Content-based adaptive network model to analyze the effect of graphene oxide on cement hydration process and its main hydration products

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Abstract. Graphene oxide nanomaterials can significantly alter and enhance the microstructure of cementitious materials, thus improving their mechanical properties and durability and bringing about a variety of functionalities of cementitious materials. In this paper, the role of graphene oxide (GO) on cement hydration process and its important hydration products, calcium hydroxide (CH) and hydrated calcium silicate gel (C-S H), was investigated under an adaptive network model. Various GOs were characterized analytically using high atomic force microscopy and transmission electron microscopy techniques, and both the hydration process and the concentration of their hydration products were measured in freshly mixed aqueous mortars with various GO admixtures using heat of hydration, X-ray diffraction studies and thermal reanalysis tests.

Keywords: Graphene oxide; cement hydration; hydration products; investigation of effects.

1. Introduction

Cement is the main component of cementitious materials, which gradually solidifies and hardens after contact with water, during which cement clinker particles will undergo various chemical reactions with water, resulting in the formation of crystals such as hydrated calcium silicate gel (C-S-H), calcium alumina crystal (AFt), calcium hydroxide crystal (CH) and its single sulfur type calcium sulfoaluminate crystal (AFm), etc. The microstructure they produce is the basic source of the toughness of cementitious composites. The microstructure they produce is the basic source of toughness of cementitious composites. However, because the hydration process of cement is complex and variable, the shape and structure of the hydration process are subject to various degrees of change, which leads to a large number of microcracks in the internal microstructure of cementite, which is the source of both the problem of brittleness and low toughness of cementitious materials and the problem of poor resistance of cementitious materials to environmental corrosion. Therefore, the problem of brittleness and low toughness of cementitious materials can be really improved fundamentally only if some techniques can be used to change the internal microstructure of cementite [1].

2. Experiment

2.1. Raw materials

The reference cement is P I type 42.5 pure silicate cement, and the chemical composition and physical properties of the cement are shown in Table 1~Table 2.

In the graphene oxide dispersion (G325), the solid concentration of graphene oxide is about 3 mg/mL. The water reducing agent is a high efficiency water reducing agent (PCE) of polycarboxylic acid anion, the famous product is Sika Visco Crete 3301. The initial fixed concentration of the water reducing agent is 46.3%, and for practical application, it is diluted to 15% of the fixed concentration with deionized water.

2.2. Paste preparation

Polycarboxylic acid water reducing agent can also be used as GO dispersion solution in the process test of producing GO cement slurry. Firstly, according to the preparation ratio of the test, the required GO solution is mixed with cement to become the specified amount of water reducing agent on average, and then placed in the ultrasonic cleaning machine (55 kHz) for 10min ultrasonic dispersion, and then mixed as a slurry. The cement-cement ratio of the cement slurry used for this experiment was 0.35, and the amount of water-reducing agent incorporated was 0.8% of the total cement content. GO was added to the cement using an equal amount of aqueous solution instead of water, so that the solid admixture ratio of GO reached 0.01%, 0.03% and 0.05% of the cement mass, respectively. The specific preparation quantity ratio is shown in Table 3. The preparation method of the slurry refers to Chinese national standard GB/T8077-2000.

Table 1. Chemical and mineral composition of cement clinker.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	f-CaO	C_3S	C_2S	C_3A	C_4AF
22.10	4.53	3.43	64.9	3.35	0.4	0.51	0.92	56.07	21.08	6.21	10.43

Table 2. Physical properties of cement.

Sample	Dosage of GO *w*/%	Mix proportion/g		
		Cement	Water	PCE
Blank	0	300	103.15	2.4
G325 01	0.01	300	93.15	2.4
G325 03	0.03	300	73.15	2.4
G325 05	0.05	300	53.15	2.4

PCE—Polyearboxylate superplasticizer.

Table 3. Mix proportion of cement pastes.

Fineness 0.08/%	Density/(g·cm^{-3})	Specific surface area/(m^2·kg^{-1})	Standard consistency/%	Soundness / mm	Setting time/min		Flexural strength/MPa		Compressive strength/MPa	
					Initial	Final	3 d	28 d	3 d	28 d
0.6	3.15	350	25.6	0.5	132	198	5.6		27.5	

3. Test Method

3.1. Heat of hydration test

The hydration of cement is a process that continuously gives off heat, and the calculation of the heat of hydration that occurs when the clay hydrates can simply reflect whether the cement hydration process is a different chemical reaction in the presence of other substances. TAM Air material and cement hydration heat isothermal calorimeter experiments were used. The test temperature was set at 25°C and the test time was 3 days [2]. Before testing, it was required to ensure that the heat capacity of the specimen and the reference sample were the same. The reference sample used for the instrument was 21.5930 g of quartz sand. The specific heat capacity of quartz sand is 0.76 J/K.g, the specific heat capacity of water is 4.18 J/K.g, and the specific heat capacity of cement is 0.75 J/K.g. Therefore, when fixing the water-cement ratio and heat capacity, the mass of cement and water required for the test can be calculated separately. The specific sample amounts for the test were 7.4156 g of cement and 2.5954 g of liquid, where the liquid included water and graphene oxide solution. In addition, due to the high weighing requirement, the required amount of each sample can be weighed after 100 times magnification when configuring the liquid, stirred well and then weighed the liquid of the mass used for the test. For the test, when the thermal equilibrium of the instrument is completed, the weighed various specimens are injected into a 20 mL ampoule, mixed quickly and uniformly and then placed in the calorimetric channel for the test [3].

3.2. X-ray diffraction analysis

X-ray diffraction (XRD) can be used to characterize the content of various crystal minerals and crystal hydration products during the hydration of cement. A Bruker D8 advance type X-ray diffractometer was used for the experiments. After preparing the paste, the (hardened) paste was taken out at a certain age according to the test conditions, impregnated with anhydrous ethanol solution for 24 h to terminate the hydration and then dried in an electric oven at 50°C for 24 h. The specimens to be tested were then crushed into a fine powder, sieved through 80 um, and a certain amount of powder was placed on a specimen tray and placed in a specimen bin for testing.

3.3. Thermogravimetric analysis

When the specimen is maintained to a certain age, the specimen is taken out, and the hydration is terminated with anhydrous ethanol solvent, and then it is powdered (after 80um sieve) and put into an electric oven to bake at 105℃ until constant weight, and then 1~2 specimens are placed in alumina ceramic crucible with an analytical balance, and put into a muffle furnace to heat up to 1000℃ for 3h to clear the non-evaporated water. After dehydration, the sample and crucible were cooled to the appropriate temperature in a dryer. Then the burn-off is weighed and calculated and the degree of hydration of the cement is estimated according to the following formula.

$$m_w = \frac{(100 - m_L)m_1 - 100m_2}{m_2} \tag{1}$$

Where: mw is the chemically bound water content (%); ML is the burn loss of the cement (1.25 for the base cement); m1 is the mass of the sample before the test (g); .m2 is the amount of the specimen after the measurement (g). The amount of CH generated during the hydration reaction of the cement was analyzed qualitatively with a NETZSCH STA449F5 simultaneous thermal analyzer. After removing the specimens at a certain age, the samples were treated in the same way as described in the X-ray diffraction analysis. Weigh 10~30mg specimens and place them in an alumina crucible for testing. The test temperature was controlled from 50 to 950°C, with a maximum rate of rise of 10C/min, and was kept under nitrogen throughout [4].

4. Test Results

4.1. Effect of graphene oxide on the exothermic hydration of cement

Figure.1 shows the velocity curves of the exothermic stages of hydration of silicate materials with different GO admixtures. From Figure 5-1, it can be found that no significant change in the thermal velocity profile of cement hydration was observed when GO was incorporated, and the velocity of the reaction time of each step was basically the same.

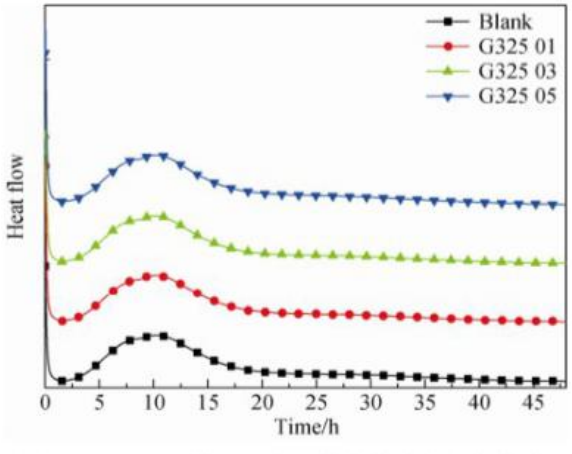


Figure 1. Hydration exothermic rate curve of cement at different GO dosing.

The rate of cement hydration forms a great negative impact on the stability of the finished cement after setting and hardening. Therefore some scholars, such as Lin and Lv, have proposed the promotion effect of GO on cement hydration, and according to this theory, one of the important factors that GO improves the material mechanical stability of cement is the promotion effect of GO on the hydration rate of cement. However, the heat of hydration experiments can confirm that the addition of GO has no significant effect on the hydration rate of cement, i.e., GO does not have an effect on cement hydration [5]. The reason for the increased effectiveness of GO on the material mechanics and durability of cement, etc., is not significantly related to its effect on the hydration rate.

4.2. Chemically bound water testing of hardened graphene oxide cement pastes

Figure.2 shows the variation of GO dosing on the concentration of chemically bound water of cementite at different ages. From Fig. 5-2, it can be found that the concentration of chemically bound water gradually increases with the increase of age temperature.

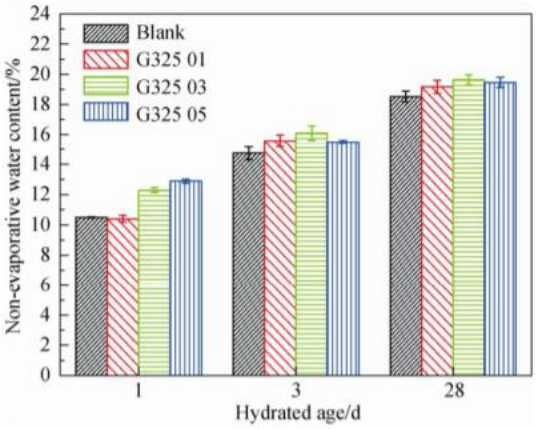


Figure 2. Effect of GO dosing on chemically bound water content at different hydration ages.

From the point of view of chemically bound water, the incorporation of GO seems to have a certain promotion effect on the hydration process of cement. This obviously contradicts with the results of the heat of hydration of cement. Since the heat of hydration is the most intuitive and accurate reflection of the hydration process of a material, it can be inferred that the results of the determination of the chemically thermally bound water content are incorrect in the presence of GO. And assuming that the actual hydration process of the building rock does not change, the only factor that produced an error in the calculation results is that the independent water removed at 105°C was not sufficient, while some other independent water was retained in the building rock under the influence of GO and was lost only at higher temperatures, thus producing an error in the calculation results [6].

4.3. Thermogravimetric Analysis of Hardened Graphene Oxide Cement Slurry

Figure.3 shows the TG-DTA curves of GO cement bodies with different admixtures after 1.3 d and 28 d of hydration, respectively. From the figure, it can be found that as the hydration time range increases and the hydration strength increases, the overall weight loss temperature of the hardened cement bodies also undergoes a corresponding range of increase. For a certain age range alone, the weight loss of the specimens gradually increases with respect to the control group due to the increase in GO admixture. This difference is especially obvious in 1 d of hydration, and then gradually decreases as the age range of hydration increases. The interception of TG specimens can be obtained from 110 to 400°C (due to the increase in silicate. The proportion of hydrated calcium silicate gels in the material is larger compared to calcium alumina, and calcium alumina crystals often undergo dehydration and dissolution before 100°C, and the decomposition rate can even exceed 98% at 110°C. Therefore, only the fusion water of the gel and the volatilization of its intrinsic physisorbed water, collectively referred to as gel weight loss, are affected in this temperature range) and at 400-500°C (CH decomposition) [7].

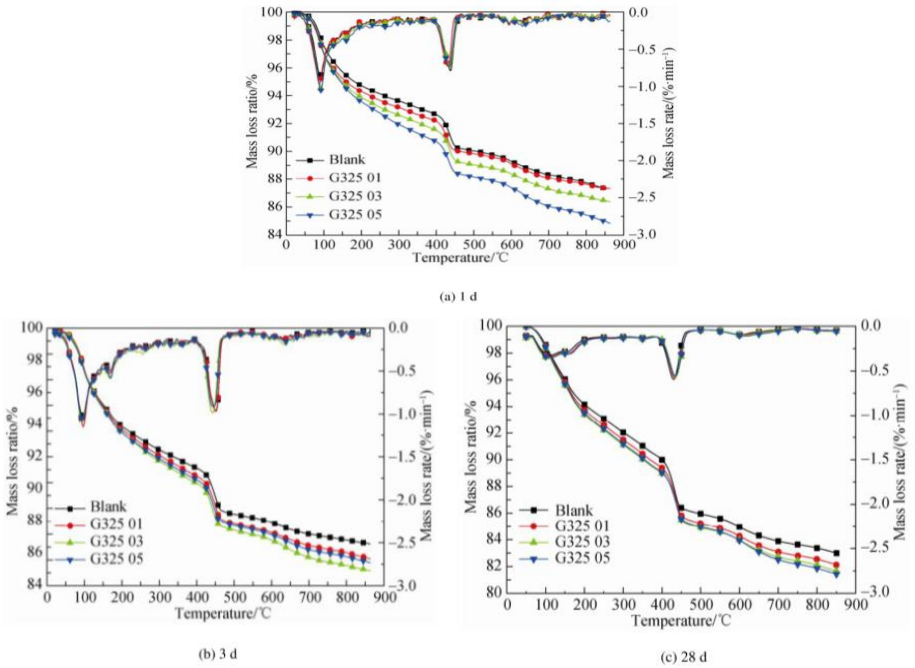


Figure 3. TG-DTA curves of GO cements with different dosing levels at different hydration ages.

Figure.4 and Figure.5 represent the gel weight loss and CH content of the hardened cement slurry for different GO and admixture types at different hydration age ranges, respectively. The .TG-DTA analysis of the cement with different admixtures of GO at different age ranges was utilized to quantify the main. The hydration process produced CH and gel weight loss by thermal decomposition method.

From the analysis of the calculated results, on the one hand, it can be further confirmed by the quantitative analysis of CH that GO does not have a significant effect on the total amount of CH produced in the cement hydration process. In addition, by quantifying the weight loss of gel composite products at 110~400C, it can be judged that various blended GOs have a significant effect on the gel composites hydrated by cement. For silicate cement products, the hydrated calcium silicate gel is the main gel material product among the hydration products, and both its and CH amounts are generated by the hydration process of calcium silicate minerals, so when it is confirmed that GO has no effect on the amount of CH generated in the cement structure during hydration, it is also confirmed that GO has no effect on the amount of C-S-H generation in the main gel material product, and the chemical influence combined with no effect on the water evaporation weight loss [8]. Therefore, the addition of GO directly affects the properties of the gel pores in the first place, so that the free water present in the gel pores does not evaporate completely at 105°C. The effect of GO on the "reorganization of the flocculation structure" within the cement paste not only affects the rheology of the paste, but also has a profound effect on the microstructure of the paste during the hardening process has a profound effect on the microstructure of the paste during the hardening process.

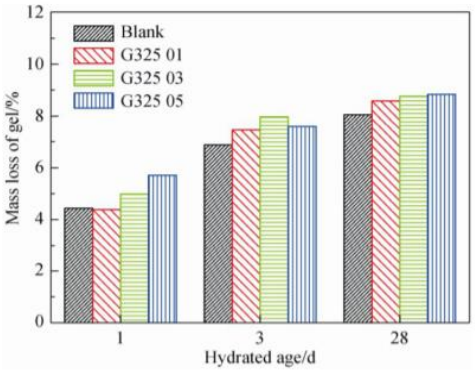


Figure 4. Effect of GO dosing on cement gel quality loss at different hydration ages.

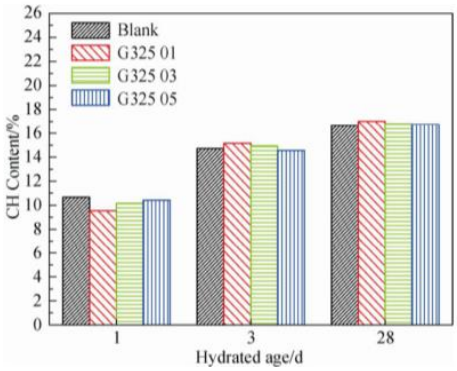


Figure 5. Effect of GO dosing on cement CH content at different hydration ages.

4.4. Nitrogen adsorption testing of hardened graphene oxide cement pastes

Figure.6 to Figure.8 show the nitrogen absorption pore size distribution curves and cumulative pore volume curves of GO-hardened cement paste within various ages in turn. According to the difference of pore size, the pores in the hardened cement bodies are divided into gel pores (≤10 nm, capillary pores (10~1000 nm) and large pores (>1000 nm), of which the capillary pores, in turn, can be divided into small capillary pores (10~100 nm) and large capillary pores (100~1000 nm).

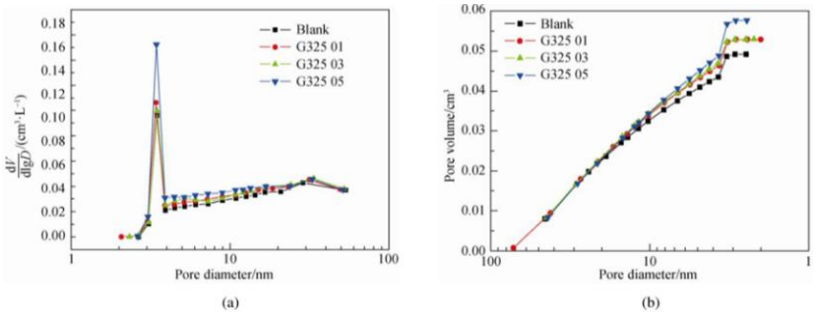


Figure 6. Nitrogen adsorption pore size distribution curve of GO hardened cement paste at the age of 3d.

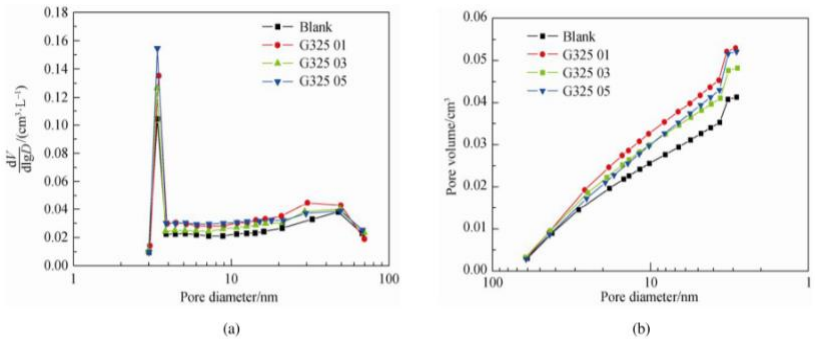


Figure 7. Nitrogen adsorption pore size distribution curve of GO hardened cement paste at 7d age.

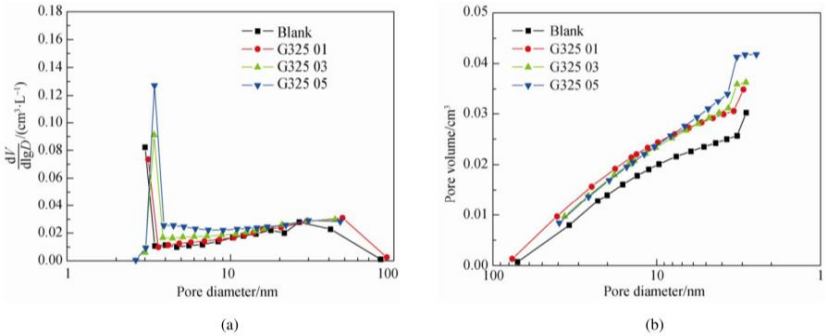


Figure 8. Nitrogen adsorption pore size distribution curve of GO hardened cement paste at 28d age.

The pore size of the hardened cement slurry measured by the nitrogen adsorption method ranges from 1 to 100 nm, and through the measured pore size distribution curve, we found that the most available pore size in the region of 1 to 100 nm is about 3.5 nm, which is the gel pore size. And by analyzing the test results we can find that the addition of GO has a great effect on the gel structure in the hardened cement paste, which can significantly increase the gel pore volume in the hardened cement paste and has the function of further refining the pore structure of the hardened cement paste, and this effect also becomes more and more prominent with the increase of GO dosing [9].

4.5. XRD testing of hardened graphene oxide cement pastes

Figures.9 show the XRD spectra of the cement slurry with GO doping above 0.03% and the blank group. The results of the analysis found no new diffraction peaks due to GO production, but the very important difference occurs in the part of the CH crystal around 18°. The brightness of the diffraction peaks at this area is significantly reduced due to the GO incorporation. To investigate this difference, small-angle diffraction was made on the samples in the range of 18° to 22°, respectively

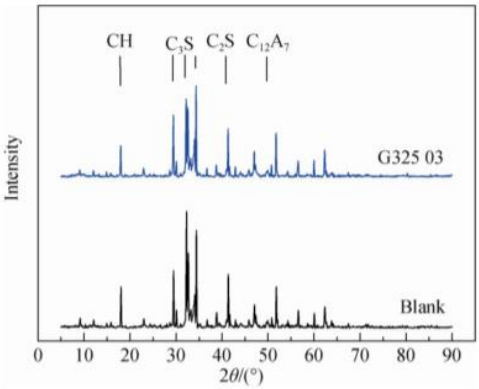
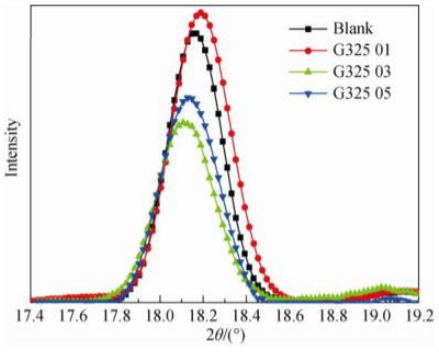


Figure 9. XRD spectra of hardened cement paste with different GO doping at 3d age.

Figures.10 show the XRD spectra of the materials with different GO doping near 18° at 1d, 3d and 28d of hydration. It can be seen from the figures that the diffraction peak intensities and peak bandwidths of the different materials at each time interval differ quite significantly. The factors affecting the intensity of the lattice diffraction peaks are mainly the amount of microcrystalline volume on the corresponding crystalline faces of the 2 crystals; the amount of the corresponding crystalline content. And the thickness of the corresponding crystalline surface microcrystals, which can be calculated by Debye-Scherrer's equation as follows:

$$D=\frac{K\cdot\gamma}{B\cdot\cos\theta} \tag{2}$$

Where: D is the average thickness of the grain in the direction perpendicular to the crystal plane, microcrystal size (nm); K is the Scherrer constant, equal to 0.89; y is the X-ray wavelength, equal to 0.1549 nm; B is the sample diffraction peak half-height width (rad); 0 is the diffraction angle (rad)



(a) 1 d

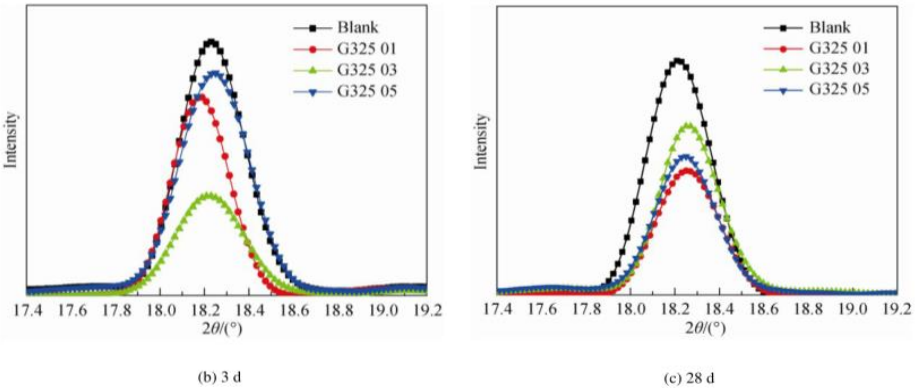


Figure 10. CH-XRD spectra of hardened cement slurry with different dosing of GO at different ages.

Figure.11 shows the CH (001) crystalline surface microcrystalline scale of various GO-doped cements at various hydration age regions. The effect of GO doping on the microcrystalline size differs due to the difference in age regions. At 1d of hydration, the microcrystalline size of CH increased correspondingly due to the increase of GO doping; at 3d and 28d of hydration, the microcrystalline volume of CH decreased correspondingly due to the increase of GO doping. The effect of different GO dopants on the microcrystal volume is more prominent in hydration 3d. However, when considered together, the addition of GO acts on the crystals of CH in the microcrystalline size level of the (001) crystalline plane of CH and also has some refinement effect on the crystals of CH [10].

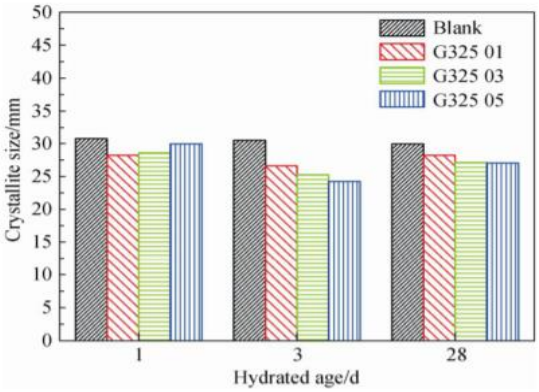


Figure 11. Size of CH(001) crystalline surface microcrystals of GO cements with different doping levels.

According to the intensity analysis of the characteristic CH peaks, the intensity of the peaks of GO-intermediated materials is much weaker than that of the control group in general, despite the fact that there is no consistent pattern of variation in the intensity of the CH peaks of GO materials with different degrees of internal admixture due to the increase in the hydration time range. This also indicates that the presence of GO leads to the conversion of a higher fraction of CH in the cement hydration reaction to other crystalline states [11]. Based on the calculation of the winding peaks of the XRD spectra and the calculation of the microcrystal size, it can be concluded that GO has a significant role in changing the crystal size and crystalline shape of CH, one of the most dominant hydrated substances, in the cement hydration reaction. Thus GO can also have the function of further refining the crystallite size of CH.

5. Conclusion

The effects of graphene oxide on the hydration process and hydration results of cement were described by heat of hydration test, TG-DTA test, and XRD test, respectively. The results show that (1) graphene oxide does not have a significant effect on the hydration process of cement, and the high oxygen-containing functional groups of graphene oxide itself do not affect the hydration of cement

as envisioned; (2) graphene oxide also has a great influence on the formation of pores in the gel structure produced by the cement paste after hardening, and due to the increase of graphene oxide doping, it can hold more gel-like pores in the free water, which can refine and close the porous structure at a certain level; (3) oxidation of multilayer graphene, which also has an important effect on the morphology of the main substance of cement hydration, a calcium hydroxide. The production of multilayer graphene after oxidation can not only have a significant inhibitory effect on the preparation of hexagonal flaky crystalline calcium hydroxide, but also refine the thickness of crystalline calcium hydroxide.

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