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Influence of 2D rGO nanosheets on the properties of OPC paste

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ABSTRACT

In this experimental study, the effects of 2D reduced graphene oxide (rGO) sheets on the properties of Portland cement paste in comparison to popularly reviewed nanomaterials like aluminium oxide nanopowder (n-Al₂O₃) and colloidal silicon dioxide nanoparticles (n-SiO₂) were investigated. The addition of 0.02% rGO sheets by weight of cement increased the 7 and 28 days flexural strength up to 70% and 23% respectively when compared to control paste. Moreover, its incorporation substantially decreased the sizes of pores/voids in the paste, even compared to the other nanomaterials, as characterized by Mercury Intrusion Porosimetry (MIP) and 3D X-ray Computed Tomography (CT) aided with image analysis technique. The assessment of Portlandite content by Thermo-gravimetric Analysis did not indicate major differences between the pastes, with the exception of the paste incorporating nano-silica. Microstructural analysis by Fourier Transform Infrared Spectroscopy, X-ray diffraction and Scanning Electron Microscopy did not reveal any major differences between the control paste and the pastes incorporating nanomaterials, despite the significantly lower amounts that were used in the paste.

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1. Introduction

The diffusion of deleterious ions through the pore network of cementitious materials can be arrested by incorporating nano-sized materials, which have a high surface area to volume ratio. Minor additions of nanomaterials such as carbon nanotubes, nano silica, nano alumina and graphene nanosheets, which are effectively dispersed in the cement matrix, are beneficial in enriching the mechanical and durability properties [1]. The nanomaterials are suggested to be super-sorbents that physically adsorb the free water to a large extent. Due to such effects, the nanomaterials are perceived to act as nucleation sites for the growth of hydration crystals at early ages, which ultimately results in reducing the fraction of unhydrated cement [2,3]. Further, the issue of reduced workability that is caused because of the use of the high surface area nanomaterials can be overcome by the use of surfactants, which also help in reducing the agglomeration effect of nanomaterials due to van der Waals forces [4–7]. In addition to high

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surface area, the shape and structure of nanomaterials also play an important role in microstructural alterations of the cementitious compounds [8].

Graphene, a 2D planar sheet of single atom thickness having sp² bonded carbon atoms arranged in a honeycomb lattice pattern, gives excellent in-plane mechanical (modulus of elasticity 1100 GPa), thermal (conductivity 5300 W/mK), optical transparent, and electrical (conductivity 2000 S/cm) properties [9].

Lv et al. [10] have attributed the aforementioned behaviour of morphological changes to shape effects by the dispersion of graphene oxide (GO) into the cement mortar. It was reported that flower-like planar clusters at low GO dosage and polyhedral and lamellar form of hydration crystals were densely formed due to the effect of high GO dosage into OPC paste. The study claims that such flower clusters were easily produced in holes and cracks of the cementitious composites. By performing thermal analysis, Gong et al. [11] have reported that 0.03% GO by weight addition into cement paste increases the generation of Portlandite and nonevaporable water up to 6% and 9% respectively. Further, they also reported that the compressive, tensile and flexural strengths were increased up to 38%, 79% and 60% respectively compared to control





Concrete Concrete Composites specimens.

Bulk synthesis of graphene is difficult to achieve because of the significant van der Waals forces in these sheets of high surface area (2630 m²/g) that cause irreversible agglomeration or even restacking to form graphite. Kuila et al. [12] have suggested that such an effect was overcome with the help of using Chemical Oxidation/Modified Hummers' method to synthesize graphene oxide. This method proves effective in synthesizing chemically converted graphene sheets which are able to form stable colloids through electrostatic stabilization. Without the use of surfactants, effective dispersion is achieved through hydrazine reduction of graphene oxide under controlled conditions [13]. The resultant material is termed as 'Reduced' Graphene Oxide (rGO).

In this study, the influence of reduced graphene oxide (rGO), dry aluminium oxide nanopowder (n-Al₂O₃) and colloidal silicon dioxide nanoparticles (n-SiO₂) on the properties of cement pastes such as workability, compressive and flexural strength, mass porosity and water sorptivity index were determined after curing for 7 and 28 days. Then the effect of nanomaterials on the pore refinement of OPC paste was investigated using Mercury Intrusion Porosimetry (MIP) and 3D X-ray Computed Tomography (CT) studies. Further, the alterations in microstructure of cement paste due to the addition of nanomaterials were characterized using Fourier Transform Infrared spectroscopy (FTIR), X-ray Diffraction technique (XRD), Thermo-gravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM) techniques.

The motivation behind choosing the popularly reviewed nanomaterials such as $n-Al_2O_3$ and $n-SiO_2$ for the comparative evaluation against the rGO cement composites was due to their effective dispersion into the cementitious matrix without the use of any surface modification agents [14,15].

2. Experimental

2.1. Materials

A top-down approach was followed to extract the rGO from natural graphite by redox reaction. Three steps such as prereduction, sulfonation and post-reduction were followed to synthesize rGO. Sodium borohydride was used for the pre-reduction of rGO at 80 °C for 1 h in order to remove the major amount of oxygen functionalities from graphene oxide. Then the water solubility (dispersion in water) was improved by adding sulfanilic acid in an ice bath for 2 h. In this stage, controllable structural defects were allowed to avoid alteration in the properties of graphene. In the post reduction process, hydrazine solution was mixed with as-synthesized graphene oxide and stirred at 100 °C for 24 h using rapid synthesizer. A majority of oxygenated groups are removed other than acid functionalities during such a reaction. Before its use, the synthesized graphene oxide of sheet sizes ranging from 5 nm to 1500 nm was kept under observation for 6 h to examine the stability of colloids [16,17]. The transformed colour of GO to rGO during its synthesis is shown in Fig. 1a. The TEM image of synthesized rGO as presented in Fig. 1b, indicating a wrinkled surface texture (image obtained from JEOL 3010 Transmission electron microscope). 53 grade ordinary Portland cement (OPC) conforming to IS 12269-1987 and polycarboxylic ether (PCE) based superplasticizer as dispersion agent were used in this study. Table 1 shows the chemical composition of the cement.

Dry aluminium oxide nanopowder $(n-Al_2O_3)$ of mean size less than 50 nm and silicon dioxide nanoparticles of average size 12 nm dispersed in deionized water $(n-SiO_2)$ having surface area of 40 m²/ g and 225 m²/g respectively were obtained from Sigma-Aldrich. Energy dispersive X-ray analysis was performed on the nanomaterials, and the results are shown in Fig. 1c.

2.2. Sample preparation

Four different cement paste mixes with a water to cement (w/c) ratio of 0.32 and dispersion agent (PCE) of 0.05% by weight of cement were prepared. Table 2 specifies the type and amount of nanomaterials used in the different mixes.

For better dispersion, pre-mixing of the nanomaterials along with deionized water and PCE were carried out using a magnetic stirrer for 15 min, followed by ultrasonication in an ultrasonic bath for next 30 min Fig. 2 shows the well-dispersed rGO solution (black coloured liquid) used in this study.

For paste preparation, the ingredients were mixed in a high speed Hobart mixer for 12 min. After mixing, the mini slump test was conducted to determine the flowability; the remaining paste was used for casting specimens of size $25 \times 25 \times 25$ mm and $20 \times 20 \times 160$ mm for determining the compressive and flexural strength respectively. Consolidation was performed using a vibration table. The specimens were demolded after 24 h and then cured in saturated limewater solution at room temperature ($25 \pm 2 \degree$ C) for 7 and 28 days.

2.3. Testing methods

A mini slump cone as shown in Fig. 3a was used for conducting the mini slump test in order to determine the workability of cement paste. The procedure specified by Collins et al. [18] was followed in this study. To determine compressive and flexural strength, the specimens were tested at a loading rate of 143 N/sec and 50 N/sec respectively. Both tests were performed using Controls C9842 testing machine on different frames having the capacities of 250 kN and 15 kN respectively.

Water sorptivity test was performed on the specimens of size $25 \times 25 \times 12.5$ mm (sliced from the 25 mm cubes) after 7 and 28 days. After curing, the specimens were stored in acetone for the next two days to arrest the hydration followed by air drying for two days. Further, the dried specimens were kept in a shallow tray of size not less than 150×75 mm with roller arrangement as shown in Fig. 3b. Then the tray was filled with limewater solution (5 g per 1 L of distilled water). The final water level was maintained slightly above the bottom edge of the specimen. The mass of the specimen was measured at specified intervals such as 0, 3, 5, 7, 9, 12, 16, 20 and 25 min. Before weighing, the adsorbed water at the specimen surface was removed with a moist cloth. Finally, the vacuum saturated mass of the specimens was measured.

The influence of rGO, n-Al₂O₃ and n-SiO₂ on the microstructure of cement paste cured for 28 days was characterized using XRD, FTIR, TGA and SEM. The paste samples were ground using mortar and pestle and sieved through 75 μ m sieve for XRD, FTIR and TGA testing. Bruker XRD machine was used to determine the crystalline phases formed in the nanocomposites and the control paste. IR absorption spectra were collected using PerkinElmer FTIR instrument for all paste samples. Netzsch TGA testing machine was used for determining the amount of Portlandite in pastes cured for 28 days. For SEM investigation, the fractured surface of paste sample was tested using FEI Quanta 400 FEG-SEM device. To enhance its conductivity, a 3 nm thick Gold/Palladium layer was coated over the surface of the specimen.

The effect of nanomaterials on the pore structure of OPC paste was characterized using MIP and 3D X-ray CT. Firstly, the distribution of gel pores (<10 nm) and capillary pores (10 nm–10 μ m) in a paste sample of size 7 × 7 × 7 mm was determined using Thermo Scientific Pascal 140/440 series MIP instrument. Secondly, the distribution of pores/voids (>100 μ m) in a paste sample of size 10 × 10 × 10 mm was determined using tomographic images acquired through GE phoenix v|tome|x s 3D X-ray CT testing machine.



Fig. 1. a. GO transformed into rGO, b. TEM image of the synthesized rGO and c. EDS spectrum of the nanomaterials used in the study.

Table 1

Chemical composition of 53 grade OPC (conforming to IS 12269-1987) used in this study.

Name of the compound	CaO	SiO ₂	Al_2O_3	Fe ₂ O ₃	SO_3	MgO	Cl
% by weight	62.16	20.95	5.14	3.06	3.08	1.33	0.009

Table 2

Amounts of the different nanomaterials added into OPC paste.

Type of mix	Control	rGO	n-Al ₂ O ₃	n-SiO ₂
Nanomaterials (% by wt.)	-	0.02	0.20	4.0

Additionally, multiple slices from the acquired tomographic images were processed and analysed using the software named Image Pro Premier 9.1 to determine the pore area fraction of the slices which is better explained in subsection 3.7.

3. Results and discussion

3.1. Mini slump spread, compressive and flexural strength

The relative increase/decrease (expressed as %) of the experimental results with different nanocomposites compared with the control paste is presented in Table 3.

The addition of rGO, $n\text{-}Al_2O_3$ and $n\text{-}SiO_2$ in OPC paste was seen to reduce the workability by 13%, 11% and 24% respectively



Fig. 2. Well dispersed rGO solution (black coloured liquid) used in this study.

Fig. 3. a. Mini slump cone test apparatus and b. Water sorptivity test.

 Table 3

 Relative change in performance in pastes with nanomaterials (expressed as % of control paste).

No	Paste mixes	% By wt. of cement	Percent increment or decrement					
			Compressive strength	Flexural strength	Slump spread	Mass porosity	Sorptivity Index	
			7/28 days	7/28 days		7/28 days	7/28 days	
1	Control	_	100/100	100/100	100	100/100	100/100	
2	rGO	0.02	120/122	170/123	87	80/96	82/104	
3	n-Al ₂ O ₃	0.20	132/123	204/123	89	89/93	70/151	
4	n-SiO ₂	4.0	145/141	218/104	76	76/81	89/170	

compared to the control mix. As mentioned earlier, these nanomaterials are super sorbents having high surface area, and lead to the absorption of maximum amount of available free water in the early ages [19–21]. Due to such an effect, the early strength enhancement achieved by the pastes with different nanocomposites (rGO, n-Al₂O₃ and n-SiO₂) was found comparatively higher when compared to the 28 days strength enhancement results as mentioned in Table 3. In particular, the 2-dimensional (sheet-like) rGO even at small concentrations (0.02% by weight) proved efficient in comparison with the 3-dimensional spherical/ angular nanomaterials such as n-Al₂O₃, and n-SiO₂. The good performance of rGO can be attributed to its quality of better dispersion in a polar solvent like water, the shape and size factors, and the presence of functional groups such as carboxyl and hydroxyl on the structure of the graphene sheets [9,10].

3.2. Mass porosity and water sorptivity index

The relative increase/decrease (expressed as %) of the mass porosity and water sorptivity index results with different nanocomposites and the control paste are presented in Table 3. The results indicate that the nanomaterials (rGO, n-Al₂O₃, and n-SiO₂) in OPC paste at initial ages led to a decrease in the water sorptivity (and porosity) compared to the control mix. Pore refinement due to the presence of nanomaterials and increased production of hydration compounds such as C–S–H, C–H, AF_t and AF_m at early ages are the possible reasons for this effect. However, at later ages, the high surface area nanomaterials cause an increase in the water sorptivity (porosity in all the pastes is almost the same) possibly owing to the super-absorbing behaviour.

3.3. XRD pattern and IR spectra

The X-ray diffraction pattern and the Infra-red spectra shown in Fig. 4a and Fig. 4b were obtained from the different nano-composites and the control paste cured in limewater solution for 28 days.

No major differences could be seen in the diffraction patterns of the different pastes, indicating similar mineralogical compositions. In case of IR spectra, the peaks attributed to O–H bend ~1645 cm⁻¹, S–O stretch ~1118 cm⁻¹, SiO₄ ~ 950 cm⁻¹ vibration representing the presence of free water, ettringite and silicates were observed in all pastes cured for 28 days. Secondly, the peaks attributed to C–O stretch ~1414 cm⁻¹ and C–O bend ~874 cm⁻¹ vibration representing the presence of CO_3^2 were also obtained in the pastes with nanocomposites (rGO, n-Al₂O₃, and n-SiO₂) and the control paste, which is indicative of carbonation.

3.4. Thermogravimetric analysis

The TGA curves of the pastes with different nanocomposites and the control paste cured for 28 days are shown in Fig. 5. Table 4 presents the gravimetric changes that were obtained from the pastes.

The peaks P_1 and P_2 specified in the TGA plot indicate the gravimetric changes due to decomposition of Ca(OH)₂ and CaCO₃ respectively. The presence of the CaCO₃ can be attributed to the original cement (~4% in the cement used), as well as to the conversion from hydrated lime due to carbonation. The total Ca(OH)₂ is therefore calculated by adding the Ca(OH)₂ after 28 days from the TGA study along with the approximate quantity of Ca(OH)₂ that



Fig. 4. a. XRD pattern and b. IR spectra of the different pastes cured for 28 days.



Fig. 5. TGA curves of the different pastes cured for 28 days.

Table 4

Gravimetric changes (in percentage) obtained from the TGA study.

decreased value when compared to the other pastes after 28 days. Such an effect is well supported with the help of compressive strength results of $n-SiO_2$ paste.

3.5. Scanning electron microscopy images

High resolution SEM images were obtained for the pastes with the different nanocomposites to observe the morphological changes at high magnification due to the incorporation of nanomaterials (rGO, n-Al₂O₃ and n-SiO₂). Fig. 6a-b shows the morphology of rGO cement composite cured for 28 days. It was found that the production of thin non-uniform platelets and entangled network of rod like crystals were observed at various locations in the rGO sample after 28 days.

Fig. 7a-b shows the morphology of $n-Al_2O_3$ cement composite cured for 28 days. The images show the presence of rod like crystals within the C–S–H matrix and the production of cloud-like C–S–H which is non-uniform in texture due to the addition of crystalline alumina nanomaterials into the cementitious matrix.

Fig. 8a-b shows the morphology of $n-SiO_2$ cement composite cured for 28 days. Here, the pozzolanic conversion due to the addition of reactive silica nanoparticles caused the formation of a homogeneous textured C–S–H matrix at various places in the n-

Mix designation	Control	rGO	n-Al ₂ O ₃	n-SiO ₂
$P_1-\%$ Dehydroxylation of Ca(OH)_2 ~430-480 °C $P_2-\%$ Decarbonation of CaCO_3 ~600-780 °C Total Ca(OH)_2 in % by mass	6.04	7.15	8.06	4.11
	13.98	11.77	11.57	10.32
	14.14	13.62	14.38	9.50

Note: P_1 corresponds to the removal of water from Ca(OH)₂, so the mass change in TGA is adjusted to the Ca(OH)₂ content by multiplying by the ratio of molecular masses of Ca(OH)₂ and H₂O. Similarly, as P₂ corresponds to the removal of CO₂ from CaCO₃, the mass change in TGA is adjusted to the CaCO₃ content by multiplying by the ratio of molecular masses of CaCO₃ and CO₂. Further, the total Ca(OH)₂ is then calculated as the sum of P₁ and stoichiometric quantity of CH from P₂ (assuming the reaction as: Ca(OH)₂ + CO₂ \rightarrow CaCO₃ + H₂O).

transforms to calcite by carbonation.

From the results in Table 4, it can be seen that the potential C–H is similar in rGO and n-Al₂O₃ pastes when compared to control paste. In the case of n-SiO₂, the rapid conversion of C–H to C–S–H products due to pozzolanic reactivity was the reason behind the

SiO₂ sample after 28 days.

3.6. Porosimetry results

Fig. 9 shows the MIP result of the different nanocomposites and



Fig. 6. Secondary electron images of the pastes with rGO nanocomposite after 28 days.



Fig. 7. Secondary electron images of the paste with n-Al₂O₃ nanocomposite after 28 days.

the control paste cured for 28 days — in each plot, two curves are presented — the cumulative intrusion curve and the differential intrusion curve. Table 5 presents the evaluation of the pore structure features of the pastes such as amount of gel and capillary pores, threshold pore diameter and most likely diameter obtained from MIP data. While the ranges for gel and capillary pores were classified based on Aligizaki [22], the threshold diameter was selected as the pore size beyond which there was a sudden increase in the intrusion, and the most likely diameter was chosen as the peak from the differential intrusion curve.

It can be seen from the results that the well-dispersed rGO in OPC paste was found to decrease the capillary pores up to 32.1% compared to the control paste due to factors such as pore refinement and increased production of cement hydrates as observed from the TGA results. However, the rGO addition was found to increase the gel pores in cementitious matrix up to 36.5% when compared to control paste possibly due to the increased formation of C–S–H gel. Gong et al. [11] have observed similar MIP results in OPC paste containing 0.03% GO addition by weight cured for 28 days. In case of n-Al₂O₃ and n-SiO₂, the gel and capillary pores were found increased to a significant extent when compared to control paste due to agglomeration/bundling of such nanomaterials within the cementitious matrix. However, as reported earlier in the paper, the mechanical performance of such mixes was found to be increased compared to the control paste. This might be due to better particle packing between the nanoadditives and the cementitious compounds.

3.7. 3D X-ray CT images

The CT scans were performed at the Centre for Non-destructive Evaluation (CNDE), Indian Institute of Technology Madras. Different pastes of sample size $10 \times 10 \times 10$ mm were scanned using an X-ray source generated at a voltage and current of 120 kV and 70 μ A



Fig. 8. Secondary electron images of the paste with n-SiO₂ nanocomposite after 28 days.



Fig. 9. Porosimetry results of the different pastes cured for 28 days.

respectively. Additionally, the scanning rate was maintained around 4 ms per image, in order to have a voxel resolution up to $20 \ \mu m$ approximately during reconstruction of images. Caesium lodide based flat panel detector was equipped inside the CT testing

Table 5
Pore structure features of the pastes cured for 28 days obtained from MIP data.

Paste mixes	Gel pores <10 nm in mm ³ /g	Capillary pores (10 nm–10 $\mu m)$ in mm $^3/g$	Threshold diameter in nm	Most likely diameter in nm
Control	10.69	48.58	26.8	14.7
rGO	14.60	33.01	20.7	12.9
n-Al ₂ O ₃	26.97	60.58	39.1	27.1
n-SiO ₂	23.42	57.76	28.6	20.4



Fig. 10. a. GLV adjusted, b. Reconstructed and c. Transparent CT image of the paste sample.



Fig. 11. Colour-coded 3D CT images of the cement paste obtained before and after Porosity analysis using the software VGStudio MAX. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 12. Histogram representing the distribution of voids present in the different pastes determined using the Porosity/Inclusion Module available in the software VGStudio MAX.

machine to convert the X-rays into light. The output data obtained from the X-ray CT run after the end of scanning period was a 2D radiograph of the paste specimen. The radiographs were extracted with the help of a data acquisition software named Phoenix datos|x CT. Later, the 2D data were reconstructed and processed with the software named VGStudio MAX version 2.2 which helps to visualise the 3D imaging of the samples.

The reconstructed CT image which is of 'n' number of voxels is a spatial distribution of the linear attenuation coefficient, which is expressed in terms of Grey Level Value (GLV), with brighter and darker regions corresponding to higher and lower value of attenuation coefficient. To visualise the presence of pores/voids inside the cement paste, the GLV of the CT image was slightly adjusted as shown in Fig. 10a. The reconstructed and transparent version of CT image of the paste sample subjected to GLV adjustment which helps to visualize the distribution of pores/voids inside the sample is shown in Fig. 10b-c.

The image reconstruction software VGStudio MAX is supplied with an optional add-on module named Porosity/Inclusion Analysis (http://www.volumegraphics.com/en/products/ vgstudio-max/porosityinclusion-analysis). This provides a range of algorithms allowing porosity/inclusions to be located within the object and yields quantitative information about these defects (voids/pores). The module is a bundle of different algorithms and modes which allows to specially investigate on pores or imperfections with high contrast (air voids) or low contrast (loose material). It also helps to examine the material with open defects that have cut through the surface or enclosed defects. Different parameters such as pore to pore distance, sphericity, and userdefined surface can be estimated using this analysis module. After the analysis run, the detailed information about each individual defect (pores/inclusion) such as its volume, projected size (Feret's diameter) and position in the material are obtained. The pores/inclusions present in the material are colour-coded in all 2D and 3D views and are also acquired along with the analysis data.

In this study, the analysis module was tested on the CT image of the paste specimens to determine the volume and diameter of the pores/voids present in the system. The only input parameters that are required to run the analysis are lower and upper bound of



Fig. 13. CT slice of the paste sample before and after analysis performed using Image analysis technique (Image Pro Premier 9.1).

the pore/void volume which are expected to be present in the material. Hence, the minimum voxel resolution of the CT image was up to 20 μ m, and the safe void volume (minimum threshold value) was fixed to have a voxel resolution of 100 μ m to avoid misleading results. After running the analysis using the module, the output data consists of parameters such as void volume, void diameter (Feret diameter), voxel counts, and coordinates of the each defect present in the system. In addition, the colour-coded 3D views of the analysed CT image were also collected from the software. Figs. 11 and 12 present the different colour-coded CT images of the paste sample analysed with the Porosity/Inclusion module and histogram of the distribution of pores/voids present in the different pastes cured for 28 days.

The histogram results suggest that the addition of nanomaterials (rGO, n-Al₂O₃ and n-SiO₂) in OPC paste was found to refine the pores/voids to a significant extent when compared to control paste. In particular, the incorporation of rGO was found efficient than the other nanomaterials (n-Al₂O₃ and n-SiO₂) in refining the voids distribution in cement paste as clearly evident from the histogram results shown in Fig. 12.

The influence of nanomaterials (rGO, n-Al₂O₃ and n-SiO₂) on refining the pores/voids was further established by determining the pore area fraction of CT slices of the paste sample. Such determination was conducted with the help of image analysis technique performed over the CT slices. Image Pro Premier version 9.1 was the software used for this analysis. The reconstructed CT image was sectioned into multiple slices (around 200). Then the pore area fraction of the slices was acquired with the use of area measurement and batch processing tools present in the image analysis software. Fig. 13 shows an unanalysed and analysed image of the paste sample obtained from the software Image Pro Premier 9.1. The output data obtained from the software were converted into a histogram representing the distribution of pores/voids in the different pastes as shown in Fig. 14.

The results reconfirm the observations of the porosity analysis presented earlier, that the addition of nanomaterials (rGO, $n-Al_2O_3$ and $n-SiO_2$) in OPC paste refines the pores/voids to a significant extent compared to control paste. It is evident that the porosity seen in the rGO slices is at a lower level compared to the $n-Al_2O_3$ and $n-SiO_2$ pastes.

4. Conclusions

The mechanical, durability and microstructure performance of cementitious paste incorporating nanomaterials such as rGO, n-Al₂O₃ and n-SiO₂ at concentrations of 0.02%, 0.20% and 4.0% by weight respectively was reported in this paper. The key findings are summarized as follows:

- 1. The addition of nanomaterials (rGO, n-Al₂O₃ and n-SiO₂) reduces the workability of OPC paste.
- 2. The use of nanomaterials increases the compressive and flexural strength of cementitious paste at early and later ages. In particular, the mechanical performance of 0.02% rGO nanosheets was found efficient than the spherical/angular shaped nanomaterials (n-Al₂O₃ and n-SiO₂).
- 3. The nanomaterials decrease the mass porosity and water sorptivity of OPC at 7 days compared to the control paste. However, there is a marginal increase at 28 days, possibly owing to the sorbing nature of these materials.
- 4. Morphological alterations in the microstructure of OPC paste due to the addition of nanomaterials (rGO, n-Al₂O₃ and n-SiO₂) were observed from the SEM images. Thermal analysis, IR spectra and XRD pattern indicate that the pastes with nanocomposites (rGO, n-Al₂O₃ and n-SiO₂) after 28 days were identical compositionally to OPC paste, with the exception of the lower C–H content in n-SiO₂ by thermal analysis because of the pozzolanic reaction.
- 5. The porosity analysis (surface and volume) by X-ray tomography suggests that the incorporation of nanomaterials was found useful in refining the pores/voids (100 μ m-3 mm) to a significant extent than the control paste cured for 28 days. The improved performance of rGO paste was also seen in the MIP studies. However, the gel (<10 nm) and capillary pores (10 nm -10μ m) were found increased due to agglomeration of nanomaterials such as n-Al₂O₃ and n-SiO₂ in OPC paste, as observed from MIP results. The overall results clearly show that the performance of 2D rGO was more convincing than n-Al₂O₃ and n-SiO₂ in terms of refinement of pores/voids and capillary pores in OPC paste as determined from tomography and porosimetry results.



Fig. 14. Histogram representing the pore area fraction of the CT slices of the different pastes determined using the image analysis technique (Image Pro Premier 9.1).

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