Research Article

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Effect of nano-silica as cementitious materials-reducing admixtures on the workability, mechanical properties and durability of concrete

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Abstract: Nano-silica (NS) is one of the most important nanomaterials in recent years. It is used as a new cement-based composite reinforcement in building materials because of its high volcanic ash activity. In order to achieve the goal of carbon peaking and carbon neutralization, combined with the research idea of cementitious materials-reducing admixture for concrete, under the condition of reducing the amount of cement in concrete by 20%, the influence of different dosages of NS on the setting time and mechanical properties of concrete was analyzed. In addition, the shrinkage performance, impermeability, and resistance to chloride-ion permeability of concrete were also studied. The results show that under the same curing conditions and ages, when the NS dosage is 2.5%, the compressive strength and splitting tensile strength of the specimen after 28 days of curing are the highest, reaching 40.87 and 3.8 MPa, which show an increase by 6.6 and 15.15%. The shrinkage performance of concrete increases with the increase in NS dosage. In addition, when the NS dosage is 2.0%, the durability of concrete has also been greatly improved. The impermeability of concrete increased by 18.7% and the resistance to chloride-ion permeability increased by 14.7%. Through microscopic analysis it was found that NS can promote the hydration reaction, generate more hydration products such as calcium silicate hydrate (C–S–H), enhance the interfacial adhesion between the matrix and the aggregate, and form a closer interfacial transition zone. Moreover, the addition of NS also reduces the cumulative pore volume in concrete, refines the pore size, and makes the internal structure of concrete denser.

Keywords: nano-silica, cementitious materials-reducing admixture for concrete, workability, durability, pore structure

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1 Introduction

As the primary infrastructure material, concrete plays an essential role in China's industrialization, urbanization, and modernization and plays a vital role in developing the world economy. After 70 years of development, China ranks first in its cement production capacity, varieties, and consumption worldwide. By 2020, China's cement production reached 2.37 billion tons, accounting for about 60% of the world's total annual output. However, the rapid development of the cement industry has also brought a series of environmental problems. By calculation, according to the current level of the cement industry, the production of 1 ton of cement clinker emits about 940 kg of carbon dioxide. Carbon dioxide emissions from the cement industry account for about 20% of the total carbon dioxide emissions from industrial production in China. The cement industry is facing enormous pressure to reduce its carbon dioxide emissions. On March 15, 2021, General Secretary Xi Jinping hosted a meeting to explicitly incorporate carbon peak and carbon neutralization into the overall layout of ecological civilization construction, which is related to the sustainable development of the Chinese nation and the construction of a community of shared future for humanity [1].

In order to achieve the goal of low carbon and environmental protection, on one hand, many studies have been conducted on geopolymer recycled concrete and fiber-reinforced concrete [2–4]. On the other hand, the emergence of nanomaterials provides new research directions and research ideas for modified cement-based materials and also provides new development opportunities for realizing national carbon peak and carbon neutralization. Nanomaterials are materials with at least one dimension in the three-dimensional space (1–100 nm) or composed of them as basic units, which are high-tech materials [5]. With the development of nanotechnology, its unique volume effect, surface effect, quantum size, and other characteristics have been gradually discovered, and many analytical testing methods have been born, which gradually enables people to reveal the microstructure of cement-based materials from the nanometer scale. At present, carbon nanotubes [6,7], graphene [8], graphene oxide [9,10], nano-silica (NS) [11,12], and nano-calcium carbonate [13,14] have been used by a large number of scholars to regulate the microstructure of cement-hardened paste to enhance the mechanical property and durability of concrete or endow concrete with multi-functionalities. Compared with other nanomaterials, NS has higher pozzolanic activity and can react with calcium hydroxide ($Ca(OH)_2$) to release heat to promote hydration. At the same time, NS can effectively refine ($Ca(OH)_2$) crystal and generate calcium silicate hydrate (C–S–H) with strong cementation and a large specific surface area, which reduces the content of calcium hydroxide on the surface of aggregate and improves the interface strength between cement slurry and aggregate [15–19]. In addition, NS can physically fill the gaps of cementitious materials, capillary pores, and calcium silicate hydrate crystals in concrete, making the concrete denser and improve its strength [20–22]. Li *et al.* [17] found that NS and micro-silica (MS) can significantly improve the carbonation resistance, water permeability resistance, chlorine salt resistance, and sulfate resistance of cement mortar, and adding 1% NS can achieve the same effect as adding 10% MS. Li *et al.* [23] found that NS and MS co-doping can have a synergistic effect, making the microstructure of concrete dense, thereby improving the durability of concrete. However, due to the large specific surface area of NS particles, the water demand for cement paste increases sharply. This leads to more absorption of free water causing a decrease in the slump and increase in the viscosity of the concrete mixture, finally reducing the workability of concrete [24–26]. Although NS has been proved to be a potential cement-based reinforcement, effective and appropriate use of NS in cement-based materials is still a matter of concern. Many researchers replaced the same mass of cement with NS in high-strength concrete and high-performance concrete to improve the mechanical properties and durability of concrete. Few people use NS as a cementitious materials-reducing admixture for concrete to replace more cement in concrete, and ultimately achieve the effect of energy-saving, emission reduction, economic and environmental protection.

In this article, combined with the research idea of cementitious materials-reducing admixture for concrete, the influence of different dosages of NS on the workability of concrete mixture and the mechanical properties and durability of concrete is studied by performing experiment under the condition of reducing the amount of 20% cement in concrete. In addition, the mechanism of the performance of NS-modified concrete with different dosages was discussed in depth from the microscopic point of view by conducting X-ray diffraction (XRD), scanning electron microscopy (SEM), and mercury intrusion porosimetry (MIP) tests.

2 Experiments

2.1 Experimental materials

Ordinary Portland cement (P.O42.5) produced by Yangchun Cement Co., Ltd was used in this study. Its chemical composition and performance parameters are shown in Tables 1 and 2. Natural sand with water absorption of 2.32% provided by Chongqing Concrete Lei Building Materials Co., Ltd was used as the fine aggregate. Gravel of 5–10 mm and 10–20 mm provided by Chongqing Concrete Lei Building Materials Co., Ltd was used as the coarse aggregate. The technical indicators of gravel are listed in Table 3, and the particle size distribution is given in Tables 4 and 5. NS sol with a solid content of 30% and an average particle size of 12 nm produced by Zhejiang Yuda Chemical Co., Ltd was used as NS, and the main technical parameters are shown in Table 6. Polycarboxylate superplasticizer (PC)

Table 1: Chemical composition of cement

Composition	SiO_2	Al_2O_3	Fe_2O_3	GaO	MgO	SO_3	Na2Oeq	f-CaO	Loss	Cl^-
Content (%)	20.08	5.09	3.81	63.41	2.06	2.33	0.55	0.88	1.72	0.016

Table 2: Performance parameters of cement

Cement	Specific surface area (m^2/kg)	Density (g/cm^3)	Normal consistency (%)	Setting time (min)	
				Initial	Final
P.O42.5	346	3.12	24.6	96	258

Table 3: Technical indicators of crushed stone

Soil content (%)	Needle-like content (%)	Crush rate (%)	Water absorption (%)
0.4	0	5.4	0.9

Table 4: Particle size distribution of gravel (5–10 mm)

Square hole sieve (mm)	2.36	4.75	9.50	16.0
Accumulated sieving residue (%)	100	96	7	0

was provided by Xika China Co., Ltd. Its main technical parameters are shown in Tables 7 and 8.

2.2 Experimental methods

2.2.1 Preparation of NS dispersion

NS sol is a monodisperse system. Because the specific surface area and surface energy of nanoparticles are huge, there are many aggregates in NS sol, and the particle size of most aggregates is 100–400 μm [27]. Micron-sized silica aggregates not only cannot take advantage of the unique advantages of nanoparticles, but also the hydrated calcium silicate (C–S–H) formed by the reaction of volcanic ash does not have the characteristics, forming a weak interfacial transition zone in cement-based materials, affecting the performance of hardened cement paste [28–31]. Therefore, the dispersion treatment of NS is essential in the process of modified cement-based composites. To each 1,000 g NS dispersion solution 1 g PC was added and ultrasonically dispersed to prevent the reunion of NS sol. The power of ultrasonic dispersion is set to 25 W and the dispersion time is 10 min. Finally, the ultrasonic dispersion of NS is transparent to semitransparent uniform dispersion. Figure 1 shows the NS dispersion and ultrasonic dispersion equipment.

Table 5: Particle size distribution of gravel (10–20 mm)

Square hole sieve (mm)	2.36	4.75	9.50	16.0
Accumulated sieving residue (%)	100	95	9	0

2.2.2 Preparation of concrete

The mix ratio of concrete (N0) in the control group was designed according to JGJ 55 "Specification for mix proportion design of ordinary concrete" [32], and the specific mix ratio is shown in Table 9. The cement consumption in the test group concrete (N1–N7) is calculated according to the reduction rate. The reduced cement and water consumption are supplemented with sand and stone to keep

Table 6: Performance parameters of NS

Appearance	SiO_2 (%)	Na_2O (%)	pH	Density (g/cm^3)	Grain size (nm)
Microemulsion white translucent liquid	30	0.1	7.4	1.204	12.0

Table 7: Performance parameters of polycarboxylate superplasticizer

Appearance	Bulk density (g/cm^3)	pH	Water reduction	Total chloride content
White powder	0.6 ± 0.1	10.5 ± 0.5	≥25%	≤0.1%

Table 8: Laboratory apparatus

Name	Model
Single horizontal axis forced concrete mixer	HJW-60
Concrete vibration table	HZJ-A
Automatic constant stress pressure testing machine	DYE-2000S
Automatic bending and compression constant stress testing machine	YAW-300/10
Concrete penetration resistance meter	HG-80
Numerical control ultrasonic cell crusher	KBS-250
Concrete penetrometer	HP-4.0
Concrete shrinkage test environment test box	YW-40
Multifunctional high-resolution X-ray diffractometer	Empyrean
Desktop scanning electron microscopy	TM4000Plus II
Automatic mercury porosimeter	Auto Pore 9150

the sand rate unchanged. The concrete mix ratio is shown in Table 9. NS dosage is expressed as a percentage of cement quality. The prepared cement, fine aggregate, and coarse aggregate are put into the concrete mixer according to the ratio and stirred for 2 min. The aggregate and the cementitious material are mixed evenly and then the ultrasonic dispersed NS dispersion is added and stirred for 2 min. After mixing, the concrete mixture was put into the corresponding mold and vibrated to give a dense formation.

In the process of preparing concrete, under the condition of the same water–binder ratio, when NS is used as a cementitious materials-reducing admixture for concrete, with the increase of NS content, a large number of free water in the concrete is absorbed, and the slump of concrete is significantly reduced, which may make the concrete mixing and vibration insufficient. The slump of each group of concrete is different, and the actual hydration environment of cementitious materials is also different. In this case, it is of little significance to compare the test performance indexes of each group of concrete. In order to eliminate the interference caused by the hydration environment, a large number of experiments were carried out to determine the amount of water-reducing agents corresponding to different dosages of NS (Table 9). As shown in Figure 2c, each group of concrete has a similar slump (70–90 mm). After such treatment, it was ensured that the concrete has similar and good workability and it eliminates the impact of different hydration environments.

2.3 Test methods

2.3.1 Test of setting time and mechanical properties

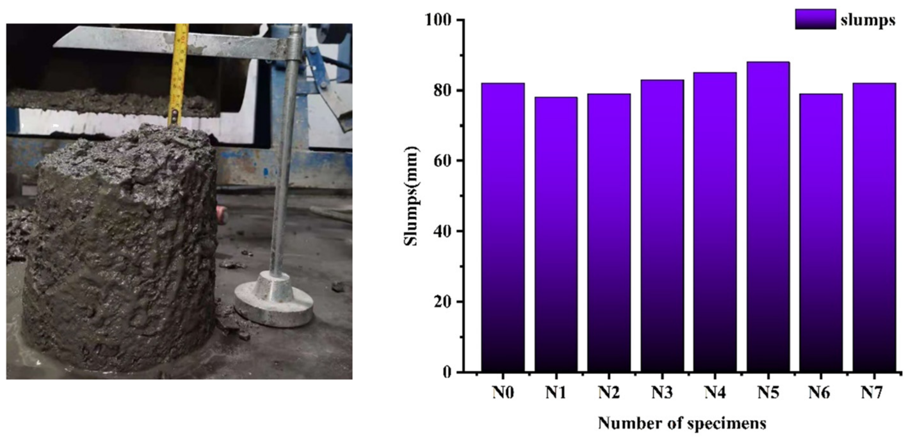
The concrete mixture was prepared, according to GB/T 50080-2002 "Standard for test method of performance on ordinary fresh concrete" [33], to test concrete initial setting time and final setting time. According to GB/T50081-2019 "Standard for test methods of concrete

(a) (b)

Figure 1: NS ultrasonic dispersion and ultrasonic dispersion equipment. (a) NS ultrasonic dispersion. (b) Numerical control ultrasonic Cell crusher.

Table 9: Proportioning of concrete

	Cement (kg/m³)	Water (kg/m³)	Coarse aggregate (kg/m³)	Fine aggregate (kg/m³)	NS (wt%)	PC (wt%)	Water–cement ratio
N0	360	215	1,095	730	0	0	0.60
N1	288	172	1,164	776	0.25	0.3	0.60
N2	288	172	1,164	776	0.5	0.3	0.60
N3	288	172	1,164	776	1.0	0.4	0.60
N4	288	172	1,164	776	1.5	0.5	0.60
N5	288	172	1,164	776	2.0	0.5	0.60
N6	288	172	1,164	776	2.5	0.6	0.60
N7	288	172	1,164	776	3.0	0.6	0.60



(a) (b)

Figure 2: Performance of concrete. (a) Slump test. (b) The slump of concrete in each group.

physical and mechanical properties" [34] the compressive and splitting tensile specimens of 100 mm × 100 mm × 100 mm concrete and the flexural specimens of 100 mm × 100 mm × 400 mm concrete were prepared, and the mechanical properties were tested at 3, 7, and 28 days.

2.3.2 Durability testing

According to GB/T50082-2009 "Standard Test Method for Long-term Performance and Durability of Ordinary Concrete" [35], the shrinkage performance, impermeability, and resistance to chloride-ion permeability of concrete were measured. In the water permeability test, the seepage height method was used to make a circular table with an upper diameter of 175 mm, a lower diameter of 185 mm, and a height of 150 mm. The average seepage height of hardened concrete under constant water pressure was measured. Shrinkage test was performed using contact method, making 100 mm × 100 mm × 515 mm prism specimens. When the shrinkage specimens were poured, stainless steel probes were inserted at the center positions of both ends of the specimens, and the initial lengths of each group of specimens were measured and recorded. Then, the specimens were immediately put into the concrete shrinkage environment test box (temperature 20°C, humidity 60%) for the test. The shrinkage of concrete was measured at the ages of 1, 3, 7, 14, 28, 45, and 60 days, respectively. The rapid chloride migration (RCM) coefficient method was used to perform the resistance to chloride ion penetration test to determine the resistance to chloride ion penetration of concrete by measuring the migration coefficient of chloride ion in the non-steady-state migration of concrete.

2.3.3 Microstructure test

Take standard curing 28-day specimens, remove surface dirt, and put in a 40°C drying oven to constant weight. The specimens were ground in a bowl, and the grinding powder was passed through an 80 μm sieve. The powder after the sieve was analyzed by XRD. XRD analysis conditions are 2–80°, 40 kV, 40 mA. The pore size and porosity of concrete specimens were studied using MIP. The microstructure of each group of concrete was studied using SEM. The specimen size was 10 mm × 10 mm × 10 mm.

3 Results and discussion

3.1 Effect of NS on setting time of concrete

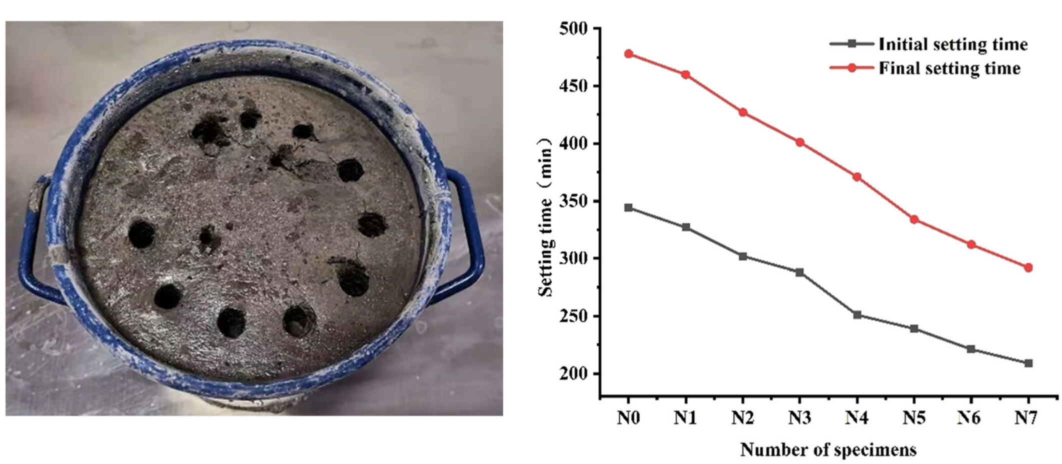
As shown in Figure 3, the initial and final setting times of the control group were 344 and 478 min, respectively. Under the same water–binder ratio, with the increase of NS dosage, concrete's initial and final setting time gradually decreases, which is similar to some previous studies [36,37], this is because NS has a strong pozzolanic activity. At the beginning of hydration, calcium hydroxide ($Ca(OH)_2$), the hydration product of cement, reacts with NS, promotes hydration, increases the exothermic rate of cement hydration, reduces the time required for hydration induction period, advances the acceleration period and deceleration period, and thus shortens the setting time of concrete.

3.2 Effect of NS on mechanical properties of concrete

As shown in Figure 4, the mechanical properties are evaluated when the specimen is cured to the specified time. Mechanical properties of specimens under standard curing for 3, 7, and 28 days are shown in Figure 5. After adding NS, the mechanical properties of concrete will be improved in varying degrees, showing a trend of first increase and then decrease. When the NS dosage was 2.0, 2.5, and 2.5%, the compressive strength of concrete reached the maximum at 3, 7, and 28 days, which were 22.58, 31.82, and 40.87 MPa, respectively, which were 15.6, 11.9, and 6.6% higher than those of the control group. When the NS dosage was 1.5, 2.5, and 2.0%, the flexural strength of concrete reached the maximum at 3, 7, and 28 days, respectively, 3.2, 4.4, and 6 MPa, which were 10.3, 18.9, and 11.1% higher than that of the control group. When the NS dosage was 1.5, 2.5, and 2.5%, the splitting tensile strength of concrete at 3, 7, and 28 days was 1.5, 2.6, and 3.8 MPa, respectively, which was 7.1, 23.8, and 15.15% higher than that of the control group.

It is worth noting that when less NS is added, the mechanics of the experimental group with a 20% reduction of cement content may be lower than that of the control group N0. For example, when the NS dosage was 0.25%, the 28 days' compressive strength, flexural strength, and splitting tensile strength of the experimental group N1 were 37.09, 5.1, and 3.1 MPa, respectively, which were 3.2, 5.6, and 6.1% lower than those of the control group N0.

SEM and XRD techniques were used to analyze the specimens after partial curing for 28 days. As shown in Figure 6, some characteristic peaks can be observed in the XRD pattern, and these peaks show different crystal structures in concrete materials. The main components are silica (SiO_2), tricalcium silicate (C_3S), dicalcium silicate (C_2S), calcium silicate hydrate (C–S–H), ettringite (AFt), and calcium hydroxide (CH). By comparing XRD



(a) (b)

Figure 3: Setting time of concrete. (a) Testing of concrete setting time. (b) Initial and final setting time of concrete.

(a) (b) (c)

Figure 4: Mechanical properties test of concrete. (a) Compressive test. (b) Flexural test. (c) Splitting tensile test.

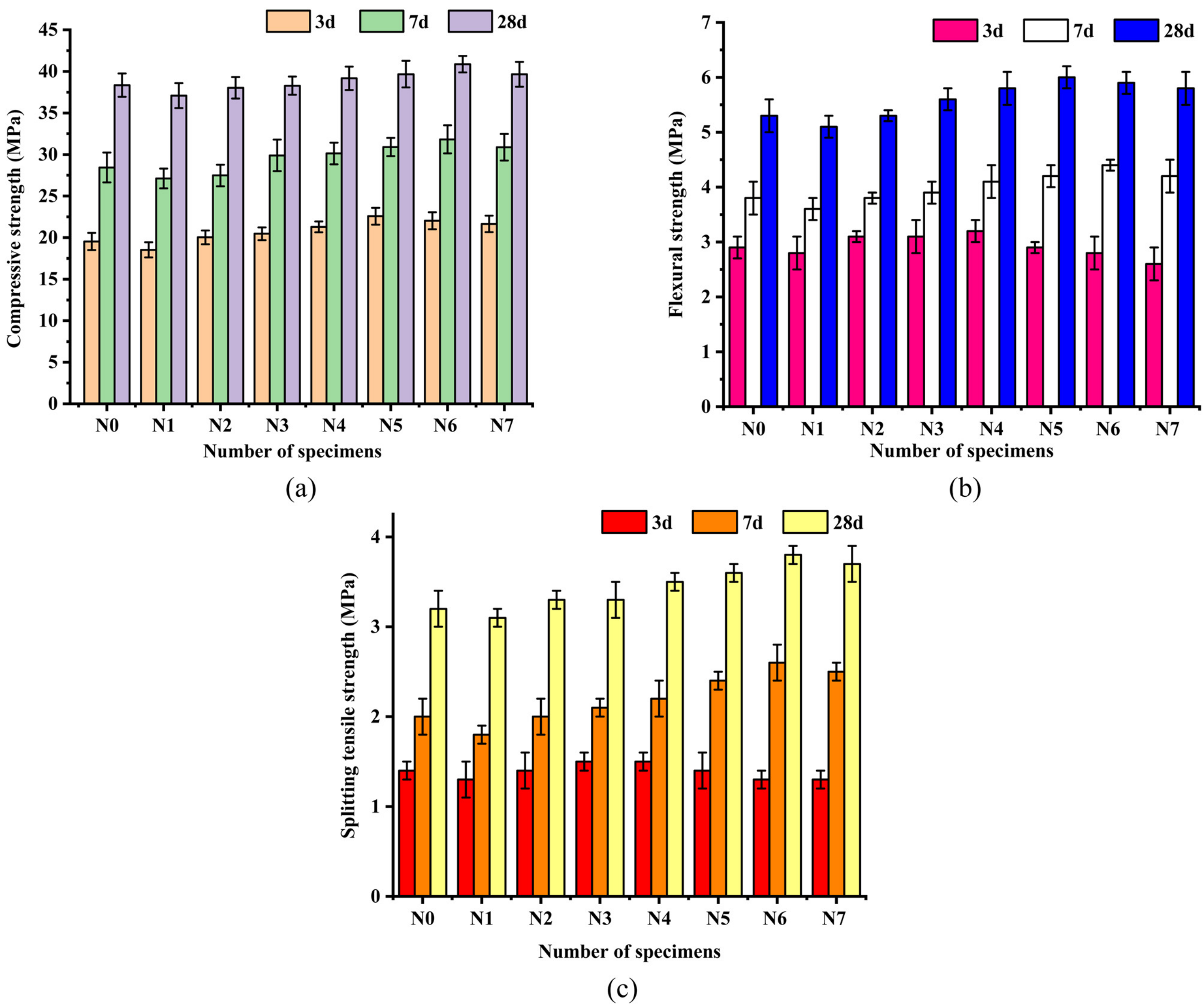


Figure 5: Mechanical properties of concrete at different ages. (a) Compressive strength. (b) Flexural strength. (c) Splitting tensile strength.

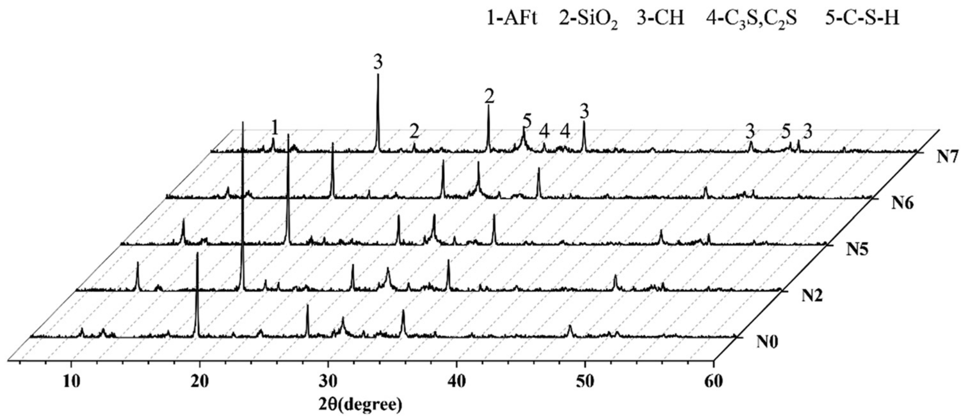


Figure 6: XRD patterns of hydration for 28 days.

patterns, it was found that the characteristic peaks of C_3S and C_2S in each group of samples were at a low level. With the increase of NS dosage, the characteristic peak of CH decreased first and then increased, while the characteristic peak of C–S–H increased first and then decreased. When the dosage of NS is 2.5%, the peak value of CH is the smallest, and the peak value of C–S–H is the largest. This is because NS shows a good pozzolanic activity and nucleation effect, which helps consume free CH in the concrete system, reduces the hydration products that cannot provide strength, and generates C–S–H to make the internal space of concrete denser, thereby enhancing the mechanical properties of concrete.

In Figure 7, it can be found that NS significantly improves the microstructure of concrete. As shown in Figure 7(a), the microstructure of the N0 sample has significant defects, the hydration products are not closely combined with the aggregate, and the ITZ is weak and there are obvious cracks. By observing Figure 7(b), it can be found that after reducing the amount of cement in concrete by 20%, the addition of 0.5% NS can promote the hydration of cement to a certain extent and form denser and regular hydration products. However, there are still cracks and incomplete packages in the interface transition zone. In Figure 7(c)–(e), it can be seen that with the gradual increase of NS dosage, the microstructure of concrete is significantly improved. The interface transition zone of the N5 specimen is dense, and the hydration products are wrapped together with the aggregate. The interface bonding between the slurry and the aggregate is significantly enhanced. Compared with the N5 specimen, the ITZ of the N6 specimen was closer. The hydration products completely wrapped the aggregate, and the hydration products changed from dispersed gel morphology to regular and orderly crystals. The crystals were intertwined to form a uniform and dense structure. This is due to the unique nucleation and filling effect of NS. The specific surface area of NS is large enough to absorb the hydration products. At the same time, C–S–H takes NS as the growth point and gradually grows from flocculent to columnar network structure with a distinct outline to improve the interface structure between cement slurry and aggregate. At the same time, the filling effect of NS can physically fill the gaps of cementitious materials, capillary pores, and calcium silicate hydrate crystals in concrete so that the concrete is denser and the strength is improved [38,39]. The N7 specimen showed that the regulatory effect of NS on the excessive zone and hydration products in the interfacial concrete began to weaken. This was because the NS dosage was too large and prone to agglomeration in concrete materials. The presence of NS aggregates not only failed to give full play to the unique advantages of nanoparticles, but also the hydration calcium silicate (C–S–H) formed by the reaction of volcanic ash did not have the cementitious characteristics, forming a weak ITZ in cement-based materials, affecting the performance of hardened cement paste, and ultimately reducing the performance of concrete.

3.3 Effect of NS on autogenous shrinkage of concrete

The shrinkage of concrete is calculated by the formula (1):

$$\varepsilon_{st} = \frac{L_0 - L_t}{L_b}, \quad (1)$$

where ε_{st} is the shrinkage rate of concrete with test period t (days), t from the determination of initial length; L_b is the measuring gauge distance of the specimen. When the contact method extensometer is used, it is the measuring gauge of the instrument. L_t is the specimen's length

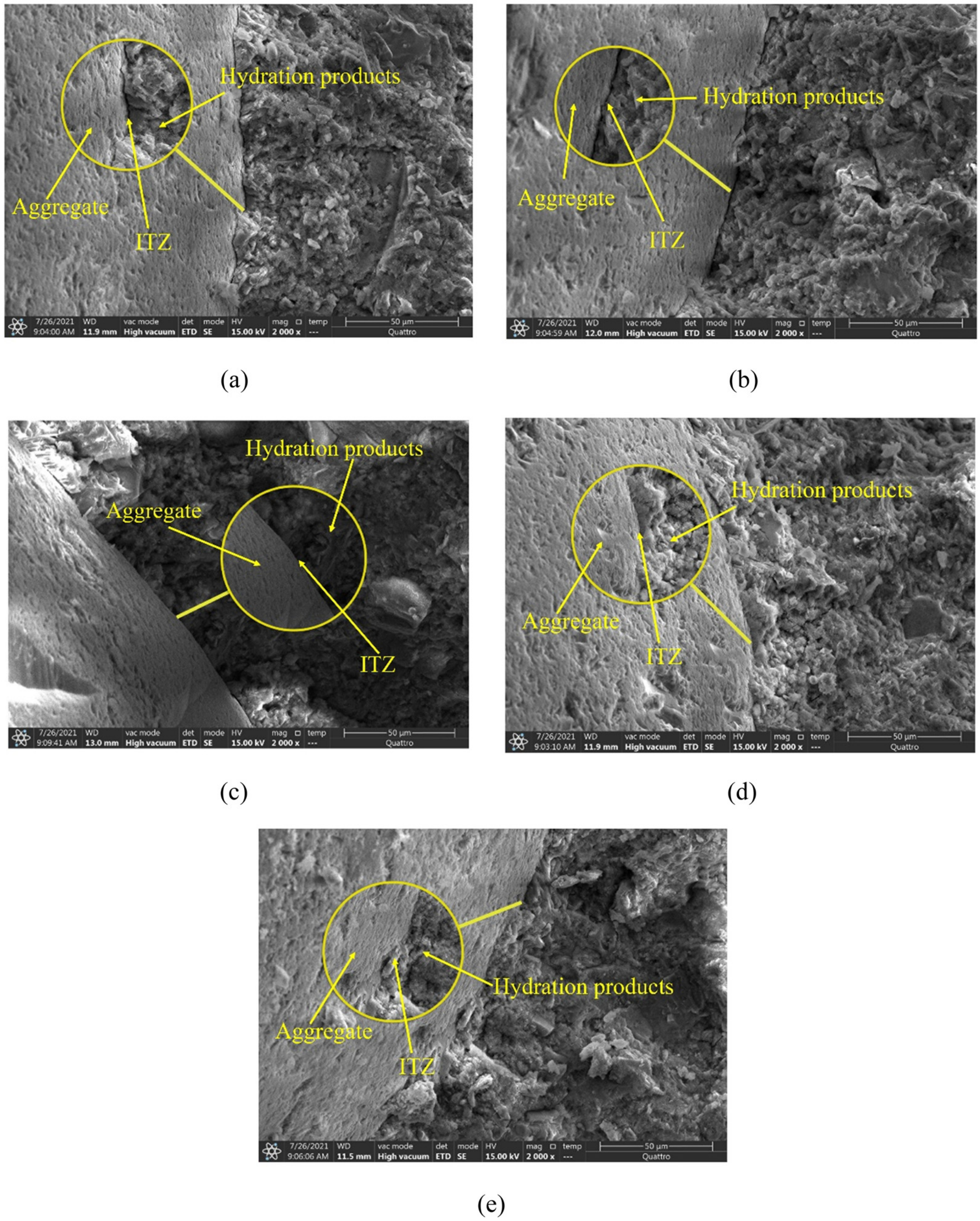


Figure 7: Micromorphology of the matrix after curing for 28 days: (a) N0, (b) N2, (c) N5, (d) N6, and (e) N7.

reading (mm) measured when the test period was *t* (days) (Figure 8).

Figure 9 shows the autogenous shrinkage values of concrete with different NS dosages at different setting times. It can be clearly seen from Figure 9 that the autogenous shrinkage of concrete increased rapidly in the early stage (especially in the first 14 days), while it increased slowly in the late stage. This is because NS has a high pozzolanic activity in the early stage. When NS is added into the concrete, the hydration process of the concrete is accelerated, and the autogenous shrinkage of concrete in the early stage is promoted. In the later stage, the hydration reaction rate of cement particles in concrete decreases gradually, and the autogenous shrinkage decreases gradually. In addition, the shrinkage of concrete specimens increases with the increase of NS content, because the autogenous shrinkage of concrete accounts for a large proportion of the early total shrinkage of concrete. For example, the shrinkage values of concrete with NS (1.0, 1.5, 2.0, 2.5, 3.0%) at 3 days were 28.7×10^{-6},

(a) (b)

Figure 8: Shrinkage performance of concrete. (a) Concrete shrinkage environment test box. (b) Horizontal shrinkage apparatus for concrete.

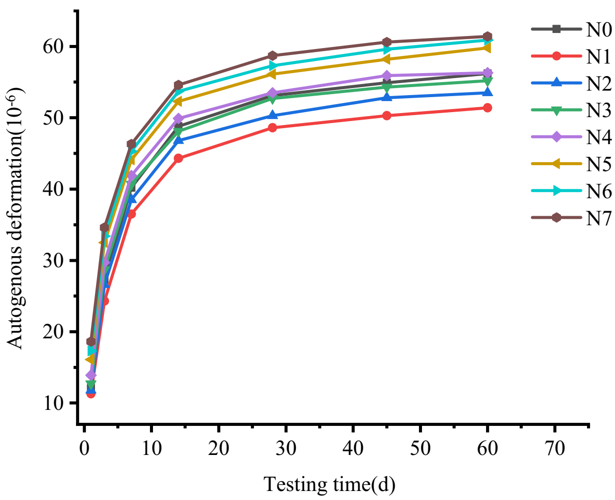


Figure 9: Shrinkage rate of concrete.

29.9×10^{-6}, 32.1×10^{-6}, 33.3×10^{-6}, and 34.6×10^{-6}, respectively, which were 5.9, 10.3, 18.5, 22.9, and 27.7% higher than those of the control group. However, the shrinkage of concrete in 14 days increased by 2.9, 5.0, 7.1, 11.3, and 15.5%, respectively, and the shrinkage in 60 days increased by 2.2, 3.1, 5.1, 8.1, and 10.5%, respectively. Notably, when NS dosage is 0.25 and 0.5%, the autogenous shrinkage of concrete in 3 days was 24.3×10^{-6} and 26.8×10^{-6}, compared with the control group decreased by 10.3 and 5.1%, 14-day shrinkage decreased by 7.6 and 3.4%, 60-day shrinkage decreased by 2.5 and 1.7%. This shows that the increase of concrete shrinkage rate decreases significantly with the increase of time. After reducing the amount of cement by 20%, the dosage of NS in concrete is lower (0.25, 0.5%), and the autogenous shrinkage value of concrete is less than that of the control group.

3.4 Effect of NS on the impermeability of concrete

The seepage height of the specimen should be calculated according to formula (2):

$$\bar{h}_i = \frac{1}{10}\sum_{j=1}^{10} h_j, \quad (2)$$

where h_j is the water seepage height (mm) at point j of specimen i and $\bar{h}_i$ is the average seepage height (mm) of specimen i.

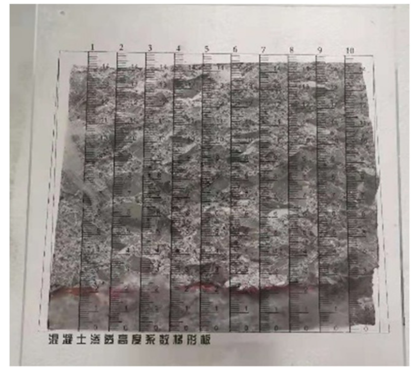
Average seepage height of a group of specimens shall be calculated according to formula (3):

$$\bar{h} = \frac{1}{6}\sum_{i=1}^{6} \bar{h}_i, \quad (3)$$

where $\bar{h}_i$ is the average seepage height (mm) of a group of six specimens.

As shown in Figure 10 and Table 10, the addition of NS has different effects on the impermeability of concrete under reducing 20% cement content in concrete. When the NS dosage was 2.5%, the average seepage height of the experimental group (N6) was 20.4 mm, which was 29.9% lower than that of the control group (N0). In contrast, when the NS dosage was 0.25%, the average seepage height of the experimental group (N1) was 28.3 mm, which was 5.6% higher than that of the control group (N0). These results show that when the NS dosage is greater than 0.5%, even if the cement content is reduced by 20%, the impermeability of concrete is still better than that of the control group, and has been enhanced to a certain extent. From the perspective of mechanism, the incorporation of NS has played a filling role, accelerated the hydration process, and became the site for the growth

(a)



(b)

Figure 10: Test on the impermeability of concrete. (a) Test instrument for impermeability of concrete. (b) Measuring average seepage height of the concrete.

of hydration products. It has greatly improved the compactness of the matrix as a whole. Moreover, NS can improve the pore structure inside the concrete, so that the pores with large pore sizes in the concrete are transformed into pores with small pore sizes, and the pore size is refined. Therefore, the impermeability of concrete is enhanced.

3.5 Effect of NS on chloride ion corrosion resistance of concrete

The chloride migration coefficient of concrete in a non-steady state should be calculated according to formula (4):

$$D_{\mathrm{RCM}} = \frac{0.0239 \times (273 + T)L}{(U - 2)t}\left(X_d - 0.0238\sqrt{\frac{(273 + T)LX_d}{U - 2}}\right), \quad (4)$$

where D_{RCM} is the non-steady state chloride migration coefficient in concrete, accurate to $0.1 \times 10^{-12}\,\mathrm{m^2/s}$; U is the absolute voltage value used (V); T is the average initial temperature and ending temperature of the anode solution (°C); L is the specimen thickness (mm), accurate to 0.1 mm; X_d is the average chloride penetration depth (mm), accurate to 0.1 mm; and t is the test duration (h).

Resistance to chloride ion erosion is an essential property of concrete, which significantly influences the durability of concrete. As shown in Figure 11c, the different penetration depths of chloride ions show that the improvement effect of different dosages of NS on the resistance to chloride ion erosion of concrete specimens is different. The average penetration depth of each specimen is tested, and the non-steady-state chloride ion migration coefficient of concrete is calculated using formula (4). As shown in Figure 11d, in the case of reducing the amount of 20% cement in concrete, the non-steady-state chloride ion migration coefficient of concrete after adding NS decreases first and then increases, indicating that the resistance to chloride ion erosion of concrete increases first and then decreases. When the NS dosages are 1, 1.5, 2, 2.5, and 3%, the resistance to chloride ion erosion of concrete shows improvement even if the cement content is reduced by 20%. The test group N5 has the best resistance to chloride ion erosion, and the depth of chloride ion erosion into concrete is the least. The non-steady-state chloride ion migration coefficient is $6.4 \times 10^{-12}\,\mathrm{m^2/s}$, *i.e.*, 14.7% lower than that of the control group N0. This is because the pore structure of concrete is refined and improved after adding NS, which reduces the connected pores in cement slurry and the connected pores in the interface between cement slurry and aggregate. At the same time, the hydration products become orderly and dense under the nucleation of NS,

Table 10: Water penetration height

	N0	N1	N2	N3	N4	N5	N6	N7
Water penetration height (mm)	26.8	28.3	26.1	24.3	23.5	21.8	20.4	21.3
Falling rate (%)		−5.6	2.6	9.3	11.2	18.7	23.9	20.5

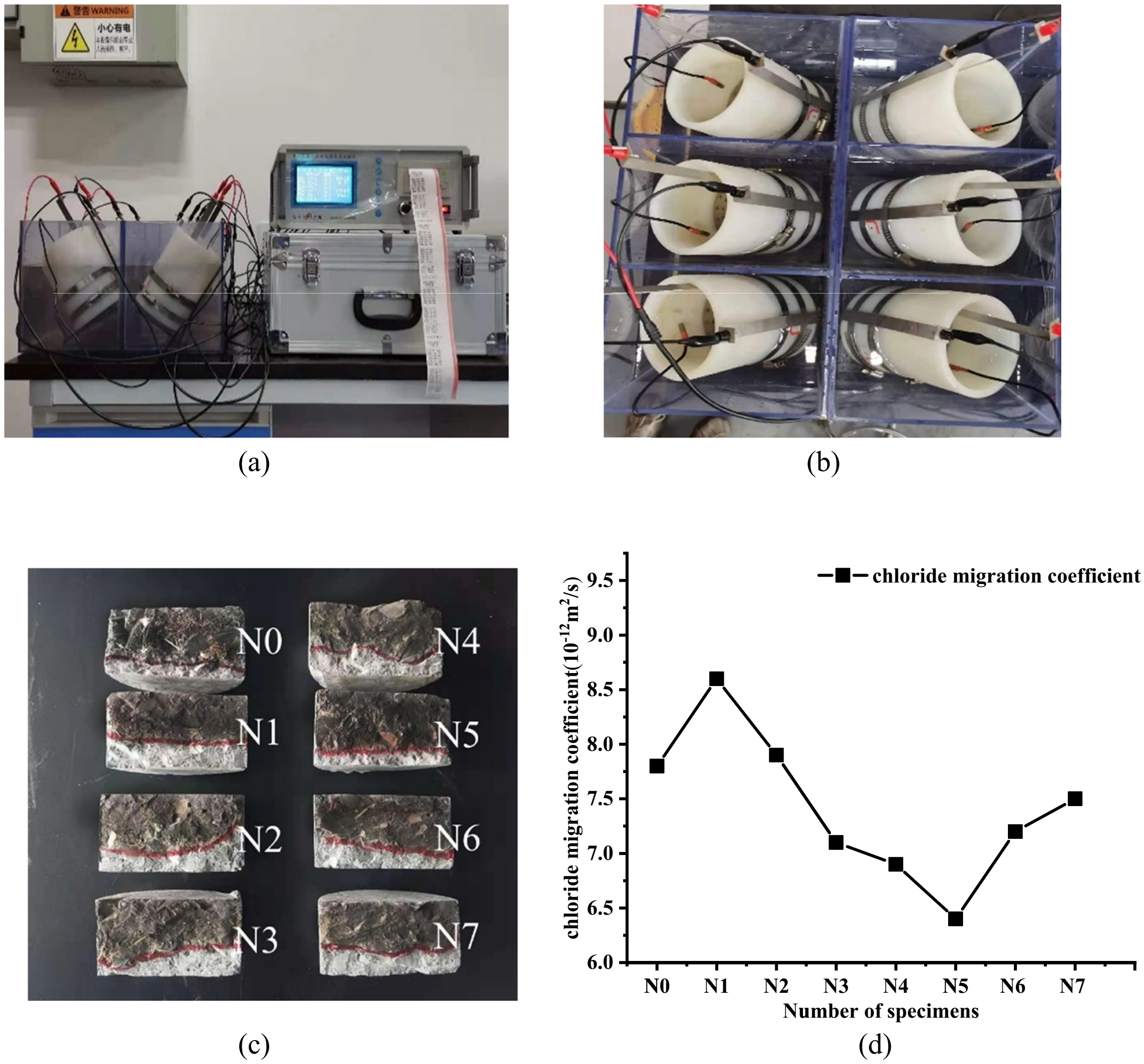


Figure 11: Chloride permeability test. (a) Multifunctional concrete durability comprehensive test instrument. (b) Chloride penetration resistance test of concrete. (c) Resistance to chloride ion permeability of different specimens. (d) Coefficient of the chloride migration.

which improves its corrosion resistance. However, under the condition of 20% reduction of cement content and low NS dosage (0.25, 0.5%), the chloride ion erosion resistance of concrete shows a decrease. The non-steady-state chloride ion migration coefficient was 8.6×10^{-12} and $7.9 \times 10^{-12}\,m^2/s$, which increased by 13.7 and 5.3% compared with the control group N0. Although NS has high pozzolanic activity, the number of hydration products of concrete cannot be compared with that of the control group on reducing the amount of cement and low dosage of NS (0.25, 0.5%). At the same time, it cannot effectively fill the pores in the concrete, resulting in the decrease of the resistance to chloride ion corrosion.

Pores in concrete have a significant impact on the strength, permeability [40], and resistance to chloride ion erosion of concrete. Therefore, the progressive mercury penetration test analysis of specimens cured for 28 days with N0 and N5. As shown in Figure 12a, the relationship of the cumulative pore volume is N0 > N5, indicating that NS can effectively reduce the cumulative pore volume of concrete and make the internal structure of concrete more compact after reducing the amount of cement in concrete by 20%. It can be seen from Figure 12b and Table 11 that the pores in N0 are mainly harmless pores, harmful pores, and more harmful pores, and the proportion of pore is 32.61, 25.72, and 27.11%, respectively. The pores in N5 are mainly less harmful pore and harmless pore, and the proportion of pore is 35.19 and 29.4%, respectively. Combined with the analysis shown in Figure 12b and Table 11, it can be found that even if the cement content in concrete is reduced by 20%, the cumulative pore volume and pore size distribution of N5 in the experimental group after

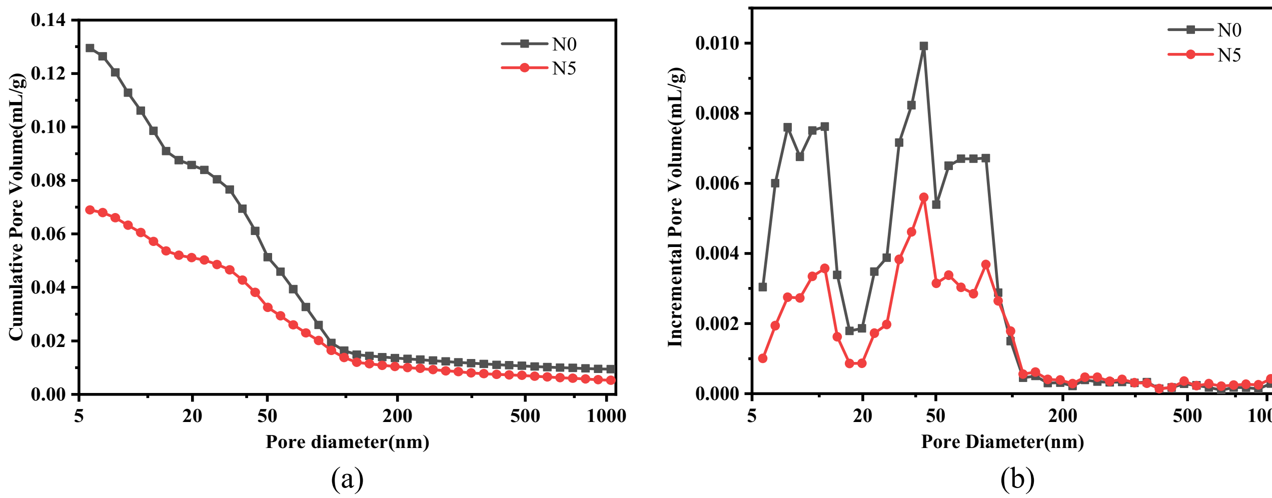


Figure 12: MIP test results. (a) Cumulative pore volume. (b) Pore size distribution.

adding NS are significantly better than those in the control group N0. Compared with the control group N0, the proportion of more harmful pores in the experimental group N5 decreased by 16.86%, and the proportion of less harmful pores increased by 21.02%. On reducing the amount of cement in concrete by 20%, it is found that the incorporation of NS makes the pores with large pore sizes in concrete transform to those with small pore size, which plays a role in refining the pore size. This also explains why reducing 20% cement content in concrete and adding 2.0% NS can improve the resistance to chloride ion erosion of concrete.

4 Conclusion

In this article, the workability, mechanical properties, durability, and microstructure of concrete by replacing NS with 20% of cement in concrete are studied in combination with the research idea of cementitious materials – reducing admixture for concretes. The main conclusions are as follows.

(1) When the NS dosage increases from 0.25 to 3% (the weight of cementitious materials), the concrete slump will be significantly reduced, and its workability needs to be improved by adjusting the amount of PC.

(2) Under the condition of reducing 20% cement content in concrete, when the standard curing age is 28 days, the compressive strength and splitting tensile strength of specimens (N6) with an NS dosage of 2.5% are 40.87 and 3.8 MPa, respectively, which are 6.6 and 15.15% higher than those of the control group (N0). The results show that the appropriate amount of NS can significantly improve the mechanical properties of concrete.

(3) Under the condition of reducing 20% cement content in concrete, specimen (N6) with 2.5% NS content has the best impermeability, which is 23.9% higher than N0. The specimen with an NS content of 2% (N5) has the best resistance to chloride ion erosion, which is 14.7% higher than that of N0.

(4) When the standard curing age was 28 days, the compressive strength of the specimen (N1) with 0.25% NS dosage was 37.09 MPa, which was 3.2% lower than those of the control group (N0). At the same time, the impermeability and chloride ion erosion resistance decreased by 5.6 and 10.26% compared with the control group (N0). The results show that under the condition of reducing 20% cement content in concrete, a

Table 11: Test results of specimen porosity

	Proportion of various apertures			
	Less harmful pore (≤20 nm)	Harmless pore (20–50 nm)	Harmful pore (50–200 nm)	More harmful pore (≥200 nm)
N0	14.56%	32.61%	25.72%	27.11%
N5	35.19%	29.4%	25.16%	10.25%

low dosage of NS cannot compensate for the loss of mechanical properties and durability of concrete.

(5) The microscopic test results show that reducing the amount of cement in concrete by 20% and adding NS can promote the formation of more hydration products such as C–S–H gel, which is helpful to form a closer ITZ inside the concrete. In addition, the cumulative pore volume in concrete is reduced, and the pore size is refined to make the internal structure of concrete denser. Finally, improving the mechanical properties and durability of concrete.

(6) The results show that NS can be used as an ideal cementitious materials-reducing admixture for concrete, and its mechanical properties and durability can be improved to some extent by adding NS under the condition of reducing the amount of 20% cement in concrete. These research results can reduce the overall cement consumption in the construction industry and thus provide new ideas for reducing carbon emissions in the cement industry. At the same time, the improvement of impermeability and chloride resistance can solve the water leakage problem of some structures, which provides a new method for improving the durability of coastal structures.

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