figure 5. An overall finding in this section is that the hydration behaviour of cement pastes modified with GO, GGBS, and LF is complex due to interdependent interactions among the components. These interactions can offset the individual drawbacks of each material, depending on their respective dosages. In Figure 5(a), for all the specimens with 10 wt% LF, the addition of 0.08 wt% GO shifted the rate of hydration curve earlier, which indicates a reduction of the induction period. However, unexpectedly, the cumulative heat of hydration all decreased to different extents with the addition of GO. This counterintuitive result may be attributed to the reduced exothermicity of the hydration process due to the modification with GO and its possible interaction with the LF and GGBS. Similar results have been reported in the study by Bhojaraju et al [14], in which they found the relationship between the maximum heat flow and the replacement GGBS content is nonlinear for GO-modified cement. Figure 5 (b) presents the results of specimens with 20 wt% LF replacement, the addition of 0.08 wt% GO shifted the rate of hydration curves to the left, but had negligible effect on the cumulative hydration heat. However, when it comes to a large replacement of GGBS, the similarity in cumulative hydration heat does not necessarily mean a similar hydration degree or a similar effect on the mechanical strength [26]. Bhojaraju et al [14] concluded that greater mechanical strength of the cementitious material can be achieved at the same cumulative heat flow, because the resulting hydration with this GO and SCMs modified mix is less exothermic. This suggests that the conversion of C3A to ettringite and the subsequent formation of AFm during Stages III and IV of the hydrations are being inhibited. To further investigate if this is true for the mixes with 10-20 wt% LF tested in this study, thermogravimetric analysis (TGA) and strength testing need to be carried out in future studies.



(a)

(b)

Fig. 5: Effect of GO on the hydration of GGBS- and LF-modified cement paste (a) 10 wt% LF (b) 20 wt% LF (Solid line for the rate and dashed line for the cumulative heat)

4. Conclusion

The combination of graphene oxide and supplemental cementitious materials such as GGBS and LF offers a promising avenue for binders with enhanced performance and reduced environmental footprint. This work demonstrated the need for optimization of the binder composition in conjunction with the addition of GO. The combination of GO, GGBS and LF significantly decreased the induction period of the hydration, especially with low GGBS contents. At high GGBS levels with the presence of LF, the hydration behaviour is more complex due to a shorter induction period, higher peak power, but lower cumulative heat released. In such cases, the total heat flow is not directly correlated with the degree of hydration or the mechanical strength because the hydration process of cements with a combination of GGBS, LF and GO can be less exothermic. This study revealed the potential of GO-modified SCM cement compositions to achieve high final degrees of hydration but lower total heat flow and less carbon footprint, which presents a practical advantage to applications such as large volume cement installations that could benefit from lower released heat, higher strength, longer durability and associated environmental sustainability.

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