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Fresh and hardened properties of GGBS-contained cementitious composites using graphene and graphene oxide

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Abstract

The addition of nanomaterials within cementitious composites affects the rheological parameters such as minislump and thixotropy. To relief this influence, the present study intends to study the addition of ground granulated blast furnace slag (GGBS) in cementitious materials containing graphene (G) and graphene oxide (GO). An experimental program is considered to measure fresh properties, compressive strength, and service life of cementitious composites. Dosages of 0.03% and 0.06% (by weight of cement) of G and GO are tested in cement pastes and mortars. GGBS in three different dosages of 15%, 30%, and 45% is investigated. A constant water/cement ratio of 0.35 is used in all mixtures. Results show that GGBS improves the yield stress and plastic viscosity of G- and GO-modified cementitious composites. Moreover, GGBS dosages of 30% and 45% compensate the reduced fluidity of 0.03 wt% of G- and GO-modified cementitious composites, respectively. The thixotropy of the composite paste containing GO decreases with the addition of GGBS. Moreover, comparable and slightly improved compressive strengths are obtained for

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mixtures containing GGBS. The results from the nomogram show a promising trend for the service life of mixtures containing G, GO, and GGBS.

Keywords*:* graphene; graphene oxide; GGBS; rheology; ICP-OES; resistivity

1. Introduction

The addition of nanomaterials to cementitious materials presents an opportunity to achieve highly durable and long-lasting materials. This can significantly increase the structural performance of building materials [1]. Recent research has focused on the reliability-based durability design of the nano-based cementitious material used in the construction industry [2-5]. To achieve this, building design codes need to account for the properties of the proposed building materials. This requires conducting different tests to provide details for addressing specific issues, i.e., rheological properties, mechanical characteristics, durability, corrosion, and service life. These tests typically require long time frames of decades to be conclusive [6].

Different nanomaterials have been used in cementitious composites, such as nano-silica [7, 8], nano-alumina [9, 10], polycarboxylates [11, 12], nano-titanium oxide [13], nano-kaolin [14, 15], nano clay, carbon nanotubes (CNT) [14, 16], and graphene-based nanomaterials (reduced graphene oxide [17], graphene oxide [2] and graphene nanoplatelets [2]). Graphene-based nanomaterials are the most innovative nanomaterials used to improve the characteristics of concretes [17]. Graphene is a material of enormous scientific interest because it is a stable two-dimensional material produced through cost-efficient chemical exfoliation techniques. Its planar hexagonal lattice exhibits nuanced electrical properties, and its high aspect ratio lends itself to many nanomechanical phenomena when used in composites [18]. In the past decade, further advancements in the field have expanded the potential of graphene by developing similar materials with different surface properties.

Graphene oxide and reduced graphene oxide contain partial surface coverage of hydroxyl and epoxide functional groups [19, 20]. As a two-dimensional material, graphene has an exceedingly high specific surface area. These minor chemical modifications dramatically impact the material properties and their dispersion and bonding with other materials [21]. This is of particular importance in applications in composites, such as in concretes, where the relative strength or weakness of the interface can be leveraged to enhance the composite properties [22]. Graphene-based nanomaterials have been shown to increase mechanical characteristics and durability in cement [23]. Graphene primarily acts as a filler and improves the microstructure of cement paste [24]. Graphene oxide arrests the formation of cracks, inhibiting crack propagation [25], and serves as a nucleation agent for calcium silicate hydrate CSH [26]. Pan et al. [27] reported that using 0.05 wt% GO can increase the composite compressive strength by 15–33%. Peng et al. (2019) [28] found that the addition of GO to cement paste improves the microstructure of cement hydration products, refines the crystal size, and forms a denser and more uniform network structure. Similarly, Lv et al. (2013) [29] confirmed that GO nanosheets could regulate the formation of flower-like crystals and considerably improve the tensile/flexural strength. Preparation and dispersion of these nanomaterials within the cementitious matrix have a critical effect on the mechanical properties [30]. However, these nanoparticles reduce the workability characteristics of cementitious pastes [24, 31-33]. Zohhadi (2015) [34] stated that in contrast to the improved compressive strength reported by other authors at low dosages, increasing the concentration graphene nanoparticles has a negative impact on workability which leads to a reduction in the compressive strength. Li (2017) [31] observed the reduction of 21% in mini-slump diameter with the addition of 0.03% of GO. Agglomeration of GO can lead to a large amount of entrapped water in the cement.

To address these issues, few researchers used supplementary cementitious materials (SCMs), including fly ash, silica fume, to compensate for the adverse effect of using nanoparticles on fresh properties [35, 36]. Wang (2017) [36] tested fly ash for improving the rheological properties of GO-modified cement-based materials. A decrease in the paste yield stress and plastic viscosity was observed with the increasing fly ash content. At 0.01 wt% of GO and 20 wt% of fly ash, the yield stress of the paste decreased 85.81%, and the plastic viscosity decreased 29.53% compared to the control sample (without fly ash and GO). At 0.03 wt% of GO and 20 wt% of fly ash, the yield stress of the paste is 50.3% lower, and the plastic viscosity decreased slightly by 5.6%. This improvement in workability characteristics is mainly because of the ball effect, particle size gradation, and lower water demand of fly ash [36]. Shang et al. (2015) [37] observed that the addition of GO into the cement causes a significant reduction in fluidity and increases the rheological parameters. They used silica fume as SCMs to compensate for the lower fluidity of GO-based cementitious materials. Li et al. (2016) [38] reported that silica fume is also effective in improving GO dispersion in cement paste. These prior studies in utilizing SCM to counteract the fluidity reduction caused by the addition of nanoparticles to cement pastes demonstrates the capacity for this methodology to be generalized to other SCMs.

Ground granulated blast furnace slag (GGBS) has been frequently studied as an SCM but has never previously been considered as a potential additive to nano-modified cement pastes. The present study seeks to investigate this potential for the purposes of counteracting the reduction in fluidity caused by the addition of G and GO. In conventional concrete mixes, the addition of GGBS, commonly in the range of 30-50%, has been shown to enhance the fluidity proportionally with the

GGBS content [39]. Regarding the affirmative influence of GGBS on concrete workability, a similar promising trend was reported by the literature [40-45]. These rheological observations correlate increased workability in the mortar with the increase in the surface area of GGBS and the fluidity of mortar was linked to the morphology of GGBS. Smoother particle surfaces yielded greater was the fluidity of the resulting mortar [46]. However, more experimental studies are necessary to confirm these experimental observations with different SCMs, especially for nanoconcrete mixtures. Hence, the current study applies GGBS to improve the fresh properties of G- and GO-modified cementitious materials. Complementary research is performed to investigate the effect of GGBS on service life characteristics of G- and GO-modified materials. The present study intends to fill the current research gap and address the following questions.

1) To what extent do the G and GO influence the fresh properties of cement paste?
2) How effective is GGBS in improving the fresh properties of cement paste containing nanomaterials?
3) What is the effect of nanomaterials on the service life of cementitious materials with GGBS?

To address these questions, an extensive experimental program has been carried out. The present study investigates different fresh properties, including (a) mini-slump spread diameter, (b) viscosity, and (c) thixotropy. Moreover, the present study considers various mechanical and durability tests to address the third objective, including the compressive strength, the conductivity of the pore solution, and the concrete resistivity. As no prior research has focused on the pore solution of mixtures containing G and GO, the present study fills this research gap. Moreover, the service life of cementitious materials is dependent on the composition of the pore solution [47-50].

A complementary durability study is presented as the third objective to quantify the impact of the pore solution changes on the durability of cement with G and GO.

2. Experimental test

2.1. Materials

ASTM Type I Portland cement (PC) was used for all mixtures with a constant water-to-cementitious material ratio of 0.35. The cement composition from quantitive X-ray diffraction is, in percent weight, 56.68% C3S, 12.22% C2S, 6.31% C3A, and 11.00% C4AF. GGBS with the chemical composition of 34.8% SiO_2, 8.5% Al_2O_3, 1.1% Fe_2O_3, 40.1% CaO, 9.7% MgO, 2.2% SO_3, and 0.7% Na_2O were used at typical replacement levels (15%, 30%, and 45%). Volume-based characteristic particle diameters of cement and GGBS were measured in isopropanol suspensions by laser diffraction, and the values are reported in Table 1. A commercial polycarboxylate ether-based polymer was used as the superplasticizer (SP) in the present investigation and was measured by weight as a percentage of the cementitious materials. In ultrapure water, the graphene particles were dispersed with a high-speed shear mixing mixer for one hour at 5000 rpm using sodium cholate [51], and graphene oxide were dispersed (4 g/l) in commercially available ultra-pure water. The dispersion quality is obtained by comparing TEM images along with visual observation. Solution cholate is a surfactant used to better disperse graphene particles in water, while graphene oxide performs better even without surfactant. Similarly, previous studies used sodium cholate as a surfactant to disperse nanomaterials in cementitious materials [34, 51]. Although there is no specific information regarding the influence of sodium cholate on the hydration process, it can deduce that the concentration of sodium cholate within cement paste is approximately 0.003

percent showing a minor influence on hydration. Fig. 1(a) presents the transmission electron microscopy (TEM) image of water-dispersed graphite with well-crystallized graphene sheets. Fig. 1(b) shows the topography of the commercially available GO. The thickness of the exfoliated graphite flakes ranged from 150 to 200 nm which is in agreement with previous studies [52], while the graphene oxide thickness is approximately 1 nm. The scanning electron microscopy (SEM) image of GGBS is also shown in Fig. 1(c). The elemental compositions and the sizes of the graphene and graphene oxide are presented in Table 2. These can significantly affect the properties of the cement matrix. Fourteen different mix proportions were used in the present investigation to form the basis of the new test results. Compositional parameters investigated were the dosages of the nanomaterials and the supplementary cementitious materials. The mixture proportions are given in Table 3. Local glacial sand with a density of 2,700 kg/m^3 and a fineness modulus of 2.56 was used as fine aggregate for testing the hardened properties of cementitious materials.

2.2. Mixing procedure and specimen preparation

The cement paste was prepared by mixing cement, GGBS (if applicable), water, superplasticizer, and an aqueous dispersion of either graphene or graphene oxide with a constant water/cementitious weight ratio of 0.35. The cement with a w/c ratio of 0.35 and 1% SP serves as the reference sample. To investigate the influence of the nanomaterials, the dosage of G and GO nanosheets was varied from 0.00% to 0.06% by weight of cement. The replacement ratio of cement with GGBS was varied from 15% to 45% by weight (15%, 30%, and 45%). Table 3 presents the mix proportions of cement paste and mortars used in the present investigation. To attain good dispersion of the nanoparticles in the paste, a mixing procedure of ASTM C1738 [53] was adopted. Water and SP were added to a high shear mixer with a water-cooling system that was selected to meet specifications. The nanomaterial dispersions were added and stirred for 15 seconds. Then, the cement was added within 60 seconds and the mixture was stirred at a speed of 4000 rpm for 60 seconds and 10000 rpm for 30 seconds. A 150-second rest was given, during which any paste adhered to the sides of the bowl was reincorporated into the batch. Then, there was a final mixing step of 10000 rpm for 30 seconds. Immediately after mixing, each of the mixtures was divided into three plastic tubes; two for the mini-slump test and one for the rheometer.

For pore solution to ensure homogeneity in the raw materials, a blend was made for each of the cementitious materials from samples taken from the storage sealed bucket at different heights. In the first case, different nano dosages (0.03 and 0.06) were studied. In all the cases, the mixing was performed uniformly (i.e. 2000 rpm for 60 s, rest for 30 s, and mix again at 2000 rpm for 90 s). After mixing, the sample was rested at ambient temperature (25°C) for 15, 45, and 90 minutes. To extract the pore solution, samples were placed in a centrifuge for 10 min at 5000 rpm. This procedure was similarly used by the literature to obtain pore solution from fresh paste [54-56]. The resulting supernatant solution was collected in a disposable plastic syringe and filtered through a syringe filter of 0.45 µm. After filtration, the pore solution was immediately diluted 1:10 and 1:100 by mass with HNO_3 (w/w) in ultra-pure water for quantifying low- (Al, Fe, Mg, Si) and high-concentration elements (Ca, K, Na, S), respectively. Diluted solutions were kept in screwcap polypropylene containers, sealed with parafilm, and stored at 4°C until the test was performed. The ICP analyses were carried out within one week of the extraction. The remaining undiluted pore solution was used for measurements of the pH and conductivity.

Four concrete samples of each composition were prepared for resistivity and three samples for compressive strength by mixing cement, GGBS (if applicable), fine aggregate, water, SP, and nanomaterials (G and GO) with the surfactant. Initially, half of the water and the remaining SP were mixed with water-dispersed nanomaterials (sonicated with half SP for 30 minutes before mixing) until a homogenous solution was obtained. Then, the cement and the aggregate were added to the mixture. Finally, the remaining water was added.

2.3. Test setups and procedures

2.3.1 Mini-conical test

For mini-slump test, a smaller version of the Abrams test was considered in the present study that followed the same characteristic of the cone described in ASTM C1437 [57]. Freshly mixed cement paste was filled in a truncated mini-cone (Top diameter 19 mm; bottom diameter 38 mm, and height 57 mm) [58], which was placed on a grid marked plate (20 x 20 mm^2). After removing the filled cone Fig. 2, the cement paste flows and reaches a steady-stable state, and the increase in the cone diameter is measured from a photo taken from the top of the set-up. This procedure was repeated just before and after the rheometer test, as shown in Fig. 3. The diameter of the fresh paste sample is the mean value of four measurements made in perpendicular directions.

2.3.2. Pre-shearing and flow test

Flow curve testing was performed with an Anton Paar MCR 301 rotational rheometer. The equipment was designed following the national institute of standards and technology (NIST) recommendations [59]. The rheometer was configured with a double spiral spindle centered on a metal shaft (Fig. 2). This tool has a diameter of 25 mm and a length of 55 mm from the bottom to the top of the spiral. During the measurements, the temperature of the outer cylinder was maintained at 23 ± 1.0 °C with a Peltier apparatus. Each cement paste sample was preconditioned with a pre-shear of 0.1 rpm until an equilibrium state was achieved, followed by a 15 second rest period. As shown in Fig. 3, the flow curve test was performed by increasing the shear rate from 0.1 rpm to 100 rpm, stepwise in 15 increments. The decreasing shear rate measurements were performed in the range of 100 rpm to 0.1 rpm in 20 increments. For each incremental measurement, the shear was maintained until an equilibrium shear stress was measured and the torque was recorded at a constant rotational speed. For the calibration of the spindle, the NIST recommended calibrated paste (Standard Reference Material (SRM) 2492 [60]) was used. To reset the shear history of the paste the up-curve is used. The data of the down curves (decreasing shear rate) were fit to the SRM 2492 certified values using the Bingham approach, as implemented in the SRM 2493 NIST certification [60]. Subsequently, the calibration factors $K\tau$ and $K\mu$ were computed with the NIST Data Calibration Tool. These parameters were used to calculate the shear rate, the shear stress, the yield stress and the viscosity of the cement pastes using the procedure explained by NIST in [60].

2.3.3 ICP-OES

A Scientific Dual View ICP-OES (Thermo Scientific 5110) was used for the elemental analyses of the pore solution. ASTM C1875 [61] was followed in the present study for ICP-OES method. In the current investigation, the values provided by the literature [54, 62] were used as a starting composition for calibration. Further, the composition of the calibration solution was modified with the results of the initial series to ensure coverage of the entire range of concentrations measured. By this procedure, the values were obtained by interpolation. The operating parameters of the ICP-OES used for the analysis are presented in Table S1.

2.3.4 Hardened properties

The resistivity of the concrete strongly depends on the microstructure of the cement paste, moisture, salt content, and temperature. The microstructure is influenced by factors such as w/c ratio, degree of hydration, and the type and amount of SCM. In the present investigation, four identical cylindrical samples of diameter 50 mm and length 100 mm were used to measure resistivity. This property was measured by the direct two probe technique (bulk electrical resistivity). This test was conducted in the presents study based on the recommendation of ASTM C1202 [63]. To ensure a uniform current density during the measurement, brass plate electrodes of the same size and shape as the end surfaces of the specimen were used. The care was taken to ensure good contact between the flat ends of the cylindrical samples and the brass electrodes by wrapping the electrodes in a damp cloth to uniform charge transfer. The plate electrodes were firmly clamped on the specimen by a 'C' clamp and electrically insulated from their environment by neoprene rubber pads. Until immediately before each measurement, the cylinders were stored in a humid room for curing. The surfaces were gently cleaned to remove any dust or loose material, and the dimensions of each specimen were recorded. The resistivity was calculated as follows.

$$\rho = RA/L \qquad (1)$$

where ρ = Resistivity in kohm-cm, R = Resistance measured in kohms, A = Area of the contact surface in cm^2, and L = length between two electrodes in cm. After each of the curing periods, three identical sample cubes of dimension 50 mm were removed from the environmental chamber. The surface moisture on the specimens was removed with a cloth prior to their being weighed. The cubes were subjected to unconfined compressive strength tests. A testing machine capable of loading up to 2000 kN was used to apply the load at a compression rate of 1 kN/sec.

3. Results and discussion

3.1 Workability

3.1.1 Mini slump

To ensure the homogeneous properties in concrete, high flowability and moderate viscosity are necessary for casting. These fresh properties assist in the proper compaction and shaping of cement-based materials while maintaining adequate cohesion stability [27]. No signs of bleeding were observed in any of these mixes. Fig. 5(a) and (c) show the variation mini-slump flow for the cement pastes with different dosages of nanomaterials (G and GO) at each time. The mini-slump diameter of the cement paste is approximately 220 mm at 7 minutes, and it was reduced to 205 mm at 22 minutes, yielding a slump of approximately 7%. Results show that as the percentage of nanomaterials increase, the mini-slump value decreases. Identical trends were observed at 7 and 22 minutes for all the mixtures. The addition of 0.06% G and GO causes reductions of 50 and 75% in the mini-slump values, respectively. Comparable results were observed at 22 minutes. This can be attributed to the larger specific surface area of the G and GO. Similar results have been reported elsewhere for cement [27, 32]. GO consists of oxygen-rich functional groups resulting in agglomeration of cementitious materials and the formation of a flocculation structure which leads to a further reduction in flowability [29, 64]. The effect of GGBS on the fluidity of the cement paste with G and GO (at contents of 0.03 wt% and 0.06 wt%) is shown in Fig. 5(b) and (d). Results show that adding GGBS, ranging from 15% to 45%, causes a considerable increase in mini-slump diameters of nano-modified cement pastes. Similar promising results were observed for unmodified cement paste containing more than 15% GGBS replacement (Fig. 5). At 15% GGBS, the unmodified cement pastes were a little lower in mini-slump diameter than the ordinary cement paste under the same solid volume fraction. This may be attributed to decrease packing density due to the irregular shape of GGBS particles [65].

With the addition of GGBS, the mini-slump flow of the nano-modified cement improves. Increases in flow diameter of approximately 31%, 109%, and 111% were observed for GO-mixtures containing 15%, 30%, and 45% of GGBS, respectively. For graphene-modified cementitious materials, 12%, 51%, and 135% increases were observed for the same dosages of GGBS. For G-modified cement, dosages of 30% and 45% GGBS were found to yield flow diameters greater than that of the control sample. However, for GO-modified cement, 45% of GGBS was required to reach the control sample flow diameter. This demonstrates that the addition of GGBS can reduce the flocculation in the cement pastes and increase the flow. Contrarily, due to the greater fineness of the GGBS particles relative to cement (Table 1), the GGBS particles can enhance the particle size gradation in the paste, which increases the fluidity of the nano-modified cementitious materials [65].

3.1.2 Static yield stress

Static yield stress indicates the degree of coagulation of concrete [66] which evolves with time as thixotropy increases. If, in the flow curves, the rate at which the shear rate increases to its maximum value is different than the rate which decreases from this value, a hysteresis loop will form, as visualized in Fig. 6 [67]. The observed hysteresis is caused by the non-Newtonian paste dynamics, which is dependent on the microstructure and composition of the material. As explained graphically in Fig. 6, a shear thickening behavior corresponds to a thixotropic hysteresis area, whereas shear thinning behavior results in a rheopectic hysteresis. In cementitious materials, the static yield stress is measured as the peak shear strength at which interparticle attractive force breakdown at low shear speeds. As shown in Fig. 7(a), the shear stress of nano-modified cement pastes is generally higher than that of ordinary cement paste, which is due to the large surface area of the nanomaterials. Moreover, the results indicate that the static yield stress of GO-modified cement is higher than G equivalent at both dosages of 0.03 and 0.06 weight percentage of cement. This may be due to the surface functionalization of GO which facilitates greater reactivity with itself and other components of the cement paste, resulting in the agglomeration and the formation of a flocculation structure [36]. It can be clearly seen in Fig. 7(a) that the cement pastes with higher dosages of nanoparticles have greater yield stresses. This increase is more significant in GO-modified cement paste as compared with G equivalents. As explained in more detail earlier, this distinction between G and GO is primarily due to the surface functional groups in GO. Fig. 7(b) illustrates the development of the static yield stress for different percentages of GGBS ranging from 0% to 45%. The shear stress of GGBS-containing mixes is lower than that of the reference mixture due to the reduced hydration between cement and GGBS. The low dosage of GGBS (15%) has no significant influence on the yield stress (Fig. 7(b)). This can be attributed to the packing density and irregular shape effects counteracting the reduced chemical activity of GGBS [65]. However, the impact of GGBS is pronounced at higher percentages (30% and 45%), because the lower reactivity dominates the other phenomena [68].

The effect of the GGBS replacement in GO-modified cement paste is shown in Fig. 7(c). Results demonstrate that 45% GGBS is the optimal dosage of GO-modified cement paste to mimic the yield stress of the reference mixture. GGBS dosages of 15% to 30% showed substantial reductions in yield stress compared to GO-modified cement alone but yielded higher yield stress than the reference mixture. This promising finding can be attributed to the filler effect of GGBS in cement, which counteracts the flocculation of GO with other components in GO-modified cement paste.

However, as there is less flocculation in G-modified cement paste, the GGBS replacement has a greater impact on the fresh properties, and reference performance can be achieved at optimum dosage of 30%. This can be mainly due to the reduction in porosity of G-contained cement paste. In the case of 45% GGBS, a few signs of bleeding were observed in G-modified cement paste.

Fig. 8 summarizes the results of the hysteresis loop test. The first five columns give the results of the nano-modified cement paste at different dosages. The latter nine columns show the impact of GGBS-containing cement with and without nanomaterials. As expected, the addition of GGBS and nanomaterials results in significantly lower hysteresis areas than the nanomaterials alone. Results presented in Fig. 8 were calculated from the experimental data shown in Fig. 9. The maximum thixotropic value of approximately 320 Nm/s was observed for the composition with 0.06 wt% GO due to the higher content of high surface area material, and GO's greater reactivity due to its functionalization. In Fig. 9, the top two rows represent nanomaterial-modified cements, while the lower rows are the mixes with GGBS and the nanomaterials. Each row is plotted on the same scale to facilitate comparison. The blue shaded portion of the loop represents thixotropic values, and red represents rheopetic which are directly compared in Fig. 8. All set of mixes showed thixotropic behavior except for the reference, 0.03 G and 15 GGBS, which expressed both thixotropic and rheopectic values (plotted as negative values). This represents that for these mixtures, after the rigorous shearing, the downward shear plot had higher torque values than the upward shear plot. A similar result was reported by Chhabra et al. [67] for materials like thick suspensions of kaolin and cornflour in water. For such materials, the equilibrium concerning the rate of structural rebuild and breakdown can tilt to either side depending primarily on the setting conditions of the samples. However, a few researchers have cautioned that negative slopes in the flow curve can occur when there is insufficient pre-shear to achieve a steady-state.

3.1.3 Dynamic yield stress and viscosity

In handling cementitious pastes, the dynamic yield stress is crucial to quantify the workability [69]. The influence of the nanomaterials (G and GO) and GGBS modified nano-cementitious materials on the rheological behavior of cement pastes, as studied in this work, can be seen in Fig. 10(b). There is an evident increase in the yield stress of the pastes at early testing times when nanomaterials are incorporated into the mixture. Large agglomerates of precipitated graphene and graphene oxide occupy a portion of the free water to wet the surface of nanomaterials. This results in an adverse effect on workability, which has been acknowledged in the literature [64]. The further enhancement of dynamic yield stress and viscosity caused by the addition of GO is observed from Fig. 10 (a and c). The additional decrease of fluidity and increase of viscosity, compared to G-modified equivalents, may be attributed to the greater dispersion and relative hydrophilicity of GO. This results in a higher specific surface area for GO, increasing its interactions with cement particles and promoting aggregation of cement grains. The functional groups on the surfaces of the GO are reduced, transferring oxygen into the cement paste, accelerating the hydration of cement and further reducing the workability [64]. Therefore, the use of other additives, such as fly ash, GGBS, silica fume, and superplasticizers, has already been recommended in the literature to offset the reduction in fluidity [37, 70]. Fig. 10 (b and d) shows the viscosity and dynamic yield stress measurements for nanomaterial-modified cement paste with different dosages of GGBS (0%,15%, 30%, and 45%). The viscosity of the reference cement was approximately 0.207 Pa-s. When 15%, 30%, and 45% by weight GGBS is added, the value of viscosity was measured to be around 0.219 Pa-s, 0.202 Pa-s, 0.140 Pa-s, respectively. As described earlier, the 15% GGBS unmodified paste experiences competing phenomena from the GGBS to modify the rheological properties, resulting in a mild increase in viscosity. However, the higher dosages of GGBS yield the expected reduction in viscosity. With the addition of the G and GO in the 15% GGBS paste, the viscosity further increases. However, for G-modified cement pastes, the 30% and 45% GGBS yielded viscosities lower than the reference. For GO, 45% of GGBS was required to attain viscosity values comparable to that of ordinary cement paste. These results are consistent with observations of the addition of other admixtures [70]. The same trends were also noted for the measurements of the dynamic yield stress.

The data presented previously enables assessing the relationship between mini-slump values and Bingham constants, including yield stress and plastic viscosity [71]. Fig. 11 shows the relation between the slump-flow diameter and the mini-slump of the nano-modified cementitious materials before and after the rheometry testing. The slump is correlated inversely with the yield stress by an exponential relationship. The data fit shows a correlation coefficient of $R^2 = 0.96$. An inverse linear relationship correlates the viscosity with an $R^2 = 0.80$. Many researchers have demonstrated the relationships between mini-slump flow, viscosity, and yield stress [72-74]. As expected, the addition of nanomaterials induces a rise in viscosity and yield stress (inversely correlated with slump flow) due to a reduction in effective free water by the mechanisms described previously. This trend increases with the quantity of nanomaterials as the number of contact points between the particles leads to greater internal friction in the paste during flow, further increasing viscosity and dynamic yield stress [72, 75, 76]. As shown in Fig. 11, the addition of nanomaterials increases the plastic viscosity linearly along with a decrease in the mini-slump value [77]. This is attributed to the high nanoparticle surface area, leading to greater Vander Waals bonding and flocculation of G and GO. Bentz et al. [78] observed a similar linear trend for the plastic viscosity to the mini-slump. The relationship between the dynamic yield stress and the mini-slump followed an exponential correlation [79]. However, the deviation of these results between different periods makes it evident that many factors influence the measured slump flow, including the hydration kinetics and differences in the concentrations of Ca, Si, Na, K, which will be explained in the next section.

3.2 Impact of nano-modified cementitious materials on pore solution

The ICP-OES compositional analysis of the pore solution of each mixture at different times is shown in Table 4. The results show a slight increase in calcium concentration in the pore solution upon the addition of nanomaterials and GGBS, at low dosages of both. The ratio between the high-concentration elements (such as K/Na) is unchanged by the addition of nanomaterials. However, there is a drastic change in these proportions with the addition of GGBS, leading to a reduction in the electrical conductivity of the pore solution of GGBS concretes. Table 4 also confirms a sharp increase in low-concentration elements upon the addition of nanoparticles at low dosage, compared to the reference cement. The same increase is visible for the nano-modified GGBS concretes. This correlates well to the enhancement of compressive strength in these concretes.

Fig. 12 shows the concentrations in pore solutions of Ca, K, Na, S, Si, and Al of cement modified with nanomaterials and GGBS at different dosages. Generally, the results show that the addition of nanomaterials causes comparable and slightly elevated pore solution concentrations of these elements compared to reference mixtures. Interestingly, the impact of GO appears to change at the higher dosage tested; switching in some cases from causing a mild increase to a minor decrease in concentrations measured. This can be attributed to the agglomeration of GO at the higher content causing a reduction in the effective nanomaterial content which is consistent with the reduced compressive strength and yield stress measured for these formulations. The addition of GGBS caused decreases in the observed concentrations of Na, K, and S, while simultaneously increasing the Si and Al contents and leaving the Ca unchanged. These observations are consistent with expectations from the chemical composition of GGBS. However, the results for the nano-modified mixtures with GGBS were varied by the element species. For Ca, Si, and Al the concentrations were enhanced compared to the equivalent mixtures with GGBS alone. In contrast, lower pore solution concentrations were observed for the other elements. This offers some explanation for the observed increase in hardened compressive strength with a simultaneous reduction in paste yield stress observed for these formulations.

The measurements of the electrical conductivity of the pore solution are slightly higher for nano-modified materials. These results are shown in Table 4. The formation factor is directly proportional to the conductivity of the pore solution [80]. For safety, the conductivity is assumed to be constant for each group of nano-modified mixes. In the present investigation, the pore solution resistivity is estimated based on binder chemistry, mix proportions [81, 82]. 80% degree of hydration is assumed for all the mixtures at 28 days [80]. A value of 18.47 (s/m) is considered for plain and nano-modified cementitious composites. Values of 16.05, 13.55, 10.95 (s/m) are considered for 15, 30, 45% of GGBS modified cementitious composites, respectively.

3.3 Impact of nano-modified cementitious materials on the resistivity of concretes

The durability of concrete strongly depends on the properties of its microstructure, such as pore size distribution and the shape of the pore connections. Fig. 14(a) compares the results of the resistivity of the nano-modified cement with the reference. With the addition of nanomaterials, there is a slight decrease in resistivity. However, the resistivity of concretes increases drastically with the addition of GGBS, as shown in Fig. 14(b). This effect was observed to increase with age and dosage to a dramatic extent. Fig. 14 (c,d) presents the change in the resistivity of the GGBS concretes with the addition of G and GO. From these results, it is clear that the dominant effect is that of GGBS. Compared to the unmodified equivalent cements, the nano modified GGBS cements show slightly lower resistivity at all ages except on the first day. This may be due to the enhanced hydration rate cause by the addition of the nanomaterials. However, for all the resistivity at the 28 days, the corrosion probable rate can be applied as per the limitations suggested by Browne et al. [83].

3.3.1 Calculation of formation factor

The formation factor is the ratio of the bulk resistivity of concrete formulation to the resistivity of the pore solution of a cement paste. It was proposed by Archie [84] to characterize the pore structure of a porous rock and similar materials. The value strongly depends on the pore geometry and connectivity of the pore network. Extensive work on concrete was conducted by Weiss and Barrett [85, 86] on the formation factor of concrete structures. Fig. 15 compares the calculated formation factors for nano-modified and GGBS-containing cement formulations considered in the present investigation. With the addition of nanomaterials, there is a slight decrease in the formation factor due to the conductive nature of the additives. Conversely, the formation factor increases drastically with the addition of GGBS. However, for combinations of nanomaterials and GGBS, all of the formation factors are significantly improved, and the corresponding corrosion probable rates are very low as per W. Jason Weiss et al. [86].

3.4 Compressive strength of concrete

Fig. 13 shows the 28-day compressive strengths of the cement formulations with and without nanomaterials and GGBS. Without GGBS, the addition of 0.03 and 0.06 wt% of G and GO resulted in significant increases in the compressive strength. This is in agreement with previous reports on the effect of carbon-based nanomaterials on strength. However, in this work, it was observed that the extent of strength improvement was reduced at the higher dosage of G and GO (0.06 wt%). As discussed previously, this may be attributed to the agglomeration of the nanoparticles, reducing their effective content in the composite. The addition of 15, 30, and 45 wt% GGBS also produced substantial increases in compressive strength. Notably, the addition of nanomaterials only increased the strength at the low dosage of GGBS. Higher contents showed significantly less improvement. Furthermore, it was observed that G offers the greatest strength improvements with low or no GGBS. Surprisingly, the compressive strength was found to increase with GO for the highest content of GGBS, in contrast to the general trend.

3.5 Estimation of the service life of concrete

To durability-based design a RC structure, the resistance of the concrete cover necessities to be measured. This section intends to work on a monograph providing empirical equation for evaluating this resistance in terms of the rate of chloride ingress through concrete, and therefore the time to initiate the reinforcement corrosion. Once the formation factor for a cement composition has been determined, the diffusion of chloride due to the permeability of the concrete can be predicted by Flick's second law of diffusion [87], given in Eq. (2). This equation can be solved for the parameter t, time, to yield a surface of solutions for possible inputs of the other parameters. These solutions are depicted graphically in Fig. 16. In the case of predicting the time of concrete failure, the C_x is the critical chloride concentration, C_s is the constant surface concentration, C_o is the native chloride concentration within the cement which is assumed to be zero, X is the depth of the reinforcement, D_o is the self-diffusion coefficient constant for a chloride ion (2.03 x 10−9 m2 /s at 25 °C), *F* is the calculated formation factor, and *t* is the time. The time-to-failure of concrete has been suggested by previous literature to be six years to be the parameter *t* plus an initiation period of six years [86].

$$\frac{(C_x - C_0)}{(C_s - C_0)} = 1 - erf\left[\frac{x}{2\sqrt{\left(\frac{D_0}{F}\right)t}}\right] \qquad (2)$$

Fig. 16 provides a nomogram of the solutions for parameter *t* for typical combinations of formation factors, chloride surface concentration, critical concentration, and the depth of reinforcement. To interpret this graphic, extend a line perpendicular to the formation factor axis at the given formation factor value through the surface concentration quadrant (Fig. S1 in Supplementary Materials). The solution for *t* is then measured in years on the axis perpendicular to this line at the point of intersection with the line which corresponds to the input surface concentration. This process can be repeated from this intersection point into the depth of reinforcement. Subsequently, the critical concentration quadrants to calculate the solution for *t* with alternate values for these parameters given on the corresponding lines in each section. Default values are assumed in this calculation to be 25 mm and 0.15, respectively.

It is worth mentioning that some limitations exist in the present study which needs to be considered for future works, including microstructural analysis of GGBS-contained nanoconcrete. For instance, the section of "estimation of service life of concrete" needs more experimental proof as the definition of concrete failure by chloride ions is not completely clear. Since concrete deterioration caused by NaCl, CaCl2 and MgCl2 have different mechanisms, it is necessary to conduct the freeze-thaw durability test (ASTM C666) or salt scaling test (ASTM C672) to provide some direct evidence showing the significant benefit of using GGBFS and G/GO.

4. Conclusions

An experimental program was carried out in the present study to determine the effect of graphene and graphene oxide on fresh paste, hardened, and durability properties of cementitious materials with varying contents of ground blast furnace slag. Mini slump, rheometry, compressive strength, ICP-OES pore solution analysis, and electrical resistivity tests were conducted in the present study, and the analysis of the results has yielded the following conclusions:

- Generally, results show that the addition of G and GO reduces the mini-slump flow diameter of the cement paste. The content of the nanomaterials has a considerable effect on this phenomenon, with 50% and 75% reductions observed for 0.06% of G and 0.06% of GO, respectively. Due to the agglomeration, GO has a higher impact on the fluidity of the mixtures as compared to G. Results show that adding GGBS to mixtures considerably increases the flow diameter, especially for dosages of at least 30 wt%. Furthermore, GGBS is more efficient in improving flow diameter in GO-modified mixtures as compared to G-modified mixtures and reference.
- The hysteresis tests show that 0.06% GO has the greatest thixotropy compared to other mixes, while a mixture containing 0.03% G is the most rheopitic. Results also show that adding GGBS to the mixtures containing G induces greater thixotropic characteristics. However, an adverse trend was observed for mixtures containing GO.
- Results show that adding G and GO results in higher viscosity and dynamic yield stress of mixtures. This effect is more potent for GO-modified mixtures than G. Adding GGBS

alone has no considerable impact on the viscosity and the dynamic yield stress. However, in the presence of G and GO, the addition of GGBS yields a significant reduction in these properties. The results indicate that reference rheological behavior can be recreated for G-modified mixtures by adding 30% of GGBS and GO mixtures with 45% GGBS.

- Results indicate that adding both G and GO creates higher compressive strength of mortars compared to the reference mixture. However, a reduction in this effect was observed at higher dosages. The addition of GGBS was shown to improve the compressive of mortars containing nanomaterials. Generally, the trend indicates that mixtures containing G have higher compressive strengths as compared to GO ones. The mixture with 0.03% G and 30% GGBS yielded the highest compressive strength among the mixtures tested.
- Results indicate that the addition of nanomaterials slightly decreases the resistivity of the cements at 28 days. However, adding GGBS causes a considerable increase in 28-day resistivities. Similar results were observed for G- and GO-modified mixtures. Additionally, results indicate that mixtures containing 0.03% GO and 45% GGBS have the highest formation factor among the compositions tested.

CRediT authorship contribution statement

Chandrasekhar Bhojaraju: Conceptualization, Idea, Investigation, Data curation, Validation, Formal analysis, Methodology, Visualization, Writing - original draft, Writing - review & editing. **Seyed Sina Mousavi**: Investigation, Formal analysis, Data curation, Writing - original draft, Writing - review & editing. **Victor Brial**: Investigation. **Michael DiMare**: Writing - review &

editing. **Claudiane M. Ouellet-Plamondon**: Supervision, Validation, Resources, Funding acquisition, Writing - review & editing.

Declaration of competing interest

The authors declare that there are no competing interests regarding the publication of this paper.

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