

Article

Experimental Research on the Properties and Formulation of Fly Ash Based Geopolymer Grouting Material

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Abstract: This paper experimentally investigated the effects of varying contents of Na₂O in a modified sodium silicate, sodium silicate moduli (M_s), and contents of granulated blast furnace slag (GBFS) on the compressive strength and drying shrinkage of fly ash (FA)-based geopolymer grouting materials at different ages. X-ray diffraction (XRD), mercury intrusion porosimetry (MIP), and scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDS) were used to study the influences of different amounts of GBFS on the microstructure and product compositions of FA-based geopolymer grouting materials. The results show that the content of Na₂O in modified sodium silicate, M_s , and the content of GBFS play a significant role in compressive strength and drying shrinkage of FA-based geopolymer grouting materials. In addition, the influence of M_s as well as the content of GBFS on the compressive strength and drying shrinkage of FA-based geopolymer grouting materials was deeply affected by curing age. The micro-performance tests and analysis clearly showed that incorporating 30 wt% GBFS can decrease the proportion of pores with large pore sizes, improve pore size distribution, and enhance the solubility of FA and further promote the formation of C-A-S-H gel within FA-based geopolymer grouting materials.

Keywords: geopolymer; sodium silicate modulus; granulated blast furnace slag; compressive strength; microstructure



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1. Introduction

Under the action of long-term harsh weather and traffic load, defects such as damage, decline of skid resistance, and cracks will gradually appear on many roads. Traditional pavement maintenance techniques generally adopt the method of first excavating to remove the damaged parts and then filling with new materials [1,2]. However, due to disadvantages, such as long cycle, high cost, and traffic impact, such a method fails to fix the damage; therefore, how to treat subgrade diseases and solve the problem of insufficient subgrade bearing capacity has become a great difficulty faced by road managers.

As a type of liquid slurry, grouting materials have the advantages of high fluidity, permeability, and compactness. The slurry penetrating the structure can be used for filling and squeezes air and water in gaps to occupy the available space and decrease porosity at cracks, thus improving the strength of the overall structure. Therefore, they are widely used to repair defects of buildings, such as subgrades, bridges, and coal mines [3–6]. Trenchless grouting reinforcement technology has gradually become the preferred scheme for subgrade reinforcement due to its advantages, such as simplicity of construction, rapid re-opening to traffic, and low price. Geopolymers, firstly proposed by Davidovits, are amorphous aluminosilicate gels depolymerised and repolymerised from aluminosilicate-rich materials that serve as raw materials under the action of an alkali activator. As inorganic

polymer materials, geopolymers demonstrate a chain structure and have excellent acid and alkali corrosion resistance, rapid hardening, and high-temperature resistance [7–10]. With the rapid development of industrialisation, a lot of industrial wastes, such as fly ash (FA) and slag, are produced. Relevant studies indicate that furnace slag contains many glassy substances with pozzolanic activity which weakly react with water. However, activated by alkaline or acidic substances, such as sodium silicate, $\text{Ca}(\text{OH})_2$, and NaOH , the active glassy substances in furnace slag are chemically activated to form gel products [11,12]. Under the action of a chemical activator, FA is chemically activated, and the resulting aluminosilicate gel can significantly improve the durability of activated products [13–15].

Scholars around the world have conducted experimental research on the performance of geopolymer grouting materials. Güllü [16] compared and investigated rheological properties of geopolymer grouting materials and FA cement-based grouting materials under different water-to-binder ratios. The research results show that geopolymer grouting materials exhibit better adaptability in material selection compared with cement-based grouting materials. Aboulayt [17] experimentally studied the rheological properties of geopolymer grouting materials formed by mixing metakaolin, FA, and stabiliser. The results implied that the addition of xanthan gum has a weak effect on the polymerisation, while it has positive effects on the stability of the grouting materials by acting on the activation solution. Roviello et al. [18] obtained a new hybrid material by synthesising a copolymer via a mixture of a polymer and an alkaline solution. Compared with pure geopolymer materials, the new material has a highly interpenetrating structure, excellent physical and mechanical properties, as well as better applicability to heat resistance and bonding of building structures. Furthermore, in terms of the effects of the activator on the performance of geopolymer grouting materials, Fernandez-Jimenez [19] investigated the influences of types of activator on the microstructure and mechanical properties of grouting materials. The research results suggested that an activator containing soluble Si is conducive to improving the chemical reaction of polymers and the strength of corresponding specimens. Criado [20–22] also found that the content and compositions of reaction products are closely related to the content of soluble Si in the activator, and the more aluminium silicate gel is produced, the higher the strength of the grouting materials. When hydroxide was selected as the activator, Lloyd [23] found that a small number of crystals with a large gap appear on the surface of FA, which greatly decreases the strength of specimens of grouting materials. Regarding the effects of mineral raw materials on the performance of geopolymer grouting materials, Yang et al. [24] fabricated FA microspheres through electrostatic adsorption and added them to an alkali-activated FA slag, which greatly improved the rheological properties of the geopolymer grouting materials. Amin et al. [25] explored influences of the content of sodium silicate solution on the fluidity of activated slag and found that the fluidity decreased with increasing amounts of sodium silicate solution. When 5% silica fume was added, the working performance of the grouting materials was improved. In the past few years, there have also been numerous reports on the shrinkage of geopolymers and their influencing factors. For example, with the increase in slag content or the concentration of the alkaline activator, Xu et al. [26] found that geopolymerization is accelerated and the shrinkage value increases. When basalt fiber was incorporated, it was also found that the capillary pores within geopolymers were improved and the pore network was refined, which generated a positive effect on shrinkage [27]. In addition, Xiang et al. [28] reported that the incorporation of Fuller-fine sand helps to increase the demand for “chemically combined” water within geopolymers, reducing the evaporation of water in a dry environment and further improving drying shrinkage.

At present, there have been few studies examining the effects of activators and mineral raw materials on the performance of geopolymer grouting materials. In this research, new FA-based geopolymer grouting materials were prepared by chemically activating FA and solid wastes of granulated blast furnace slag (GBFS) using modified sodium silicate. Eight different mixing ratios were designed to evaluate the influences of the content of Na_2O in modified sodium silicate, sodium silicate modulus (M_s), and the content of GBFS on the

compressive strength and drying shrinkage of FA-based geopolymer grouting materials at different ages. In addition, microstructures and product compositions of FA-based geopolymer grouting materials under different contents of GBFS were further studied by using X-ray diffraction (XRD), mercury intrusion porosimetry (MIP), and scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDS).

2. Experimental Program

2.1. Materials

In this research, FA and GBFS were used as ash raw materials. The chemical compositions and contents of FA and GBFS determined using an X-ray fluorescence (XRF) diffraction analyser are listed in Table 1. The particle size distributions of FA and GBFS were studied with a Mastersizer 2000 laser particle sizer and the median diameters (D_{50}) of FA and GBFS were 10.80 μm and 11.4 μm , respectively. The XRD analysis of FA and GBFS is demonstrated in Figure 1. Figure 1a shows that FA contains mullite and quartz and that a hump appears within $15^\circ \leq 2\theta \leq 35^\circ$, indicating that FA includes several glassy substances. As displayed in Figure 1b, diffuse scattering peaks occur within $20^\circ \leq 2\theta \leq 40^\circ$, suggesting that glassy substances are present in GBFS. Furthermore, a diffraction peak is seen at $2\theta = 29.5^\circ$ ($d = 0.30284$ nm), indicating that merwinite is contained in GBFS. A diffraction peak appears at $2\theta = 31.3^\circ$ ($d = 0.28545$ nm), suggesting that GBFS contains akermanite or gehlenite.

Table 1. Chemical composition of FA and GBFS (wt%).

Material	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	MnO	P ₂ O ₅	TiO ₂	SO ₃	LOI
FA	50.62	21.97	7.18	9.17	2.12	1.33	-	-	0.79	2.16	0.77
GBFS	33.00	14.82	0.23	40.80	-	-	0.32	0.01	0.66	-	2.31

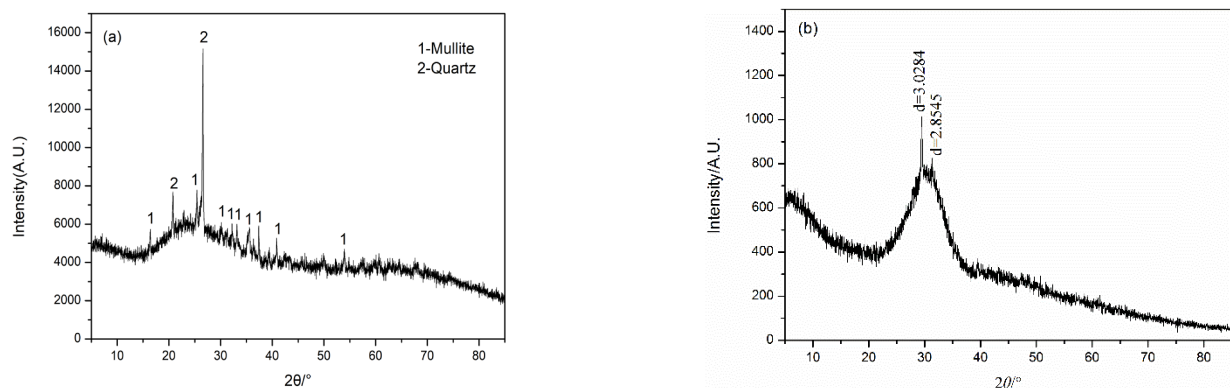


Figure 1. XRD analysis: (a) FA; (b) GBFS.

Industrial sodium silicate used in this study was provided by Nanjing Daoqin Industrial Co., Ltd. (Nanjing, China), with the contents of SiO₂, Na₂O, and H₂O being 26.2, 8.5, and 65.3 wt%. The solid sodium hydroxide with a purity $\geq 96\%$ and deionised water were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The modified sodium silicates with moduli (M_s) of 1.2, 1.4, and 1.6, and Na₂O contents of 6, 9, and 12 wt% were prepared by adding solid sodium hydroxide and deionised water into industrial sodium silicate. All modified sodium silicates were allowed to stand for 24 h before use and recovered to room temperature.

2.2. Specimen Preparation and Testing Programs

In the present study, the composite powder composed of FA and GBFS was chemically activated with the modified sodium silicate. Eight types of grouting materials were prepared according to the mass ratio of water to composite powder (W/S) of 0.45. Figure 2

illustrates the nomenclature of grouting materials and Table 2 lists the mix proportions of the grouting materials. The grouting materials were injected into cubic moulds measuring 30 mm × 30 mm × 30 mm and prismatic moulds measuring 20 mm × 20 mm × 80 mm after uniform stirring with a cement paste mixer, respectively. All specimens were immediately wrapped with polyethylene films and then placed in the curing chamber (20 ± 1 °C, RH ≥ 95%) for curing for 24 h before being demoulded.

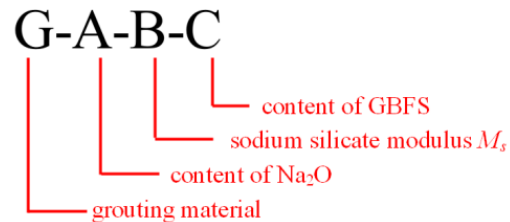


Figure 2. Nomenclature of grouting materials.

Table 2. Mix proportions for FA-based geopolymer grouting materials.

No.	Mix	Composite Powder			Modified Sodium Silicate ^a			W/S ^b
		FA (wt%)	GBFS (wt%)	M_s	Na ₂ O (wt%)	SiO ₂ (wt%)	H ₂ O (wt%)	
1	G-6-1.4	100	0	1.4	6.0	8.4	93.6	0.45
2	G-9-1.2	100	0	1.2	9.0	10.8	89.8	0.45
3	G-9-1.4	100	0	1.4	9.0	12.6	99.5	0.45
4	G-9-1.6	100	0	1.6	9.0	14.4	101.0	0.45
5	G-12-1.4	100	0	1.4	12.0	16.8	105.4	0.45
6	G-9-1.2-10	90	10	1.2	9.0	10.8	89.8	0.45
7	G-9-1.2-20	80	20	1.2	9.0	10.8	89.8	0.45
8	G-9-1.2-30	70	30	1.2	9.0	10.8	89.8	0.45

Notes: (a) The contents of compositions in modified sodium silicate are expressed by the mass of composite powder; (b) W/S represents the mass ratio of water to composite powder.

The demoulded cubic specimens were placed in the curing chamber for curing for 7, 28, and 90 days, respectively. According to the relevant test methods in GB/T 17671-2020 [29], the compressive strength of the cubic specimens cured for 7, 28, and 90 days was measured with an electro-hydraulic cement compressive tester (TYA-100C). Each compressive strength value was measured based on three specimens.

The drying shrinkage of the grouting materials at different ages was tested based on the prismatic specimens. The initial length (L_0) of the demoulded specimen was first measured using a comparator by referring to relevant test methods in JC/T 603-2004 [30]. Thereafter, the specimen was placed in a curing box to allow continued curing for 2, 3, 7, 14, 21, 28, 56, 90, and 180 days at 20 ± 2 °C and RH = 45 ± 5%. After curing, the lengths (L_t) of the specimens at different ages were measured. The drying shrinkage of the specimen was calculated in accordance with Equation (1):

$$S_t = \frac{L_0 - L_t}{L_e} \times 100\% \quad (1)$$

where S_t is the drying shrinkage percentage of the specimen at each age (%) and L_e denotes the effective length of the specimen (75 mm).

To study the microstructure of the grouting materials, samples were taken from the crushed rectangular specimen that had been cured for 28 days, immersed in absolute ethanol for 24 h and then dried in a vacuum at 40 °C for 24 h. The XRD test was then used to analyse the phases of the specimen under the scanning range of 5° to 85° at a scanning rate of 10°/min. An MIP test was conducted on the grouting materials with a 60-GT automatic mercury porosimeter to study the micropore structure. The microstructures of

the specimens were observed through the SEM–EDS test and the types of reaction products were determined according to elemental compositions in the microstructure.

3. Results and Discussion

3.1. Compressive Strength

The compressive strengths of FA-based geopolymer grouting materials cured for 7, 28, and 90 days with different contents of Na_2O , M_s , and contents of GBFS are displayed in Figure 3. Figure 3a shows that as the content of Na_2O in modified sodium silicate increased from 6.0 to 12.0 wt%, the compressive strength of the grouting materials cured for 7, 28, and 90 days increased from 6.0 to 14.1 MPa, from 12.6 to 24.4 MPa, and from 16.7 to 39.0 MPa, respectively. These findings indicate that the increased content of Na_2O in the modified sodium silicate is conducive to improving the compressive strength of the grouting materials. The main reasons for this are as follows: on the one hand, the higher the content of Na_2O in modified sodium silicate as the activator, the more alkaline the geopolymer system, which promotes the full dissolution of raw materials. The increase in the dissolution of Si and Al promotes continuous polymerization, resulting in more gel phases. On the other hand, the higher the content of Na_2O , the higher the content of SiO_2 that plays a role in cementation in the modified sodium silicate. The generation of a lot of gel phases results in denser grouting materials, thus increasing their compressive strength. In addition, the formation of hydrated ions by Na ions and more water is conducive to decreasing the content of free water as well as the content of microscopic pores in the internal structure induced by water evaporation, further slowing down the generation of microcracks and strength loss to a certain extent.

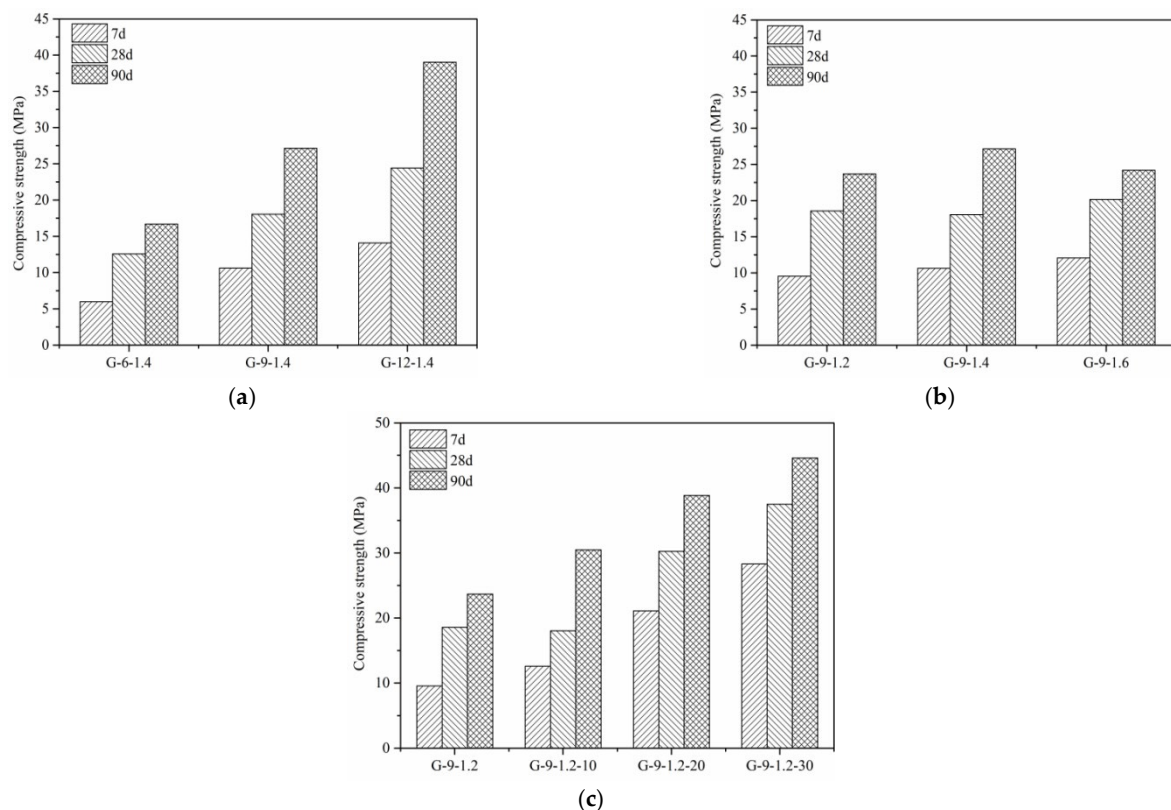


Figure 3. Effects of different factors on the compressive strength of FA-based geopolymers: (a) content of Na_2O ; (b) M_s ; (c) content of GBFS.

As illustrated in Figure 3b, with the increase in M_s from 1.2 to 1.6, the compressive strength of FA-based geopolymer grouting materials cured for 7 and 28 days increased by 2.5 and 1.5 MPa from 9.6 to 12.1 MPa and from 18.6 to 20.1 MPa, respectively. It is

noteworthy that the compressive strength after curing for 28 days decreased slightly when the M_s was 1.4. The compressive strength of the grouting materials cured for 90 days first increased, then decreased, and increased by 0.52 MPa with the increase in M_s . It can be inferred that for the grouting materials at an early age, increasing the modulus of the activator was beneficial in that it slightly increased the compressive strength. However, the compressive strength decreased with the increase in the modulus of the activator for the grouting materials at the later age. Sodium silicate is an important cementing agent. When keeping the W/S and content of Na_2O unchanged, the larger M_s is, the higher the content of silica oligomer in modified sodium silicate. Many silica oligomers precipitate on the surface of undissolved FA particles, which improves the compressive strength of the grouting materials. When M_s is high, $[\text{Al}(\text{OH})_4]^-$ produced through dissolution is immediately saturated by $[\text{Si}(\text{OH})_4]$. The subsequent polycondensation occurs between $[\text{Si}(\text{OH})_4]$ and $[\text{Si}(\text{OH})_4]$ with a high reaction activation energy. This prolongs the setting and hardening time of FA-based geopolymer grouting material, which is not conducive to practical engineering applications.

Figure 3c shows the compressive strength of FA-based geopolymer grouting materials cured for 7, 28, and 90 days after adding different amounts of GBFS: as the amount of GBFS increased from 0 to 30 wt%, the compressive strength of the grouting materials cured for 7, 28, and 90 days increased by 195%, 101%, and 88%, respectively, suggesting that the addition of GBFS was conducive to improving the compressive strength of the grouting materials. However, the increasing amplitude in compressive strength decreased slightly with the increase in curing age.

3.2. Drying Shrinkage

Figure 4 shows the drying shrinkage of FA-based geopolymer grouting materials under different amounts of Na_2O , M_s , and amounts of GBFS. From Figure 4a, the content of Na_2O in the modified sodium silicate exhibits a significant effect on the drying shrinkage of the grouting materials under a certain M_s . For instance, the drying shrinkage percentage of the grouting materials was merely increased by about 0.07% at an age of 180 days when the content of Na_2O increased from 6 to 9 wt%. When the content of Na_2O increased from 9 to 12 wt%, the drying shrinkage percentage increased by 0.36%. The generation of a certain amount of shrinkage is closely related to two types of driving forces, namely, the pore pressure and the steric hydration forces induced by the interactions between ions [31]. On the one hand, as mentioned above, increasing the content of Na_2O is conducive to decreasing the internal porosity of the material and making the internal structure more dense, which may contribute to a smaller radius of the menisci formed within the grouting material and further induce a high pore pressure, resulting in increased autogenous shrinkage. On the other hand, with the increase in Na_2O content, there were large amounts of Na^+ ions in the initial solution. With the progress of polymerization, the reduction in the concentration of Na^+ ions and the hydration shells essentially led to a decrease in the steric hydration force. Consequently, the surrounding gel pores were close to each other, which was manifested in the increase in the drying shrinkage of the specimen.

The changes in the drying shrinkage of the grouting materials with age under different M_s are illustrated in Figure 4b: the drying shrinkage of the grouting materials first decreased, then increased with the increase in M_s . When M_s increased from 1.2 to 1.6, the corresponding drying shrinkage of the grouting materials at the age of 180 days decreased from 0.29% to 0.15%, then increased to 0.29%. In addition, comparison of Figure 4a,b shows that the content of Na_2O in the modified sodium silicate exerted a more significant influence on the drying shrinkage of the grouting materials than M_s .

The changes in the drying shrinkage of FA-based geopolymer grouting materials with age under different contents of GBFS are shown in Figure 4c. As the content of GBFS increased, the drying shrinkage of the grouting materials uniformly decreased. As the content of GBFS increased from 0 to 30 wt%, the drying shrinkage decreased by 28% from 0.29% to 0.21%. The reaction product of the grouting materials was N-A-S (H) gel.

The gel contained many gel pores and capillary pores, and a large capillary force during dehydration shrinks and cracks the materials. After adding GBFS, the reaction product of the grouting materials (N-A-S (H) gel) contained some C-A-S-H gel. Compared with the N-A-S (H) gel, the resulting C-A-S-H gel had the higher elastic modulus, which is beneficial for inhibiting the shrinkage of gel materials.

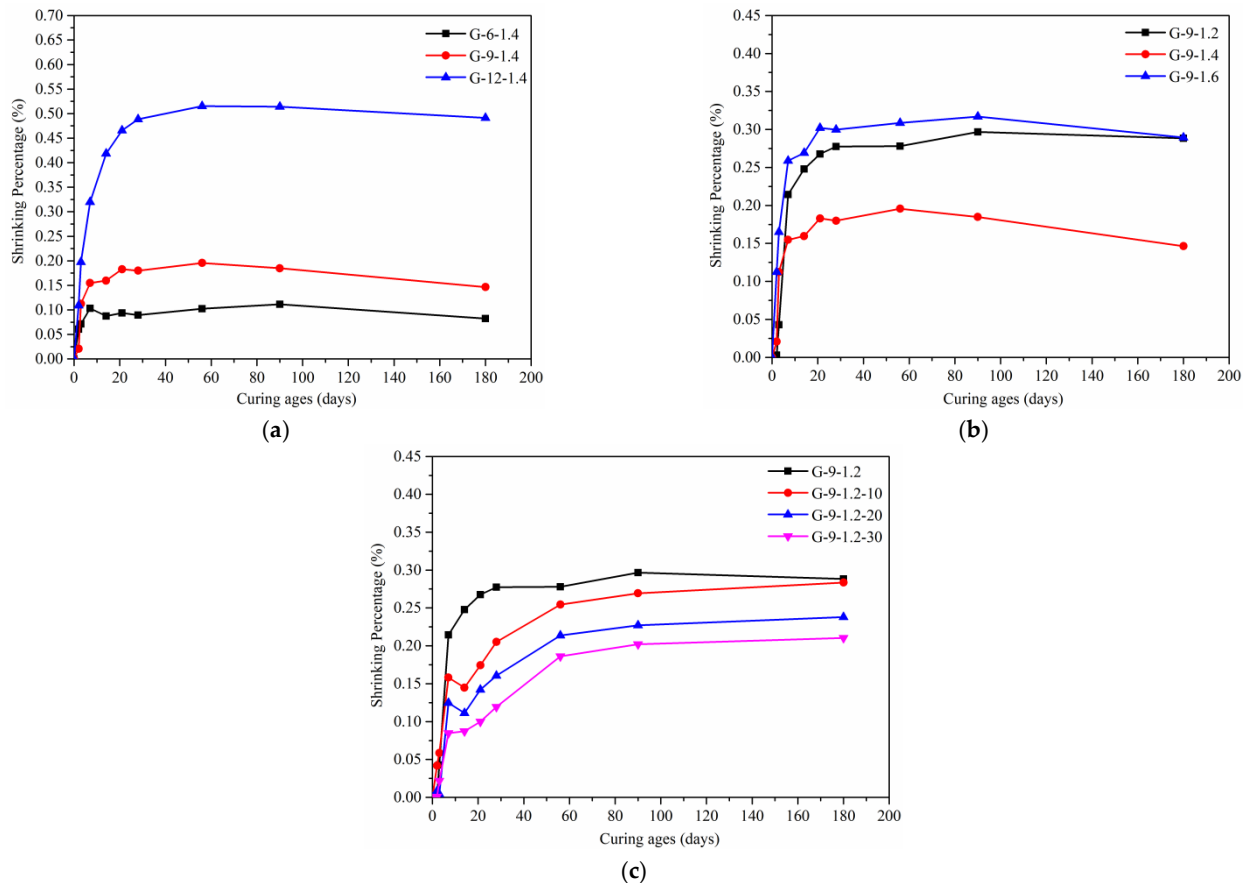


Figure 4. Influences of different factors on the drying shrinkage of FA-based geopolymer grouting materials: (a) content of Na_2O ; (b) M_s ; (c) content of GBFS.

3.3. XRD Analysis

Figure 5 displays the XRD patterns of FA-based geopolymer grouting materials under different contents of Na_2O , M_s , and contents of GBFS. The turning point in the chart (for FA-based material) is widened and shifts to a higher angle after activation with modified sodium silicate, suggesting the formation of N-A-S (H) gel due to alkali excitation [8]. As displayed in Figure 5a, it can be observed that XRD patterns of FA-based geopolymer grouting materials under different contents of Na_2O and M_s are basically consistent. The original quartz and mullite in the fly ash still existed in the diffraction spectrum of the geopolymerisation products and the corresponding positions of the characteristic peaks did not change, but the intensity of each characteristic peak was different. XRD cannot effectively characterise phase compositions of FA-based geopolymer grouting materials with N-A-S (H) gel as the main product.

As shown in Figure 5b, quartz and mullite phases were still present in FA-based geopolymerisation products after adding 0–30 wt% GBFS. With the increase in the content of GBFS, the diffraction intensities of quartz and mullite phases gradually decreased, indicating that these two phases did not participate in geopolymerisation. Furthermore, it can be inferred that the addition of GBFS increases the solubility of FA, thus improving the reaction of many FA-based polymer grouting materials. Moreover, the proportion of amorphous products significantly increased. Figure 5b shows that the hump widened and

moved to a higher angle with the increase in the content of GBFS. This is mainly because a large amount of Ca^{2+} in GBFS dissolves and participates in geopolymerisation, so that the product of FA-based geopolymer grouting materials partially converts from N-A-S(H) gel to C-A-S-H gel.

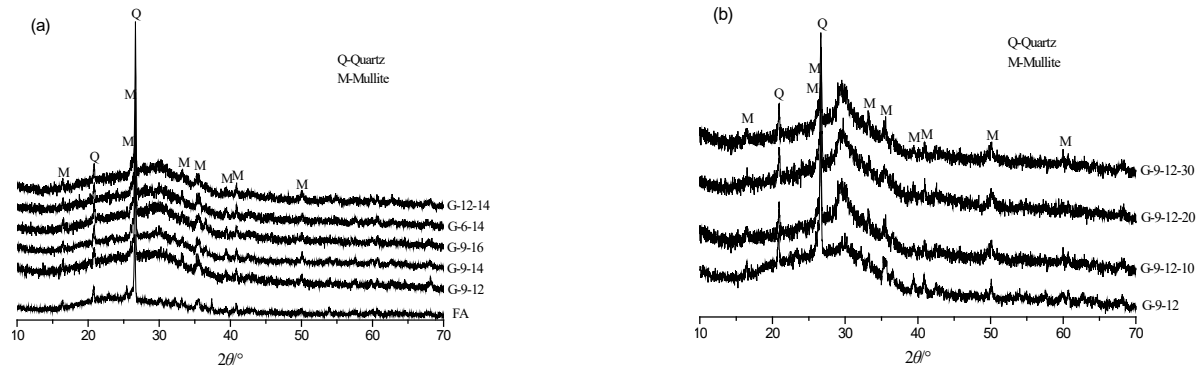


Figure 5. XRD analysis of FA-based geopolymer grouting materials: (a) parameters of modified sodium silicate; (b) content of GBFS.

3.4. MIP Analysis

The MIP test results of FA-based geopolymer grouting materials G-9-12 and G-9-12-30 are shown in Figure 6. As displayed in Figure 6a, double peaks appear in the pore size distribution of G-9-12 but not that for G-9-12-30 because many coalesced pores are present in such polymers [32]. On the one hand, after being modified by 30 wt% GBFS, the chemical reaction of FA-based geopolymers was more complete and more reaction products filled gaps inside the materials to make the structure more compact. On the other hand, GBFS plays a role in micro-aggregate filling and can also decrease the porosity of grouting materials to a certain extent. Figure 6b shows the proportion of volumes of pores with different sizes in G-9-12 and G-9-12-30. After adding 30 wt% GBFS, the proportion of pores smaller than 10 nm in the grouting materials increased from 6.83% to 27.28%, whereas those of pores with sizes of 10–20, 20–50, 50–100, and larger than 100 nm decreased by 51.56%, 79.06%, 79.14%, and 57.41%, respectively. The proportion of pores larger than 50 nm decreased from 43.16% to 23.24%. This implies that the addition of 30 wt% GBFS improves the pore size distribution of FA-based geopolymer grouting materials. It is inferred that the microstructure of the grouting materials to which 30 wt% GBFS has been added is more compact and suffers less drying shrinkage compared with grouting materials without added GBFS.

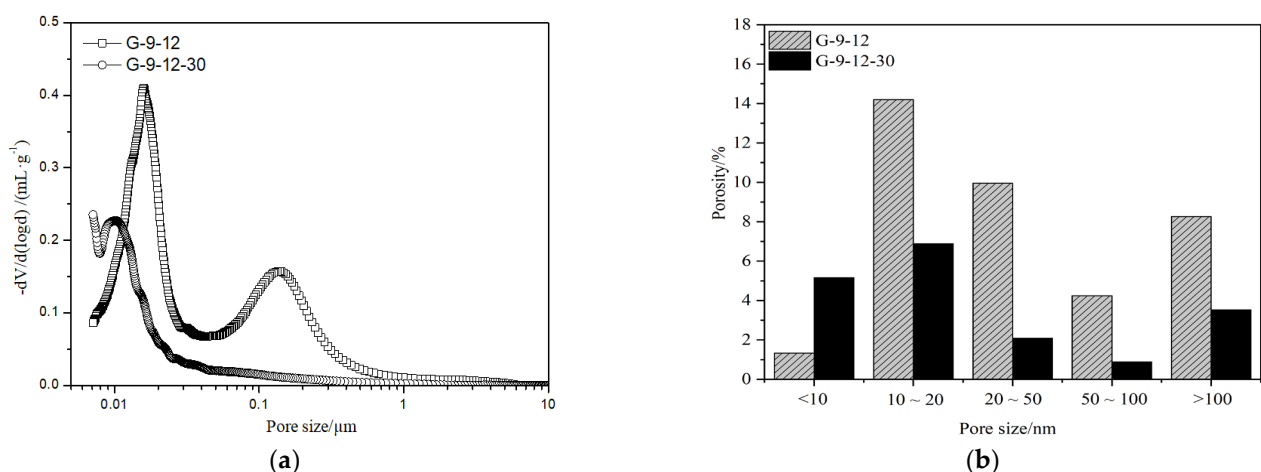


Figure 6. Pore size distribution of FA-based geopolymer grouting materials: (a) differential curves of pore size distribution; (b) proportion of pores.

3.5. SEM-EDS Analysis

Figures 7 and 8 display SEM-EDS patterns of FA-based geopolymer grouting materials G-9-12 and G-9-12-30, respectively. FA-based geopolymer grouting materials present a “chocolate cookie” structure: many undissolved FA particles are embedded in gel products or spall in the sample preparation process to leave different sizes of pores; flocculent or crystalline substances aggregate on the surface of some undissolved FA particles. In addition, there are many networked cracks in the gel products of FA-based geopolymer grouting materials, some of which are coalesced. A large gap exists between a lot of incomplete FA particles and gel products, mainly due to the dehydration and shrinkage of gel products. The research on the microstructure of geopolymers also shows that the geopolymerisation products produced by dissolution and condensation are unable to fill pores produced by the dissolution of FA particles [33].

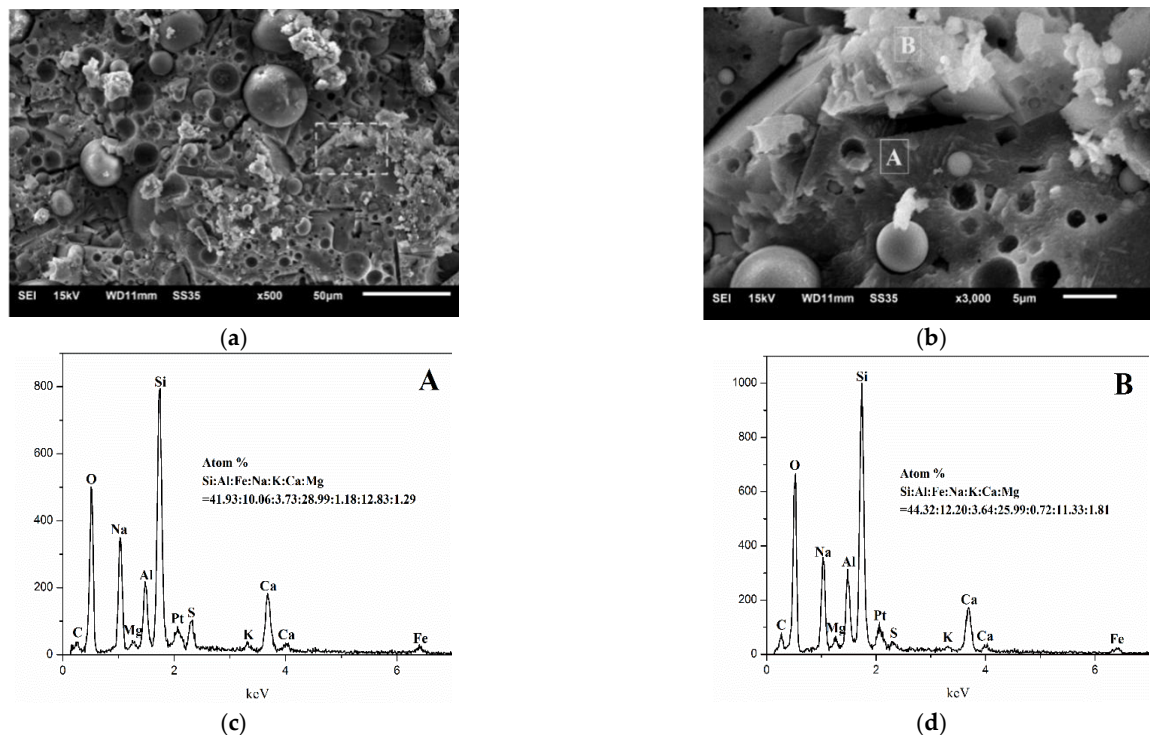


Figure 7. SEM-EDS patterns of G-9-12: (a) SEM image ($\times 500$); (b) SEM image ($\times 3000$); (c) elemental composition: Area A; (d) elemental composition: Area B.

The main elemental composition in matrix A of the FA-based geopolymer grouting materials G-9-12 was $\text{Na}_{2.88}\text{K}_{0.12}\text{Ca}_{1.28}\text{Mg}_{0.13}\text{AlSi}_{4.17}\text{Fe}_{0.37}$, which contained C-A-S-H and N-A-S(H) gel products. The main elemental composition in floccule B was $\text{Na}_{2.13}\text{K}_{0.06}\text{Ca}_{0.93}\text{Mg}_{0.15}\text{AlSi}_{3.63}\text{Fe}_{0.30}$, which also contained C-A-S-H and N-A-S (H) gel products. Both A and B were the result of the accumulation of gel particles, but the density of A was higher than that of B. It is speculated that the amount of free water in B was higher, resulting in a loose structure.

Compared with G-9-12, G-9-12-30 with the content of GBFS of 30 wt% has a more compact structure and contains fewer undissolved FA particles. The reaction activity of GBFS is much higher than FA, and glassy substances in GBFS are dissolved in activator solution, producing a large amount of Ca^{2+} . On the one hand, the dissolved Ca^{2+} from GBFS can replace some charge-balancing Na^{+} ions in the N-A-S (H) gel network, resulting in the gradual conversion of N-A-S (H) gel into C-A-S-H gel [32]. On the other hand, Ca^{2+} can decrease the bond energy of Si_{2p} , Al_{2p} , and O_{1s} , thus promoting the dissolution of glassy substances in FA. Adding an appropriate amount of GBFS is conducive to improving the compactness of the microstructure of FA-based geopolymer growing materials [34].

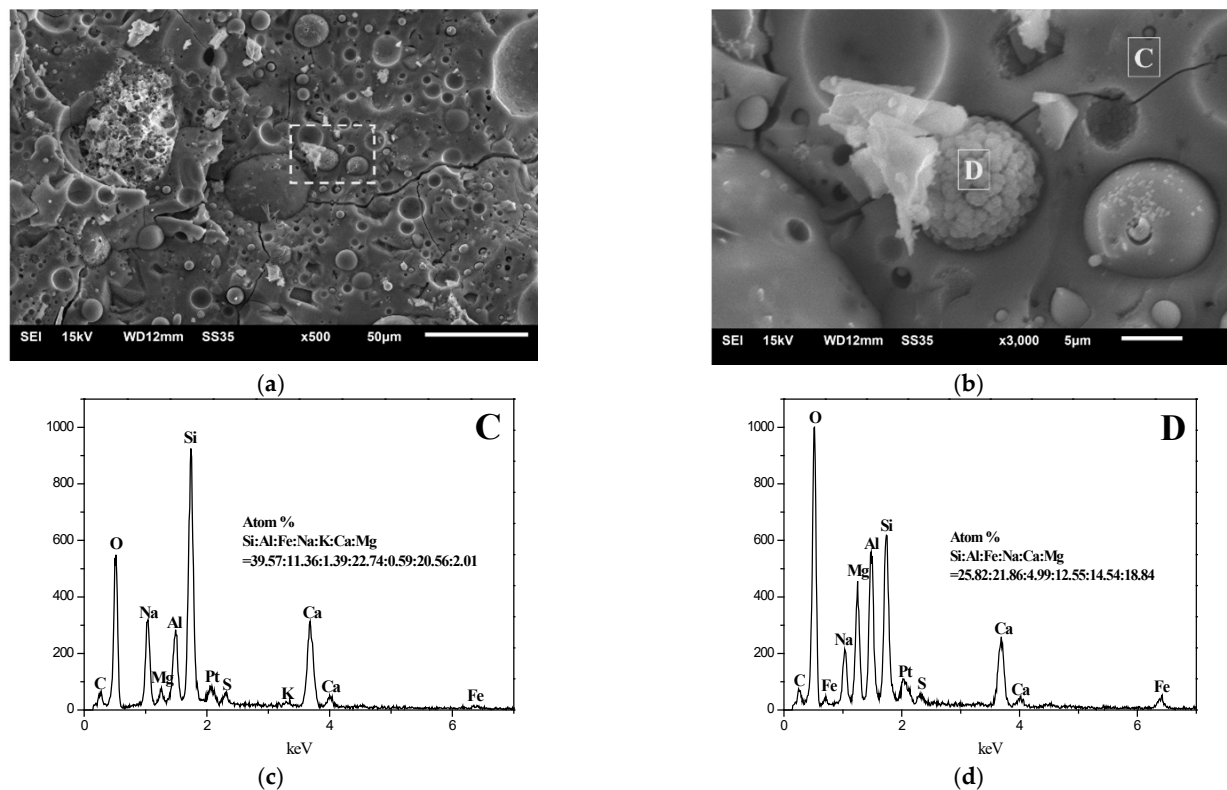


Figure 8. SEM-EDS patterns of G-9-12-30: (a) SEM image ($\times 500$); (b) SEM image ($\times 3000$); (c) elemental composition: Area C; (d) elemental composition: Area D.

The main elemental composition in matrix C of G-9-12-30 was $\text{Na}_{2.00}\text{K}_{0.05}\text{Ca}_{1.81}\text{Mg}_{0.18}\text{AlSi}_{3.48}\text{Fe}_{0.12}$, which consisted of C-A-S-H and N-A-S (H) gel products. The mushroom-shaped floccle mainly comprised $\text{Na}_{0.57}\text{Ca}_{0.67}\text{Mg}_{0.86}\text{AlSi}_{1.18}\text{Fe}_{0.23}$ as well as C-A-S-H and N-A-S (H) gel products. In comparison with G-9-12, the calcium content in the matrix of G-9-12-30 increased significantly. Therefore, it is inferred that the proportion of C-A-S-H gel in its products increased significantly.

4. Conclusions

Based on experimental research and theoretical analysis, the following conclusions are obtained:

When the sodium silicate modulus is certain, increasing the content of Na_2O in the modified sodium silicate is conducive to enhancing the compressive strength of FA-based geopolymer grouting materials. With the increase in sodium silicate modulus, the compressive strength of grouting materials with early curing age improved slightly, whereas the compressive strength of grouting materials with a high curing age first increased and then decreased. As the GBFS content ranged from 0 to 30 wt%, a significant increase was observed in the compressive strength of grouting materials; however, the increasing amplitude slowed down with curing age.

With the content of Na_2O ranging from 9 to 12 wt%, the drying shrinkage of FA-based geopolymer grouting materials showed a significant increase. It was observed that the drying shrinkage of FA-based geopolymer grouting materials was decreased with the increase in sodium silicate modulus and then significantly increased when the sodium silicate modulus was 1.6. The improvement of GBFS content has a positive effect on the drying shrinkage of FA-based geopolymer grouting materials.

XRD analysis shows that, with the increase in Na_2O content and sodium silicate modulus, the positions of the characteristic peaks of quartz and mullite do not change, and the main difference is that each characteristic peak shows a certain difference in intensity.

The increase in GBFS content could improve the solubility of FA and further promote the formation of C-A-S-H gel.

MIP and SEM–EDS analysis revealed that the incorporation of GBFS with a content of 30% helped to reduce the proportion of pores with large pore size and further improved the pore size distribution in the grouting materials as well as the conversion of the reaction products of FA-based geopolymer grouting materials from the main N-A-S(H) gel to both N-A-S(H) and C-A-S-H gel.

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