Effects of Graphene Oxide Encapsulated Silica Fume and Its Mixing with Nano-Silica Sol on Properties of Fly Ash-Mixed Cement Composites

Shun Zhou, Xiaotao Zhang, Han Zhou and Dongxu Li *

College of Materials Science and Engineering, Nanjing Tech University, Nanjing 211816, China; 201961103057@njtech.edu.cn (S.Z.); 201961103054@njtech.edu.cn (X.Z.); 201861103006@njtech.edu.cn (H.Z.)
* Correspondence: dongxuli@njtech.edu.cn

Abstract: In the present research work, the ternary effects of varying dosages of graphene oxide encapsulated silica fume (GOSF), nano-silica sol (SS), and fly ash (FA) on the rheological properties, compressive strength, the content and crystal size of calcium hydroxide (CH), porosity, water absorption, and microstructure of cement were studied. The results showed that the incorporation of SF improved the dispersion of GO in the cement matrix. GOSF was prepared through electrostatic attraction between the positively charged SF and negatively charged GO. The ternary mixture of GOSF, SS, and FA had a synergistic effect that improved the performance of cement. When the curing age of cement reached 28 days, the compressive strength reached a peak of 86.5 MPa, the minimum values of content and crystal size of CH were 11.55% and 45.69 nm, respectively, and the minimum values of water absorption and porosity were 0.0011 cm/s\(^{0.5}\) and 13.56%, respectively. In terms of microstructure, the denser structure of C-S-H gel and the regular arrangement of CH were noticed.

Keywords: silica fume; silica sol; graphene oxide; fly ash; orthogonal experiment

1. Introduction

During the curing of cement, a large quantity of calcium hydroxide (CH) crystals is developed as a part of the hydration process, which affects the bond between hydration products leading to the deterioration of the cement performance. The pozzolanic material contains SiO\(_2\), which can react with CH to form C-S-H gel. Hence, the CH content in cement is reduced, the CH crystal size is refined, and the C-S-H content is increased, thus effectively improving the properties of cement-based composites [1–3]. As an industrial by-product with pozzolanic properties, fly ash (FA) has been widely used in cement-based composites to replace cement, and the durability of cement-based composites is greatly improved by incorporating FA. FA-mixed cement not only has the characteristics of low drying shrinkage, corrosion resistance, and high later strength but also has significant environmental and economic benefits. However, due to the low activity of FA in the early stage, FA will not slowly participate in cement hydration until at least 7 days later [4]. Even at 28 days, the improvement effect of FA on cement performance was not significant, limiting the further application of FA in the field of construction [5–7]. The silica fume (SF) is also an industrial by-product and contains a large amount of SiO\(_2\). The particle size of SF is small and, therefore, can be used as filler to fill the pores between cement and FA particles to improve the bulk density of FA-mixed cement. The pozzolanic activity of SF is higher than that of FA, the addition of SF can improve the interfacial structure of FA-mixed cement, refine the interfacial CH grains, and reduce the orientation degree of interfacial CH crystals [8,9]. Therefore, the early strength of FA-mixed cement can be effectively enhanced by adding the appropriate amount of SF. However, due to the limitation of early activity, SF reacts slowly with CH within 1 to 3 days [10–12].
With the development of nanomaterials, more ideas and methods have been provided to improve FA-mixed cement performance. In the early 1990s, British scientist Taylor confirmed the existence of nano calcium silicate hydrate (C-S-H) in cement, laying the foundation for the performance of cement reinforced by nanomaterials [13]. Incorporating a small amount of nanomaterials can affect the hydration process of cement and the formation of cement hydration products, thus enhancing the performance of cement. Compared with other nanomaterials, the application of nano-silica (NS) and graphene oxide (GO) in cement has attracted much attention [14,15]. Due to the extremely high pozzolanic activity of NS, NS can quickly react with CH to form additional C-S-H gel and compact the cement matrix. The appropriate addition of NS can make up for the defects of FA-mixed cement and greatly improve the early strength of cement. Meanwhile, FA also offsets the early shrinkage of cement caused by the incorporation of NS, reducing the risk of structural cracks [16–19].

GO can accelerate the hydration process of cement by providing abundant nucleation sites and high aspect ratios and form regular hydrated crystal shapes. When GO is incorporated into the cement, it acts as a two-dimensional sheet structure to aggregate the hydration products of the cement on the surface of GO to form a denser C-S-H gel, thus improving the structure of cement [20–22]. LV et al. found that with the incorporation of 0.03 wt.% GO in the cement, the mechanical properties of cement were significantly improved [23]. Therefore, the overall performance of cement can be improved by incorporating NS and GO in the cement matrix containing SF and FA.

However, nanomaterials with small particle size and large specific surface area have a higher tendency to agglomerate, which affects their dispersibility in the cement matrix. In the cement containing SF and FA, how to improve the dispersion of NS and GO is difficult to be solved [24–26]. The agglomeration of NS seriously affects its pozzolanic activity, nucleation effect, etc. Compared with NS powder, nano-silica sol (SS) is liquid and has better dispersion stability in water. The effects of NS powder and SS on the hydration of cement were compared. It was found that compared with NS powder, SS could significantly accelerate the process of hydration and further improve the mechanical properties of cement [27–30]. GO also has similar problems, due to the strong Van der Waals self-attraction and ionization interference, GO is prone to agglomeration in the alkaline environment of cement paste, limiting its strengthening effect on cement. How to effectively disperse GO in a highly alkaline environment is a challenge [31,32].

Some researchers pointed out that the dispersibility of GO can be improved by the addition of SF [33–38]. Firstly, when SF is mixed with GO solution, GO tends to wrap around SF particles through electrostatic attraction. The electrostatic resistance offered by the same charge between the SF adsorbed with GO induces the dispersion of GO in cement, which is beneficial to improve the effect of GO on the early performance of FA-mixed cement; Secondly, SF can react with CH to generate C-S-H gel through pozzolanic reaction, which reduces the concentration of Ca$^{2+}$ around GO, thus reducing the possibility of interaction between GO and Ca$^{2+}$ [11,33,34]. Chandra studied the effects of GO, SF, and FA on the microstructure and mechanical properties of cement and found that with the incorporation of 3 wt.% and 5 wt.% SF in the cement paste, the agglomeration of GO can be reduced, and the addition of FA helped improve the fluidity of the cement paste [35]. However, the surfaces of SF and GO have the same negative charge and repel each other, so the adsorption capacity of SF to GO is limited. It is reported that with the help of positively charged amino functional groups in amino silane, the surface of SF is changed from the negative charge to the positive charge that is more suitable for adsorbing GO [36,37]. Yu et al. studied the GO wrapped on the surface of SF particles and prepared a new material with little effect on the fluidity of cement paste [38]. This method provides a good idea for the application of GO in cement.

In this paper, SF is modified by KH550 to change its surface charge, then GO is modified on the surface of SF to obtain GO encapsulated SF (GOSF). GOSF has the characteristics of both SF and GO. SF acts as a carrier to disperse GO, making GO disperse more evenly in cement paste. The effects of varying dosages of GOSF, SS, and FA on the properties
of cement are studied by orthogonal design, including setting time, fluidity, compressive strength, phase composition, etc. The test results are analyzed and modeled by Design-expert software. So far, only a few studies are available on this type of modified cement system. It is hoped that the research in this paper can provide some reference for preparing cement-based composites with excellent performance.

2. Materials and Methods

2.1. Raw Materials

Portland cement (PC, PII52.5) was purchased from Jiangnan-Onoda Cement Co., Ltd. (Nanjing, China); SF and FA were provided by Hui-feng New Materials Co., Ltd. (Suzhou, China); GO solution (7.6 g/L) was provided by Jiangnan Graphene Research Institute. Nano-silica sol solution (solid content 30%) was purchased from Xian-feng Nanomaterials Technology Co., Ltd. (Nanjing, China). The polycarboxylate superplasticizer (PCE) was provided by Jiangsu Zhao Jia Building Materials Technology Co., Ltd. (Suzhou, China), with a water-reducing rate of 40%; γ-Aminopropyltriethoxysilane (KH550) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China).

The chemical composition and particle size of the experimental materials are shown in Table 1, which are measured by XRF and a laser particle size analyzer, respectively.

Table 1. Chemical composition of cement, FA, and SF.

| Materials    | Cement | Fly Ash | Silica Fume |
|--------------|--------|---------|-------------|
| SiO₂ (%)     | 21.45  | 50.77   | 96.35       |
| Al₂O₃ (%)    | 4.33   | 27.87   | 0.465       |
| Fe₂O₃ (%)    | 3.41   | 5.04    | 0.281       |
| CaO (%)      | 63.46  | 3.31    | 0.0532      |
| MgO (%)      | 1.49   | 0.762   | 0.0325      |
| Na₂O (%)     | 0.26   | 0.704   | 0.0202      |
| K₂O (%)      | 0.57   | 2.54    | 0.02        |
| TiO₂ (%)     | 0.24   | 1.20    | 0.0271      |
| MnO (%)      | 0.14   | 0.0611  | 0.0325      |
| P₂O₅ (%)     | 0.16   | 0.245   | 0.351       |
| ZrO₂ (%)     | 0      | 0       | 1.52        |
| LOI (%)      | 1.68   | 6.63    | 0.76        |
| Median particle size (µm) | 18.33 | 15.75 | 1.636 |

The XRD patterns of Portland cement (PC) and FA are shown in Figure 1a. The XRD pattern of FA is mainly composed of broad diffraction peaks and a characteristic hump appears around 30°, indicating that the FA comprises a large number of amorphous phases. The existence of a few sharp diffraction peaks indicates the presence of mullite and quartz phases. The XRD patterns of SF and SS are the same, and the diffraction peak only appears around 22°, indicating that both SF and SS are amorphous phase. Moreover, the curve of SS is relatively smooth, whereas the SF has weak impurity peaks, validating the presence of impurities in SF. In addition, the diffraction peak intensity of SS is higher than that of SF. This may be due to the fact that the number of particles involved in diffraction differs.
2.2. Fabrication of GOSF

The surface charge of SF was changed from negative to positive with surfactant to achieve a better adsorption of GO on its surface. During this process, SF was firstly ultrasonically for 10 min to disperse the particles in ethanol. Then, the KH550 (1 wt.% of SF) was added to the deionized water and stirred for 3 min. Next, the KH550 solution was added to the SF solution and stirred for 90 min at 75 °C to obtain modified SF (MSF). The suspension was washed with ethanol and deionized water.

MSF was firstly ultrasonicated for 5 min to disperse the particles in water. Then, GO was added to the MSF solution and stirred for 60 min using magnetic stirring. The positively charged MSF and negatively charged GO were assembled together through electrostatic interaction. The supernatant was collected, and after drying, it was found that the content of GO was extremely low, indicating that almost all the GO was assembled with MSF. The GOSF was obtained after centrifugation and vacuum-drying at 60 °C for 2 days.

The preparation principle of GOSF is shown in Figure 2a. It can be seen from Figure 2b that the color of GOSF is slightly darker than that of the original SF, validating the encapsulation of SF by GO. To facilitate the comparison of subsequent experiments, the ratio of SF and GO was set as 200:1.
2.3. Preparation of the Cement Paste

The cement paste with a water-to-binder ratio of 0.4 was prepared by mixing cement, water, FA, GOSF/SF, and SS/GO. The cement, FA, and GOSF/SF were added to a mixing container and stirred for 120 s. GO/SS was ultrasonicated for 5 min to disperse the particles in water, then GO/SS solution was added into the container. The mixture was stirred at a low speed for 120 s, stopped for 15 s, and at high speed for 120 s. After the stirring process, the paste was cast into a $20 \times 20 \times 20$ mm mold and compacted 15 times on a vibration table. The samples were cured in the standard curing room ($20^\circ$C/RH 95%).

The effect of GOSF on the rheological and mechanical properties of FA-mixed cement is preliminarily studied by setting up four groups of comparative tests, which are recorded as experiment 1. The proportions of raw materials are shown in Table 2. The dosage of PCE is 0.1875 g.

| Sample        | Cement (%) | FA (%) | GO (%) | GOSF (%) | SF (%) |
|---------------|------------|--------|--------|----------|--------|
| FAPC          | 75         | 25     | 0      | 0        | 0      |
| SF-FAPC       | 71         | 25     | 0      | 0        | 4      |
| GO-SF-FAPC    | 71         | 25     | 0.02   | 0        | 4      |
| GOSF-FAPC     | 71         | 25     | 0      | 4        | 0      |

Table 2. The dosages of different materials in experiment 1.

As shown in Table 3, the orthogonal experiment with three factors and three levels is designed using Design-expert software. This is the focus of this paper, which is recorded as experiment 2. Three independent variables, such as GOSF, SS, and FA are set at the upper, middle, and lower levels, respectively, with a total of 17 groups of experiments. The dosages of GOSF, SS, and FA are varied from 4 wt.% to 8 wt.%, 0.5 wt.% to 1.5 wt.%, and 10 wt.% to 25 wt.% of total cementitious materials, respectively. The dosage of PCE is 0.7 g. The data are analyzed and modeled by Design-expert software, and the fitting equations of the independent variable and dependent variable are obtained.
Table 3. The dosages of different materials in experiment 2.

| Sample | GOSF (%) | SS (%) | FA (%) |
|--------|----------|--------|--------|
| 1      | 4        | 0.5    | 17.5   |
| 2      | 8        | 0.5    | 17.5   |
| 3      | 4        | 1.5    | 17.5   |
| 4      | 8        | 1.5    | 17.5   |
| 5      | 4        | 1      | 10     |
| 6      | 8        | 1      | 10     |
| 7      | 4        | 1      | 25     |
| 8      | 8        | 1      | 25     |
| 9      | 6        | 0.5    | 10     |
| 10     | 6        | 1.5    | 10     |
| 11     | 6        | 0.5    | 25     |
| 12     | 6        | 1.5    | 25     |
| 13     | 6        | 1      | 17.5   |
| 14     | 6        | 1      | 17.5   |
| 15     | 6        | 1      | 17.5   |
| 16     | 6        | 1      | 17.5   |
| 17     | 6        | 1      | 17.5   |

2.4. Testing Methods

2.4.1. Zeta Potential and FT-IR

The surface charges of GO and SF were analyzed by a Zeta potentiometer.

GO, SF, MSF, and GOSF were characterized by Fourier transform infrared spectroscopy (FT-IR, EQUINOX-55, BRUKER Corporation, Karlsruhe, Germany). The wavenumber range was set from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\).

2.4.2. Dispersion Stability

In this test, CH saturated solution was used to simulate the pore solution of cement. GO and GOSF were diluted to 0.01 wt.% and 2 wt.% (containing 0.01 wt.% GO) with CH saturated solution, respectively. The two diluted solutions were ultrasonicated for 5 min to disperse the particles and placed for 10 min.

2.4.3. XRD and SEM/TEM

An X-ray diffractometer (XRD, Rigaku D/Max-RB, Rigaku Corporation, Tokyo, Japan) was used to detect the phase composition of samples.

The morphology of samples was analyzed by scanning electron microscope (SEM, JEOL-IT300, JEOL Japan Electronics Co., Ltd., Tokyo, Japan) and transmission electron microscope (TEM, JEOL-2100F, JEOL Japan Electronics Co., Ltd., Tokyo, Japan).

2.4.4. Setting Time and Fluidity

According to GB/T 1346-2011 standard [39], the setting time of cement paste was measured with Vicat apparatus.

According to JC/T 1083-2008 standard [40], the fluidity of cement paste was tested.

The AMT-1 marsh time automatic tester was used to measure the marsh time of cement paste.

2.4.5. Compressive Strength and TG/DSC

According to GB/T 17671-1999 standard [41], the compressive strength of hardened cement paste was tested.

The content of CH in the samples was quantitatively characterized by TG/DSC. The temperature was from room temperature to 1000 °C, the heating rate was 10 °C/min, and the protective gas was nitrogen. The mass loss in the temperature range of 400 °C to 500 °C was caused by the decomposition of CH [42]. The decomposition process of CH can be
expressed by the following reaction Equation (1). According to Equation (2), the CH content of samples can be calculated.

\[
\text{Ca(OH)}_2 \xrightarrow{\Delta} \text{CaO} + \text{H}_2\text{O} \uparrow \quad (1)
\]

\[
m_{\text{CH}} = m_{400-500^\circ\text{C}} \times \frac{M_{\text{CH}}}{M_{\text{H}_2\text{O}}} \quad (2)
\]

where \(m_{400-500^\circ\text{C}}\) represents the mass loss caused by the decomposition of CH. \(M_{\text{CH}}\) and \(M_{\text{H}_2\text{O}}\) represents the molecular weight of CH and H\(_2\)O, respectively.

### 2.4.6. Water Absorption and MIP

According to the ASTM C1585-13 standard [43], the water absorption of samples at 28 days was tested. The samples were firstly dried to constant mass, then four sides of the samples were wrapped. Next, the initial mass of samples was recorded before immersing the samples in water for testing, where the water level is 2 mm from the bottom of the samples. The wet mass of samples were measured at different times, and the interval time was 1 min, 2\(^{1/2}\) min, 3\(^{1/2}\) min, 4\(^{1/2}\) min, 5\(^{1/2}\) min, 6\(^{1/2}\) min, 7\(^{1/2}\) min, and 8\(^{1/2}\) min. Then the water absorption of samples was calculated by Equation (3).

\[
K = \frac{(m(t) - m_0) / \rho}{A \sqrt{t}} \quad (3)
\]

The Mercury intrusion porosimetry (MIP, POREMASTER-60, Quantachrome Corporation, Boynton Beach, FL, USA) was used to detect the pore size distribution and porosity of hardened cement paste.

### 3. Results and Discussion

#### 3.1. Characterization of MSF and GOSF

It can be seen from Figure 3 that the zeta potential of SF changes from \(-64.6\) mV to +11.47 mV after modification. There are a large number of active silicon hydroxyl groups on the surface of SF. When the silicon hydroxyl groups on amino-siloxane react with the functional silicon hydroxyl groups on the surface of SF, the positively charged amino groups are grafted to the surface of SF in the form of chemical bonds. The zeta potential of GO is \(-9.89\) mV, indicating that the character of GO has a negative potential. Amino-siloxane was used to change the surface potential of SF particles, which is beneficial to the combination of SF and GO. It can be seen from Figure 4 that the modification of SF does not affect the phase composition of SF.

It can be seen from Figure 5 that the position and intensity of the infrared absorption peak of MSF have changed. The peak at 3589 cm\(^{-1}\) is the \(-\text{OH}\) peak, and there is still a hydroxyl peak after modification, indicating that the hydroxyl group on the surface of MSF does not completely react with the hydrolyzed silane coupling agent. A weaker absorption peak appears at 2883 cm\(^{-1}\) and is the C-H stretching vibration peak of \(-\text{CH}_{2}\). The peak at 1630 cm\(^{-1}\) is the unique bending vibration absorption peak of adsorbed water. The absorption peak at 1616 cm\(^{-1}\) is caused by the overlap of the N-H bending vibration of the \(-\text{NH}_{2}\) functional group and the bending vibration absorption peak of water molecules after some amino groups are grafted on the surface of SF. The peak at 1120 cm\(^{-1}\) is the anti-symmetric stretching vibration peak of Si-O-Si, and the absorption peak at 810 cm\(^{-1}\) and 474 cm\(^{-1}\) are the symmetric stretching vibration and the bending vibration of Si-O-Si, respectively. The wave peak at 694 cm\(^{-1}\) is the plane oscillating vibration absorption peak of the N-H bond. Combined with the results of zeta potential and infrared analysis, new characteristic peaks \(-\text{NH}_{2}\) and \(-\text{CH}_{2}\) appear on the surface of MSF, indicating that KH550 and SF are covalently bonded, and the chemical modification is successful. In addition, there are a large number of hydroxyl and carboxyl groups on the surface of GO. The characteristic groups corresponding to the characteristic peaks of 1720 cm\(^{-1}\), 1600 cm\(^{-1}\),
and 1400 cm\(^{-1}\) are C=O, C-C, and -C=C-, respectively. GOSF is composed of GO and SF, while the infrared analysis result of GOSF is similar to that of SF, and no obvious characteristic peak of GO is observed because the content of GO in GOSF is too low.

![Figure 3. Zeta potential of GO, SF, and MSF.](image)

![Figure 4. XRD patterns of SF and GOSF.](image)
As shown in Figure 6a, the morphology of SF is observed by SEM. The shape of SF particles is spherical. As shown in Figure 6b, the morphology of GO is observed by TEM. GO is distributed in layers with multiple layers overlapping. Figure 6c shows the TEM image of the GOSF particles and it is inferred that the GOSF particles exhibit a wrinkled texture related to the flexible GO sheets where the GO sheets and SF spheres are intertwined. The GO sheets seem to link adjacent SF spheres together, which indicates that the SF spheres are encapsulated by the GO sheets.
3.2. Dispersion Stability of GO/GOSF

To understand the dispersion stability of GO and GOSF in CH saturated solution, the dispersion test was carried out. The pore solution of cement contains a lot of Ca\(^{2+}\), which is easy to cross-link with the -COO- on the surface of the GO and makes GO agglomerate in the cement paste. As shown in Figure 7, it can be clearly seen that most of the GO agglomerates in the CH saturated solution and precipitates at the bottom of the bottle. However, in the CH saturated solution containing GOSF, the aggregation phenomenon of GO is not observed. Compared with the 0.01 wt.% GO addition, the degree of precipitation in the solution containing 2 wt.% GOSF (containing 0.01 wt.% GO) is less, which indicates that the various ions in the CH saturated solution have less influence on GOSF. This is because most GO sheets are absorbed and wrapped on the surface of SF, which separates the GO from Ca\(^{2+}\) adhering, thus reducing the flocculation behavior of GO in the CH saturated solution. Moreover, compared with nanolevel GO, micro-level SF has more negligible effects on the fluidity of cement paste.

3.3. Fluidity and Setting Time of Cement Paste

In experiment 1, to understand the influence of GOSF on the fluidity of cement paste, four groups of comparative tests were carried out. The results are shown in Figure 8. Compared with GO-SF, GOSF has less influence on the fluidity of cement paste. This is
because GO is wrapped on SF, which further improves the dispersion of GO in the cement paste and increases the fluidity of cement paste by 14.71%.

Figure 8. The fluidity of cement paste in experiment 1.

Further, in experiment 2, to study the effects of GOSF, FA, and SS on the fluidity of cement paste, fluidity and marsh time tests are carried out. The results are shown in Table 4. Due to the excessive viscosity of S3 (Sample3), S4, S10, and S12, it is easy to block the nozzle of the marsh tube, and the marsh time cannot be accurately measured. To quantify the marsh time of the cement paste, the inverse of the marsh time ($1/t_{200}$) is calculated so that the unmeasured marsh time is infinitely close to zero; then, the results of $1/t_{200}$ are analyzed. There have been a lot of studies on the conclusion that FA can improve the fluidity of cement paste [1–7]. So this paper mainly studies the influence of the dosages of GOSF and SS on the two dependent variables, $1/t_{200}$ and fluidity. The data are analyzed and modeled, and the model equations are established through multiple linear regression analysis, as shown in the following equations (Equation (4), $R^2 = 0.99$; Equation (5), $R^2 = 0.99$).

\[
\text{Fluidity} = 170.6 - (3.87 + 0.5SS + 10.05GOSF + 3.75FA)GOSF - (54.37 + 2.55SS - 4.25FA)SS - (11.3FA - 7.75)FA \quad (4)
\]

\[
1/t_{200} = 0.1 + \{(2.469SS - 4.479 - 19GOSF - 5.582FA)GOSF - (64 + 19SS + 1.218FA)SS - (19FA - 5.038)FA\} \times 10^{-3} \quad (5)
\]
Table 4. Test results of macroscopic properties of samples.

| Sample | Fluidity (mm) |Marsh Time (s)  | Setting Time (min) | Compressive Strength (MPa) |
|--------|---------------|----------------|--------------------|----------------------------|
|        |               | Initial         | Final             | C$_{3d}$ | C$_{28d}$ |
| 1      | 220           | 7.5            | 398               | 538      | 32.88     | 72.8     |
| 2      | 207           | 8.1            | 461               | 546      | 30.38     | 63.26    |
| 3      | 110           | /              | 354               | 494      | 34.38     | 60.92    |
| 4      | 95            | /              | 390               | 510      | 31.93     | 63.42    |
| 5      | 140           | 17.9           | 340               | 476      | 37.83     | 78.9     |
| 6      | 146           | 18.5           | 394               | 506      | 34.73     | 86.5     |
| 7      | 160           | 11.8           | 380               | 535      | 28.7      | 51.48    |
| 8      | 151           | 16.5           | 463               | 568      | 26.35     | 61.32    |
| 9      | 205           | 8              | 408               | 518      | 35.5      | 80.57    |
| 10     | 90            | /              | 351               | 500      | 36.75     | 78.6     |
| 11     | 215           | 7.7            | 464               | 564      | 26.51     | 58.83    |
| 12     | 117           | /              | 379               | 504      | 27.75     | 53.5     |
| 13     | 175           | 9.5            | 384               | 529      | 29.52     | 73.8     |
| 14     | 167           | 10.3           | 389               | 519      | 30.85     | 75.62    |
| 15     | 170           | 9.8            | 385               | 516      | 31.3      | 76.2     |
| 16     | 169           | 10             | 392               | 520      | 29.8      | 75.93    |
| 17     | 172           | 9.6            | 378               | 526      | 31.65     | 74.6     |

Figure 9 shows the influence of GOSF and SS on the two dependent variables. It can be seen that the change of SS content has the most obvious effect on the rheological properties of FA-mixed cement paste. When SS content increases from 0.5 wt.% to 1.5 wt.% at constant FA and GOSF content, the fluidity of cement paste is decreased from 220 mm to 110 mm (50%). As a nanoscale material, SS can easily form dense agglomerates because of its small particle size, large specific surface area, and high surface energy.

In experiment 1, when 0.02 wt.% GO is added into the cement, the marsh time of cement paste is increased by 29.6%, which is similar to the conclusion of the literature [44]. Interestingly, in experiment 2, it is found that incorporating GOSF in cement increases from 4 wt.% to 8 wt.%, i.e., GO content increases from 0.02 wt.% to 0.04 wt.%, and the marsh time is increased only by 7.4%. The reason for this phenomenon is that GO is adsorbed and wrapped on the SF surface. Compared with nanolevel GO, microlevel SF has less effect on the fluidity of the cement paste.

In addition, the setting time of samples in experiment 2 is shown in Table 4. It can be seen that the setting time of SS is the shortest. With the increase of GOSF and FA content, the setting time of cement is prolonged, which is because the decrease of cement content
leads to the delay of cement hydration. Adding SS into cement can effectively reduce the setting time of cement paste. Due to the high pozzolanic activity of SS, it is easy to combine with CH to form C-S-H gel at the initial stage of cement hydration. Therefore, the early hydration and hardening process of FA-mixed cement is accelerated.

### 3.4. Compressive Strength of Samples

The compressive strength of samples in experiment 1 was tested and the results are shown in Figure 10. Compared with SF-FAPC, the compressive strength of GOSF-FAPC at 28 days is increased by 26.67%. Due to the unique two-dimensional sheet structure, excellent mechanical properties, large specific surface area, and abundant oxygen-containing groups of GO, the hydration products are hydrated and crystallized on the surface of GO, and the compressive strength of samples is significantly improved [45]. Compared with the GO-SF-FAPC, GOSF-FAPC is more effective in improving the compressive strength of samples, and the compressive strength of GOSF-FAPC at 28 days is increased by 5%. This is because the dispersion of GO has been further improved.

![Compressive strength of samples in experiment 1.](image)

Further, to understand the effects of GOSF, SS, and FA on the mechanical property of samples, compressive strength tests were carried out. The compressive strength of samples at 3 days and 28 days (C3d and C28d) were tested. The data are analyzed and modeled, the model equations (Equation (6), R2 = 0.98; Equation (7), R2 = 0.95) are shown as follows:

\[
C_{3d} = 30.62 + (1.02\text{GOSF} + 0.013\text{SS} + 0.19\text{FA} − 1.3)\text{GOSF} + (0.69 + 0.75\text{SS} + 0.0025\text{FA})\text{SS} + (0.26\text{FA} − 4.44)\text{FA} \quad (6)
\]

\[
C_{28d} = 75.23 + (1.3 − 4.23\text{GOSF} + 3.01\text{SS} + 0.56\text{FA})\text{GOSF} − (2.38 + 5.9\text{SS} − 0.84\text{FA})\text{SS} − (1.45\text{FA} + 12.43)\text{FA} \quad (7)
\]

Because of the low reactive nature of FA, the increase of FA content results in the decline of C3d and C28d. However, the dosages of GOSF and SS have different effects on C3d and C28d. As shown in Table 4, the C3d of S5 is the highest, which is consistent with the result of the setting time, indicating that S5 hydrates faster in the early stage and the internal structure of SS is more compact. The effects of GOSF and SS content on C3d are shown in Figure 11a. When GOSF content increases from 4 wt.% to 8 wt.% at constant FA content, C3d is decreased by about 2 MPa. When SS content increases from 0.5 wt.% to 1.5 wt.% at constant FA content, C3d is increased by 4.5%, the enhancement effect of SS on C3d is not obvious. This is similar to the reports of Du et al. [46], when the content of nano-silicon in cement increases from 1 wt.% to 2 wt.%, the increase of compressive strength of cement was less than 5 MPa. The reason for this phenomenon is that SS has a higher influence on the rheological properties of cement paste, and therefore, the increase of SS content in cement leads to excessive fluidity loss that further leads to the high viscosity of cement paste. It is not conducive to the uniform distribution of various materials in cement paste, limiting the reinforcement effect of SS on C3d. The influence of GOSF and SS
Even in the cement mixed with 25 wt.% FA, when 1 wt.% SS and 8 wt.% GOSF are added into the cement, C\textsubscript{28d} can reach 61.32 MPa, which is higher than the standard compressive strength of PII52.5 cement at 28 days. This shows that the mixing of GOSF and SS can effectively compensate for the early strength decline of FA-mixed cement. However, the content of GOSF and SS needs to be appropriate, the excessive content of GOSF is not conducive to the development of the early strength of cement. The effect of SS content on C\textsubscript{28d} is consistent with the reports of Sharma [47]. When SS content was 0~1 wt.%, C\textsubscript{28d} was positively correlated with it. While SS content was more than 1 wt.%, C\textsubscript{28d} was negatively correlated with it. The addition of SS makes the internal hydration products of the cement become denser; however, the dense hydration products wrap part of the un-hydrated cement particles, which limits the further hydration of the cement particles.

![Figure 11](image_url)

**Figure 11.** Compressive strength of samples at 3 days (a) and 28 days (b) vs. the dosages of GOSF and SS.

### 3.5. Water Absorption Test

The water absorption can indirectly reflect the microcracks and pores structure of cement. The effects of GOSF, SS, and FA on water absorption of samples at 28 days (K\textsubscript{28d}) are studied. The model equation (Equation (8), R\textsuperscript{2} = 0.9) is shown as follows:

\[
K_{28d} = [15.2 - (1.75 + 0.25SS + 1.1GOSF + 0.25FA)GOSF + (1.875 + 4.65SS - 3FA)SS + (1.625 + 1.15FA)FA] \\
\times 10^{-4}
\]  

(8)

It can be seen from Figure 12 that GOSF has a positive effect on reducing K\textsubscript{28d}. When GOSF content is increased from 4 wt.% to 8 wt.%, K\textsubscript{28d} is decreased by 21.74% at most. Moreover, the appropriate quantity of SS can reduce K\textsubscript{28d}, and when SS content is less than 1%, K\textsubscript{28d} decreases with the increase of SS. In other cases, K\textsubscript{28d} increases with the increase of SS. The addition of SS increases the viscosity of cement paste, which causes the uneven distribution of various materials in the cement past, increasing pores and microcracks in cement hydration products.
Figure 12. The effects of GOSF and SS on water absorption of samples.

3.6. Porosity Test

The pores in cement are classified into three types as per the pore diameter, namely harmless pores (<20 nm), less harmful pores (20–200 nm), and harmful pores (>200 nm) [48]. The porosity above 20 nm in the samples is calculated, and the results are shown in Table 5. The model equations (Equation (9), $R^2 = 0.97$; Equation (10), $R^2 = 0.87$) are shown as follows:

$$P_{3d} = 21.23 + (0.34 - 0.14\text{GOSF} + 0.045\text{SS} + 0.025\text{FA})\text{GOSF} - (0.13\text{SS} + 0.17\text{FA} + 0.18)\text{SS} + (0.83\text{FA} + 1.47)\text{FA}$$

(9)

$$P_{28d} = 13.8 + (5 \times 10^{-4}\text{GOSF} - 0.09\text{SS} + 0.17\text{FA} - 0.46)\text{GOSF} + (0.13\text{SS} - 0.5\text{FA} + 0.39)\text{SS} + (1.25\text{FA} + 0.33)\text{FA}$$

(10)

| Sample | Water Absorption | CH Content | Porosity | Crystal Size |
|--------|------------------|------------|----------|--------------|
|        | $K_{28d}$ (cm/s^{0.5}) | $CH_{28d}$ (%) | $P_{3d}$ (%) | $P_{28d}$ (%) | $S_{3d}$ (nm) | $S_{28d}$ (nm) |
| 1      | 0.0019           | 14.37      | 20.76    | 13.91        | 51.82         | 48.87         |
| 2      | 0.0015           | 13.03      | 21.67    | 13.66        | 48.56         | 47.26         |
| 3      | 0.0023           | 13.85      | 20.16    | 14.39        | 49.49         | 48.1          |
| 4      | 0.0018           | 12.58      | 21.25    | 13.78        | 50.08         | 48.56         |
| 5      | 0.0013           | 14.47      | 20.25    | 15.3         | 52.17         | 45.69         |
| 6      | 0.0011           | 13.77      | 20.55    | 13.56        | 50.14         | 45.66         |
| 7      | 0.002            | 12.7       | 23.24    | 16.21        | 52.89         | 48.56         |
| 8      | 0.0017           | 11.55      | 23.64    | 15.13        | 48.26         | 47.18         |
| 9      | 0.0016           | 14.31      | 20.43    | 14.03        | 50.8          | 47.81         |
| 10     | 0.0026           | 13.44      | 20.57    | 16.27        | 49.49         | 46.8          |
| 11     | 0.0022           | 12.88      | 23.61    | 15.08        | 50.47         | 47.8          |
| 12     | 0.002            | 12.23      | 23.08    | 13.85        | 49.49         | 47.36         |
| 13     | 0.0016           | 13.53      | 20.84    | 13.85        | 50.82         | 46.21         |
| 14     | 0.0015           | 12.92      | 21.46    | 13.67        | 51.13         | 45.8          |
| 15     | 0.0015           | 13.48      | 21.04    | 13.8         | 51.52         | 46.35         |
| 16     | 0.0014           | 13.53      | 21.59    | 13.98        | 50.75         | 45.63         |
| 17     | 0.0016           | 13.24      | 21.22    | 13.72        | 51.63         | 46.6          |

Due to the low activity of FA, it mainly plays a filling role in the composite cement system. Therefore, with the increase of FA content, $P_{3d}$ and $P_{28d}$ show an upward trend. When FA content increases from 10 wt.% to 25 wt.%, $P_{3d}$ and $P_{28d}$ increase by 15% and 11.58%, respectively. This shows that with the progress of hydration, the negative effect of FA on porosity is gradually decreased because FA has participated in the hydration reaction.
Figure 13 shows the influence of GOSF and SS on the porosity of cement. From the results, it is clear that the addition of more SS leads to the lowering of the $P_{3d}$ value. However, the increase in GOSF content results in higher $P_{3d}$. Due to the extremely high pozzolanic properties and nucleation effect, SS can react with CH in the early stage of cement hydration to accelerate cement hydration and form dense hydration products. When the SS content increases from 0.5 wt.% to 1.5 wt.%, $P_{3d}$ is reduced by 3%. When the GOSF content increases from 4 wt.% to 8 wt.%, $P_{3d}$ is increased by 5.4%. When the GOSF content increases, the hydration rate of the cement decreases, resulting in the decrease of the internal structure density of cement and the increase of porosity. With the hydration of cement, the reaction activity of GOSF increases gradually, and GOSF can react with CH to form C-S-H gel. Therefore, with the increase of GOSF content, $P_{28d}$ gradually decreases, which is consistent with the test results of water absorption. In conclusion, the appropriate amount of GOSF and SS can effectively reduce the pore size in the modified cement system.

![Figure 13](image_url)

**Figure 13.** The porosity of samples at 3 days (a) and 28 days (b) vs. the dosages of GOSF and SS.

### 3.7. Effect on CH Content

Figure 14 shows the TG/DSC curve of samples in experiment 2, which is used to detect the change of CH content in cement. The TG curve is the mass loss of samples during the heating process, and the DSC curve shows the endothermic peaks caused by the decomposition or dehydration of hydration products. As shown in Figure 14, in this composite cement system, the endothermic peaks around 120 °C are formed by the dehydration of C-S-H gel and ettringite, the endothermic peaks of around 440 °C and 650 °C are formed by the decomposition of CH and CaCO$_3$, respectively.

According to the results of TG, the CH content of samples at 28 days ($CH_{28d}$) is quantitatively analyzed. The results are shown in Table 5. When FA content increases from 10 wt.% to 25 wt.%, $CH_{28d}$ is decreased by 16.12%. The reasons are as follows: (1) FA replaces part of cement and reduces the amount of cement involved in hydration reaction, resulting in the decrease of hydration products; (2) With the incorporation of FA in cement, the fluidity of cement paste is improved, GOSF and SS are more evenly dispersed in cement paste and can react with more CH; (3) FA reacts with CH through the pozzolanic effect.

The model equations (Equation (11), $R^2 = 0.9$) was shown as follows:

$$CH_{28d} = 13.29 - 0.56GOSF - 0.31SS - 0.83FA$$  \hspace{1cm} (11)
Figure 14. TG-DSC diagram of samples at 28 days.

According to the results of TG, the CH content of samples at 28 days (CH\textsubscript{28d}) is quantitatively analyzed. The model equations (Equation (11), R\textsuperscript{2} = 0.9) was shown as follows:

\[ 
\text{CH}_{28d} = 13.29 - 0.56 \text{GOSF} - 0.31 \text{SS} - 0.83 \text{FA} 
\]

Figure 15 shows the effects of GOSF and SS on CH\textsubscript{28d}, with the increase of GOSF and SS content, CH\textsubscript{28d} decreases. It can be seen from Figure 14 that the mass loss peak of S5 at 440 °C is the most obvious, indicating that the CH content of S5 is the most. In general, more hydration products lead to a denser microstructure and higher compressive strength, but this is not consistent with the obtained compressive strength test results. The reason is that GOSF and SS have a pozzolanic effect, which generates a new C-S-H gel phase while consuming CH. As a result, the CH content of S6 is lower than that of S5, but the compressive strength of the former is 19.11% more than that of the latter.

3.8. CH Crystal Size

Figure 16 shows the XRD patterns of samples in experiment 2. When the content of GOSF, SS, and FA changed, no new diffraction peak appeared, indicating that the type of cement hydration products did not change. The crystal shape and size of hydration products have an important influence on the properties of the cement. The refined CH crystal is beneficial to the compaction of cement. The CH crystal size can be determined by the XRD test. The main reflection of the (001) crystal plane of CH is around 18° and the crystal size of it can be calculated by Debye–Scherrer formula (Equation (12)):

\[ 
D = \frac{K \cdot \gamma}{B \cdot \cos \theta} 
\]
3.8. CH Crystal Size

Figure 16 shows the XRD patterns of samples in experiment 2. When the content of GOSF, SS, and FA changed, no new diffraction peak appeared, indicating that the type of cement hydration products did not change. The crystal shape and size of hydration products have an important influence on the properties of the cement. The refined CH crystal is beneficial to the compaction of cement. The CH crystal size can be determined by the XRD test. The main reflection of the (001) crystal plane of CH is around 18° and the crystal size of it can be calculated by the Debye–Scherrer formula (Equation (12)):

\[
D = \frac{K \cdot \gamma}{B \cdot \cos \theta}
\]

\[(12)\]

\(D\) is the average thickness of the crystal grains perpendicular to the crystal plane, crystal size (nm); \(K\) is the Scherrer constant, equal to 0.89; \(\gamma\) is the X-ray wavelength, equal to 0.1549 nm; \(B\) is the half-height width of the sample diffraction peak (rad); \(\theta\) is the diffraction angle (rad).

The influence of GOSF and SS on the crystal size of FA-mixed cement is studied. The model equations (Equation (13), \(R^2 = 0.84\); Equation (14), \(R^2 = 0.84\)) are shown as follows:

\[
S_{3d} = 51.17 + (0.96SS - 0.19GOSF - 0.65FA - 1.17)GOSF + (0.082FA - 0.99SS - 0.39)SS - (0.11FA + 0.19)FA
\]

\[(13)\]

\[
S_{28d} = 46.12 + (0.7GOSF + 0.52SS - 0.34FA - 0.32)GOSF + (1.37SS + 0.14FA - 0.11)SS - (0.05FA - 0.62)FA
\]

\[(14)\]

GOSF and SS have positive effects on refining the CH crystal size of samples at 3 days and 28 days (\(S_{3d}\) and \(S_{28d}\)). Figure 17 shows the influence of GOSF and SS on the CH crystal size. GOSF contains GO and SF, where GO is a two-dimensional sheet structure that facilitates the cement hydration products to aggregate and grow on the GO surface. As pozzolanic materials, SF and SS can react with CH to form a dense C-S-H gel. When the dosages of GOSF and SS increase from 4 wt.% and 0.5 wt.% to 8 wt.% and 1.5 wt.%, \(S_{3d}\) decreases by 8.75% and 2.58%, respectively. This is similar to the reports of Ye [18], where SS can refine the crystal size of CH. As the hydration proceeds, the crystal size of CH decreases gradually, \(S_{28d}\) is generally smaller than \(S_{3d}\), and the \(S_{28d}\) of S6 shows the least value. Mixing GOSF and SS in FA-mixed cement can synergistically refine the CH crystal size.
3.9. Morphology of Samples

The compressive strength of samples can reflect the change of its internal hydration products from the side. According to the shift in $C_{28d}$, five groups of samples are selected for SEM analysis, namely S5, S6, S7, S9, S10, to observe the microstructure of samples and analyze the effect of GOSF, SS, and FA on the hydration products. As shown in Figure 18, sheet-shaped CH, irregular C-S-H gel, and a small amount of unreacted FA particles can be observed in each sample, and some samples also contain needle-shaped ettringite.

By comparing Figure 18a,b, it is inferred that both S5 and S6 have relatively dense C-S-H gel and a lower quantity of sheet CH on the surface of samples. Compared with S5, S6 has a denser C-S-H gel structure, more regular CH arrangement, fewer pores, and small-sized sheet structures. It can be seen from S6 that the polyhedral hydration crystals are embedded and interwoven into each other to form a regular and compact microstructure. The possible reason behind this phenomenon is that with the increase of GOSF content, SF and GO are increased simultaneously. Compared to the samples with the lower GO content, the higher GO content is more conducive to forming the regular microstructure of cement [23]. SF has pozzolanic activity, so it can react with CH to generate more C-S-H gel, reduce the gel porosity, and improve the mechanical properties of cement. Comparing Figure 18a,c, it is found that with the addition of a higher FA content, the more unreacted FA is present. In addition, S7 also contains a large number of loose C-S-H gel and needle-like ettringite. The structure of hydration products in S7 is relatively loose and interlaced, which is not conducive to the development of the mechanical properties of cement. Comparing Figure 18d,e, it can be seen that S10 has more pores than S9. Obvious clustered hydrated crystals can be observed on the surface of S10, which is due to the difference in SS content. When the content of SS is high, SS reacts with CH and acts as a nucleation site to generate hydration products, forming the cluster structure. In addition, with the increase of SS content, the rheological property of cement paste is decreased, increasing cement porosity.
Figure 18. SEM images of samples at 28 days (magnification is 5000).

4. Conclusions

In this study, the ternary effects of GOSF, SS, and FA on the rheological properties, mechanical properties, the content and crystal size of CH, porosity, water absorption, and microstructure of cement are studied. The results are as follows:

(1) The negatively charged GO is adsorbed and coated over the positively charged SF through electrostatic attraction to obtain GOSF. Compared with GO, the interaction between GOSF and Ca\(^{2+}\) is weaker, so the dispersion of GOSF in CH saturated solution
is improved. The adsorption of GO on SF mitigates the fluidity-reducing effect of GO on the cement paste and increases the fluidity of cement paste by 14.71%.

(2) GOSF and SS can significantly improve the hydration and hardening process of FA-mixed cement, thus improving the early and later mechanical properties of FA-mixed cement. The incorporation of GOSF and SS offered an effective modification of hydration crystals, resulting in reducing CH content and refining grain size of the cement composites, which is beneficial to the compaction of cement.

(3) GOSF and SS can effectively improve pore size distribution and reduce the water absorption capability of FA-mixed cement. Because GOSF and SS can react with CH to form additional C-S-H gel, the C-S-H gel structure becomes significantly denser, thus converting the harmful pores into harmless pores and less harmful pores. In addition, SS can act as a nucleation site to form cluster hydration products in FA-mixed cement.

(4) Incorporating GOSF and SS in the FA-mixed cement can compensate for the strength loss caused by FA, and the addition of FA helps improve the fluidity of the cement paste containing GOSF and SS. The ternary mixture of GOSF, SS, and FA has a synergistic effect that improves the performance of cement, which provides some reference for the preparation of cement-based composites with excellent performances.

(5) From this work, the technology of improving the dispersion of nanomaterials in cement paste by modifying nanomaterials to the surface of supplementary cementitious materials is further deduced. For example, the feasibility of modifying SS to the surface of SF and the feasibility of using FA instead of SF to disperse GO need to be further studied.

Author Contributions: Writing—original draft, S.Z.; Validation, X.Z.; Data Curation, H.Z.; Writing—review & editing, Validation, D.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (No. 51872137) and Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The authors would like to acknowledge the assistance from Xiaotao Zhang, Han Zhou, Dalong Liao and Jiawei Jiao from Nanjing Tech University.

Conflicts of Interest: The authors declare no conflict of interest.

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