

Experimental Study on the Properties of Nano-Silica Modified Fly Ash-Cement Composite Grouting Materials

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ABSTRACT

Pursuing low-carbon development in green mining requires improving the efficiency of solid waste utilization. This study developed a high-strength green cement-based composite grouting material using silicate cement and fly ash as the primary cementitious materials, with its toughness enhanced by the incorporation of nano-silica (NS). Various testing methods, including slurry property and mechanical strength tests, as well as advanced techniques such as XRD and SEM, were employed to comprehensively analyze the effects of NS dosage on hydration products, working properties, setting time, and mechanical strength. The results demonstrate that adding NS effectively reduces the initial setting time of the fly ash-cement composite slurry. Moreover, as the NS dosage increases, the fluidity, hydration rate, and compressive strength of the composite slurry initially increase and subsequently decrease. At an NS dosage of 1%, the composite slurry achieves optimal performance, with a 1% increase in fluidity, a 5.9% reduction in initial setting time, and compressive strength improvements of 12.6% and 37.8% at 3 and 90 days, respectively. Microscopic characterization indicates that the addition of an appropriate amount of NS significantly enhances the volcanic ash effect, consuming substantial amounts of Ca(OH)_2 and generating abundant hydrated calcium silicate products. In addition, the unhydrated NS can also play a filling effect, significantly improving the matrix's densification. These findings provide new insights into the development of cost-effective, high-performance green grouting materials for deep coal mine engineering, offering both theoretical and practical significance.

KEYWORDS

Silicate cement; Nano-silica; Fly ash; Grouting materials; Mechanical properties

1. INTRODUCTION

Silicate cement-based grouting materials are extensively applied in coal mine engineering for perimeter rock reinforcement, filling, and borehole plugging because of their low cost, excellent flowability, and high durability [1]. Fly ash-cement composite grouting materials, containing spherical particles, enhance slurry fluidity and material compatibility. However, their high water precipitation rate and low early strength limit broader applications. Recent research demonstrates the

successful use of nanomaterials to modify fly ash-cement grouting materials through doping. Consequently, optimizing the mechanical properties and stability of fly ash-cement slurry using nanomaterials has become a critical challenge in deep-well soft rock tunnel grouting reinforcement technology. Studies indicate that trace amounts of nanomaterials effectively enhance cement hydration, improve matrix mechanical properties, and increase densification [2-3]. The study revealed that nano-silica enhances secondary hydration and strengthens slurry development by reacting with calcium hydroxide during cement hydration. Hu et al. [4] explored how nano silica influences the mechanical properties of pulverized coal cement slurry. Han et al. [5] highlighted that nano-silica forms a stable dispersion system among pulverized coal cement particles, preventing settlement and segregation via spatial resistance and electrostatic repulsion, thereby enhancing slurry stability.

Based on this analysis, this paper employs silicate cement and fly ash as the primary cementitious materials and incorporates NS as an admixture to develop a high-strength green cement-based composite grouting material. It examines the impact of NS dosage on the precipitation rate, fluidity, setting time, and compressive strength of fly ash-cement composite slurry and investigates the correlation between micro-morphology and macro-mechanical properties to expand its application in coal mine roadway grouting reinforcement. XRD and SEM characterizations were employed to investigate the intrinsic relationships between components, microscopic morphology, and macroscopic mechanical properties of NS-modified fly ash-cement composite slurry, aiming to enhance its application in coal mine tunnel grouting reinforcement

2. MATERIALS AND METHODS

2.1. Test Raw Materials

The cement (OPC) used in this study was produced by Huainan Shunyue Cement Co., Ltd. and is classified as ordinary 42.5 silicate cement. Its chemical composition and performance parameters are presented in Fig. 1(a) and Table 1, while its XRD pattern, shown in Fig. 1(b), reveals tricalcium silicate (C3S) and dicalcium silicate (C2S) as the primary mineral components. The fly ash (FA) was supplied by Rong Changsheng Environmental Protection Material Company. Its XRD pattern, presented in Fig. 1(c), indicates that the main crystalline phases are mullite and quartz, with 73.2% vitreous content. The technical indices of fly ash are listed in Table 2.

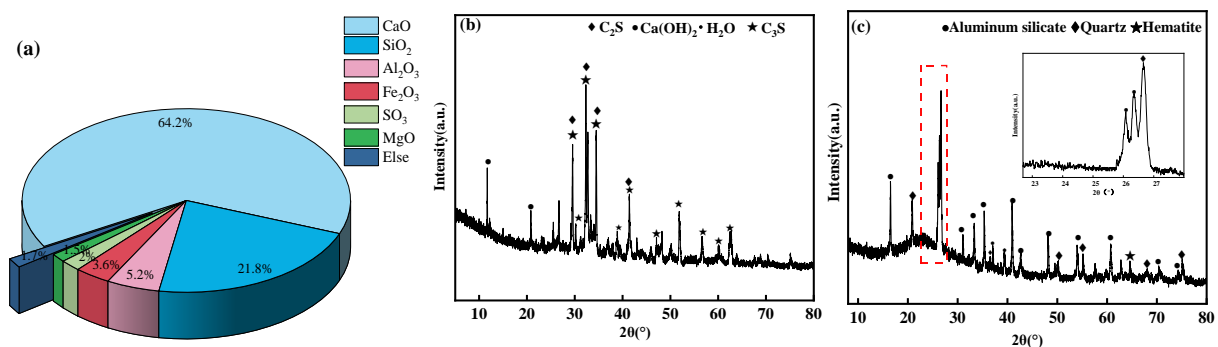


Figure 1. The raw material component and XRD pattern of grouting materials: (a) pie chart of silicate cement composition, (b) XRD pattern of silicate cement, (c) XRD pattern of fly ash

Table 1. Performance parameters of Portland cement

Typology	Chloride ion content /%	Specific surface area /($\text{m}^2 \cdot \text{kg}^{-1}$)	Heat loss /%	28 d Compressive strength/MPa	Incipient condensation time /min	Time of final coagulation /min
Cement	0.012	326	1.52	48.6	185	325

Table 2. Technical index of fly ash

Name	Loss/%	Fe ₂ O ₃ /%	SiO ₂ /%	Al ₂ O ₃ /%	CaO/%	Na ₂ O/%	MgO/%	K ₂ O/%
Fly ash	2.48	3.87	53.36	29.09	2.27	0.66	0.81	0.98

2.2. Grouting Material Proportioning Experiment

As shown in Table 3, a one-factor test was designed. Appropriate proportions of silicate cement, fly ash, and various dosages of glass fiber powder were weighed, added to the mixer, and stirred at high speed for 120 seconds. Based on a water-solid ratio of 0.7 (water/cement + fly ash), a measured quantity of tap water was added and stirred at high speed for 180 seconds to ensure a uniform and precipitation-free slurry, resulting in six distinct proportions of NS-modified fly ash-cement composite grouting materials. The slurry properties, mechanical characteristics, and microstructure were subsequently characterized.

Table 3. Sample ratio of grouting materials (% , mass ratio)

Test piece	Cement	Fly ash	NS	Water
N1	100	15	0	80.5
N2	100	15	0.5	80.5
N3	100	15	1	80.5
N4	100	15	1.5	80.5
N5	100	15	2	80.5
N6	100	15	3	80.5

2.3. Slurry Characterization Tests

Precipitation rate: Inject 50 mL of grouting material into a cylinder and allow it to stand for 1 hour. Measure the levels of the upper water layer and the lower slurry layer in the cylinder, and calculate the water precipitation rate as the percentage of the two.

Fluidity: Pour the prepared slurry into a truncated conical mold with dimensions of 60 mm × 70 mm × 100 mm (height × upper inner diameter × lower inner diameter). Lift the mold, allowing the slurry to flow freely on a glass surface until it stabilizes as a circular shape. Measure the diameter of the circle to determine the degree of flow.

Setting time: Following GB/T1346-2011 standards, "Test Methods for Water Consumption, Setting Time, and Stability of Standard Consistency of Cement," a Vicat meter was employed to measure the initial and final setting times of the grouting materials.

2.4. Compressive Strength Tests

The prepared slurries were poured into 40 mm × 40 mm × 40 mm specimen molds, oscillated to remove air bubbles, smoothed, and placed in a curing box at a constant temperature and humidity for 24 hours. After 24 hours, the molds were de-molded and maintained under standard curing conditions at (20 ± 2) °C and 95% relative humidity for different durations (3 d ± 2 h, 7 d ± 2 h, 28 d ± 2 h). Compressive strength tests were conducted using the RMT Rock Mechanics Tester (RMT-150, Wuhan Branch of CAS), designed by the Institute of Geotechnical Research, Chinese Academy of Sciences, with a load rate of 0.2 kN/s and a maximum range of 400 kN.

2.5. Micro Performance Tests

An X-ray diffractometer (XRD, Shimadzu, Japan, XRD-6000) was used to analyze the components of the nodular body specimens, with internal standard semi-quantitative analysis performed using titanium dioxide and Cu K α ($\lambda = 1.54060 \text{ \AA}$) radiation as the incident wavelength. Additionally,

scanning electron microscopy (SEM, Hitachi, Japan, S-3000 N) was utilized to observe the microscopic morphology of NS-modified fly ash-cement stone specimens.

3. SLURRY CHARACTERIZATION RESULTS

3.1. Slurry Characteristics

In grouting projects, slurry viscosity is a critical parameter that determines the effective flow time and spreading range of the slurry. Precipitation within the slurry reduces the free water volume, thereby altering its viscosity and time-dependent characteristics. Fig.2 illustrates the variation in the water precipitation rate of NS-modified fly ash-cement composite grouting material over 30 min. The water precipitation rate of the composite grouting material decreases as the settling time increases. The water precipitation rates for the N1-N6 slurries are 7.2%, 5.4%, 4.5%, 3.8%, 2.9%, and 1.2%, respectively, indicating that as the NS dosage increases, the precipitation rate of the composite fly ash-cement grouting material gradually decreases. Compared with the control group N1, the bleeding rates of slurry groups N2 to N6 decreased by 25%, 37.5%, 47.2%, 59.7%, and 83.3%, respectively. These results demonstrate that the addition of NS reduces the water precipitation rate of fly ash-cement slurry and enhances its stability [6].

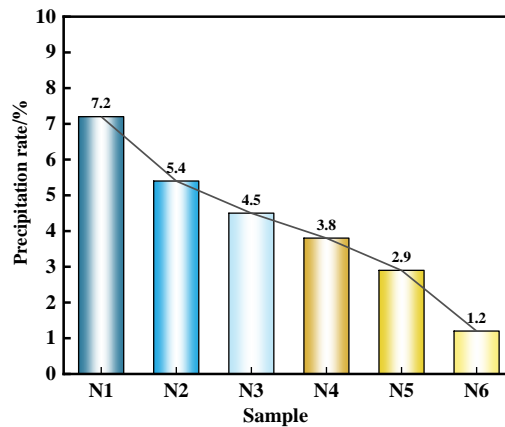


Figure 2. Water evolution rate of NS-modified fly ash - cement composite grouting materials

Fluidity represents the macroscopic diffusivity of the gelled slurry. Fig.5 shows the evolution of the flowability of composite slurry with different NS doping with time. With the increase of NS dosage, the slurry fluidity increases and then decreases, and the slurry no longer flows after 7 min, it reaches the critical value of fluidity, and when it exceeds the critical value, the slurry will tend to stabilize until it stops flowing. The fluidity of the control group of N1 is 228 mm, and the fluidity of N2-N6 is reduced by 13.2%, 18.1%, 20.7%, 22.5% and 43.3% compared with that of the control group. The results showed that the van der Waals forces and electrostatic effects of nanomaterials tend to trigger particle agglomeration thereby reducing the flowability of the slurry, while nano-silica has a more significant effect on the fluidity of cement slurry due to its higher specific surface area [7].

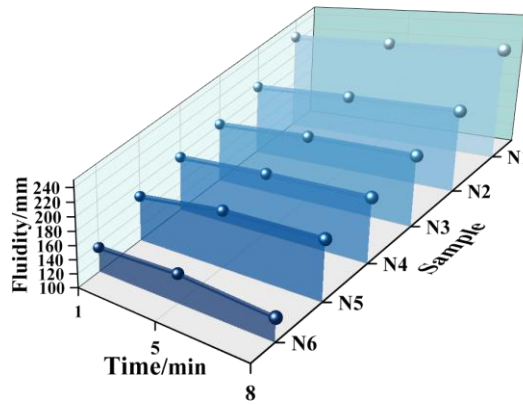


Figure 3. Fluidity of NS-modified fly ash-cement composite grouting materials

Achieving an appropriate setting time is essential for ensuring optimal grouting performance. Fig. 4 presents the initial and final setting times of various composite grouting materials. The final setting time decreases initially and then increases with the increase in NS dosage, while the initial setting time decreases consistently. The initial setting time of N1 is 619 min., while the initial setting times of N2 to N6 are reduced to 3.7%, 6.3%, 5.9%, 6.8%, and 9.0% of that of N1, respectively. This behavior occurs because nanoparticles, due to their small size, act as fillers and exhibit directional adsorption after being incorporated into the slurry. They also consume more free water for hydration, which decreases as agglomerates form with increasing NS dosage [8].

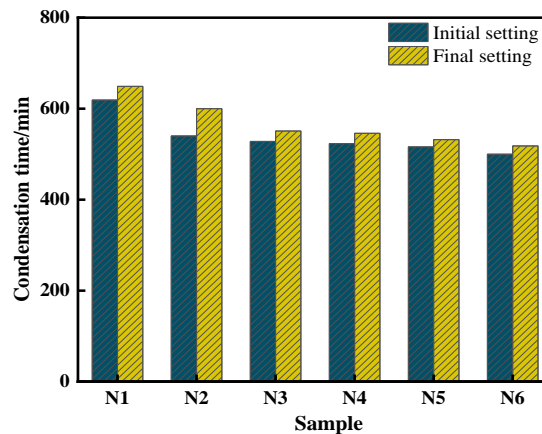


Figure 4. Setting time of NS-modified fly ash-cement composite grouting materials

3.2. Compressive Strength

Fig.5 illustrates the compressive strength of NS-modified fly ash-cement composite grouting material nodules at various curing ages. The compressive strength of the control group (N1) was 5.437 MPa after 3 days of curing. With NS modification, the compressive strength of the fly ash-cement composite grouting material initially increased and then decreased within the dosage range of 0.5–3%. At an NS dosage of 1% (N3), the early strength reached its optimum, showing a 10.7% improvement compared to the control group (N1). As the curing time increased, the mechanical properties of the nodular body improved continuously. At 90 days, the compressive strength followed a similar trend with NS doping, with the N3 specimen achieving the highest compressive strength of 21.325 MPa, 98% higher than that of N1. However, with higher NS dosages, NS particles tended to agglomerate and exhibit uneven distribution within the matrix, introducing defects and pore structures. This negatively affected the material, increasing porosity and reducing the mechanical properties of the nodular body [9].

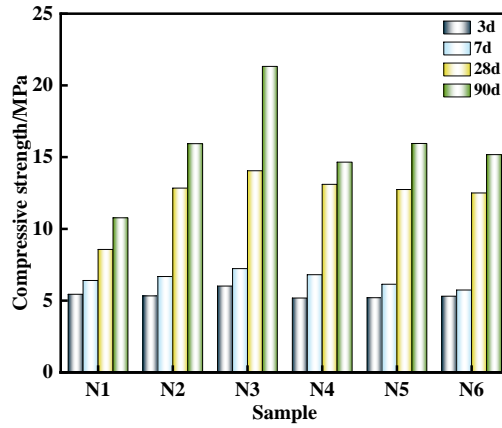


Figure 5. Compressive strength of NS-modified fly ash-cement composite grouting materials

3.3. XRD Analysis

Fig.8 presents the XRD patterns of nodular bodies from modified fly ash-cement composite grouting material cured for 28 days with varying NS dosages. The main hydration products of the grouting material are C-S-H, Ca(OH)₂, and Calcite (AFt), as observed in the figure. The presence of CaCO₃ results from the carbonation of surface Ca(OH)₂ in the air during the curing process, while C₂S, C₃S, quartz, and mullite correspond to unhydrated particles. The Ca(OH)₂ peak initially increases and then decreases with rising NS dosage, while the AFt peak gradually diminishes. This behavior is attributed to the role of NS in promoting Ca(OH)₂ generation.

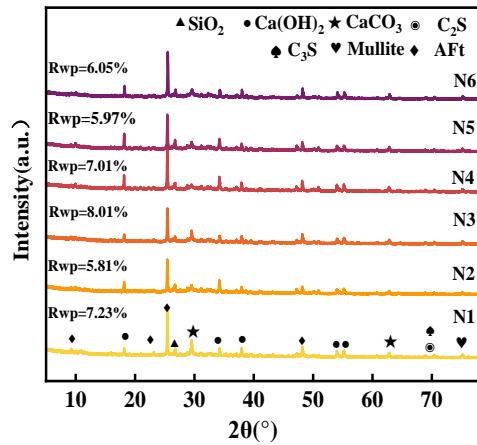


Figure 6. NS modified fly-cement composite grouting materials XRD pattern

3.4. Micro-morphological Analysis

Fig.7 illustrates the micro-morphological evolution of the composite grouting material nodular body cross-section with varying NS dosages. Fig.7(a, b) displays SEM images of the fly ash-cement grouting material nodular body, revealing numerous spherical fly ash particles. Hydration products, including lamellar Ca(OH)₂ and C-S-H gel, are visible, and the overall structure appears loose with numerous pore structures. Fig.7(c, d) presents SEM images of the 0.5% NS-modified fly ash-cement composite grouting material. Compared to the control group (N1), the hydration in this sample is more complete, with significantly increased gelation products that lap and cross-link with flaky Ca(OH)₂. The overall structure is denser, and pore space is noticeably reduced compared to N1. At an NS dosage of 1% (Fig.7e, f), the C-S-H cementation product develops further. The C-S-H and lamellar Ca(OH)₂ are interconnected by AFt and interspersed, forming a denser overall structure, with some NS particles filling the pores. With higher NS dosages, as shown in Fig.7(g-l), numerous pores

and defects appear in the matrix. Hydration products become unevenly distributed, reducing the density of the solidified body and negatively impacting its mechanical properties.

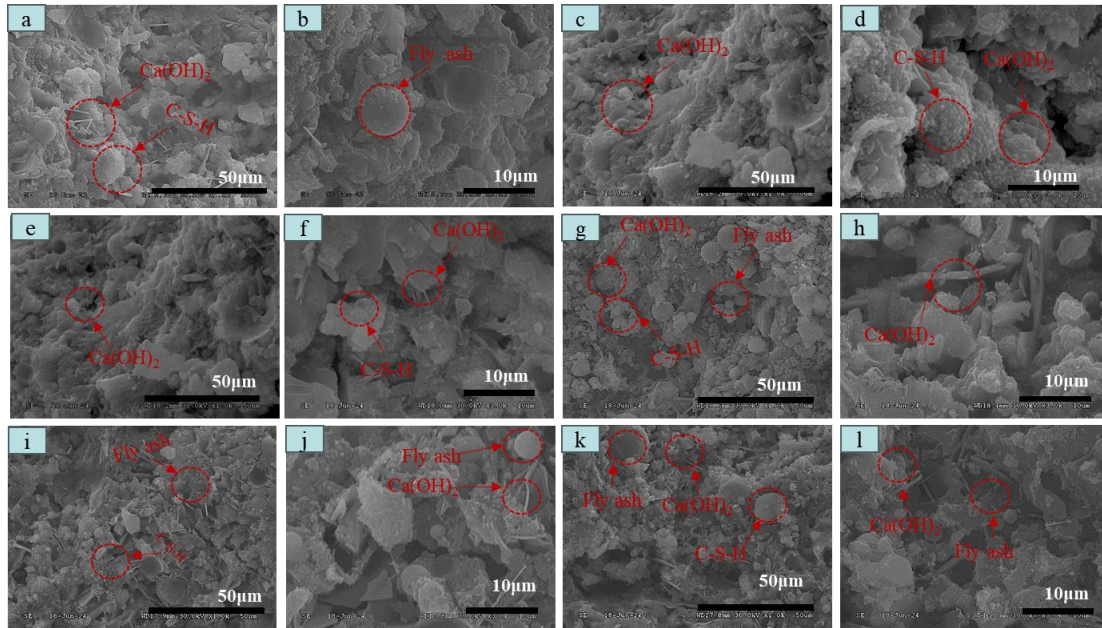


Figure 7. SEM cross-section of NS modified fly ash-cement specimens after 28 d curing time: (a, b) 0%, (c,d) 0.5%, (e, f) 1%, (g, h) 1.5%, (i, j) 2%, (k, l) 3%

4. CONCLUSION

- (1) A novel high-quality green cement-based composite grouting material was developed using silicate cement and fly ash as cementitious materials, with NS as an admixture. The results demonstrate that NS modification reduces the setting time of fly ash-cement slurry, and increasing NS dosage leads to a gradual decrease in mobility and water precipitation rate.
- (2) The dosage of NS significantly impacts the mechanical strength of fly ash-cement composite grouting material. The compressive strength of the nodule body initially increases and then decreases with rising NS dosage. At an NS dosage of 1%, the nodule body achieves optimal mechanical strength, with 3 d and 90 d compressive strengths of 6.1 MPa and 21.325 MPa, representing improvements of 10.7% and 98%, respectively, compared to the control specimen.
- (3) Microscopic characterization confirms that suitable NS modification enhances the volcanic ash activity of fly ash, generates significant amounts of Ca(OH)_2 , consumes existing Ca(OH)_2 , and produces abundant C-S-H cementitious products. This modification improves the degree of polymerization, reduces matrix porosity, and provides a robust structural foundation for enhanced mechanical properties.

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