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Sulfate corrosion resistance of foundation concrete with nano-particles

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Abstract. With the rapid development of modern industry, the foundation soil and the underground water in some areas are severely polluted by the corrosive medium affecting the durability of foundation concrete. Sulfate corrosion is one of the major factors leading to the destruction of foundation concrete. The sulfate corrosion resistance of foundation concrete with nano-particles (nano-SiO₂ and nano-CaCO₃) under the action of dry-wet cycle is experimentally studied, and compared with that of plain foundation concrete. The test results indicate that, under the action of dry-wet cycle, the sulfate corrosion resistance of foundation concrete is significantly improved with the addition of nano-particles. With the increasing content of nano-particles, the sulfate corrosion resistance of foundation concrete gradually rises to its peak and then drops step by step. The sulfate corrosion resistance of foundation concrete with nano-SiO₂ is superior to that of foundation concrete with the same amount of nano-CaCO₃. When the content of nano-SiO₂ and nano-CaCO₃ is respectively 2.0 % and 1.0 % by weight of binder, the sulfate corrosion resistance of foundation concrete is the best. Because the pore structure of concrete is improved with the addition of nano-particles, as nano-SiO₂ can react with Ca(OH)₂ and nano-CaCO₃ can react with C₃A, nano-particles can significantly enhance the sulfate corrosion resistance of foundation concrete.

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1. Introduction

The natural environment is damaged with the rapid development of modern society because the industrial waste and household garbage are discharged randomly. The site soil and underground water in some areas are polluted seriously. The building foundation has close contact with the site soil and underground water, so the site soil and underground water contaminated by corrosive medium can affect the durability of foundation concrete. In addition, the sulfate corrosion is one of the key factors causing damage to foundation concrete. Because the building foundation is concealed, the corrosion phenomena are very difficult to discover, and are hard to control and repair. Except that the industrial and household waste can lead to the existence of corrosive ion in the site soil and underground water, the site soil in some areas contains corrosive ion in itself, such as SO₄²⁻, which can give rise to the rapid failure of foundation concrete due to severe sulfate corrosion. Sulfate erosion of foundation concrete exists in many other countries, such as America, Germany, Canada and Japan. Consequently, it is essential to enhance the sulfate corrosion resistance of foundation concrete.

Nano-materials attract more and more attention due to their unique physical and chemical properties. With the reduction in manufacturing costs, the application field of nano-materials is more and more extensive. It has been proven that nano-materials can improve the mechanical properties and durability of concrete. Nano-materials gives lower heat of hydration, improved durability together with the responsiveness to hydrogen sulfate and hydrogen chloride attacks when equated to the standard concrete [1–10]. However, the research on the sulfate corrosion resistance of concrete with nano-materials is so limited at present.

Zhang et al. [11, 12] studied the sulfate corrosion resistance of foundation concrete with nano-particles in freeze-thaw environment, and the test results showed that the addition of nano-kaolin, nano-SiO₂ and nano-CaCO₃ can improve the sulfate corrosion resistance of foundation concrete to different extent. When the content of nano-kaolin, nano-SiO₂ and nano-CaCO₃ can is respectively 3 %, 2 % and 2 %, the life of sulfate corrosion resistance of foundation concrete is respectively increased by 99.33 %, 127.98 % and 106.40 %. Li et al. [13] studied the effect of nano-CaCO₃ on the performance of concrete with fly ash in the dry-wet cycling environment, and the corrosion resistance of fly ash concrete is greatly enhanced when the content of nano-CaCO₃ is 1 %.

Nano-SiO₂ has high pozzolanic activity, can quickly participate in cement hydration reaction, and can consume Ca(OH)₂ in cement hydration products; Nano-CaCO₃ can improve the pore structure of concrete, and the price is low, with reasonable economy. Therefore, in this paper, nano-SiO₂ and nano-CaCO₃ are mixed into the foundation concrete to study the change rules of physical properties (relative dynamic elastic modulus) and mechanical properties (compressive and flexural strength) of nanoparticle foundation concrete against sulphate corrosion and its modification mechanism of the sulfate corrosion resistance of foundation concrete with nano-particles under the action of dry-wet cycle. And the sulfate corrosion resistance is compared with that of plain foundation concrete.

2. Methods

2.1. Materials and mixture proportions

The cement used is Portland cement (P.O42.5). The fine aggregate is natural river sand with a fineness modulus of 2.43. The coarse aggregate used is crushed basalt with a diameter of 5–31.5 mm. The properties of nano-particles (SiO₂ and CaCO₃) are given in Table 1.

Table 1. Properties of nano-particles.

Item	Diameter (nm)	Purity (%)	Specific surface area (m ² /g)	pH value
nano-SiO ₂	20	99.9	640 ± 60	6–8
nano-CaCO ₃	30	99.0	–	9.3

The water-to-binder (the sum of cement and nano-particles) ratio used for all mixtures is 0.44, and the sand ratio is 34 %. The mixture proportions of concretes per cubic meter are shown in Table 2. The water-reducing agent (FDN, one kind of β-naphthalene sulfonic acid and formaldehyde condensates, 1.5 % by mass of binder) is adopted to ensure the good workability of fresh concrete, and act as a better dispersant to prevent the agglomeration of nano-particles in cement paste. Besides, the defoamer (tributyl phosphate) is employed with a mass ratio of 4 % to superplasticizer to eliminate air bubbles generated during the dispersion of nano-particles.

Table 2. Mix proportions of concretes (unit: kg/m³).

Mixture type	Water	Cement	Sand	Coarse aggregate	Nano-SiO ₂	Nano-CaCO ₃	FDN	Defoamer
PC	165	375	645	1240	–	–	4.31	–
NS05	165	373.1	645	1240	1.9	–	4.31	0.172
NS10	165	371.2	645	1240	3.8	–	4.31	0.172
NS20	165	367.5	645	1240	7.5	–	4.31	0.172
NS30	165	363.7	645	1240	11.3	–	4.31	0.172
NC05	165	373.1	645	1240	–	1.9	4.31	0.172
NC10	165	371.2	645	1240	–	3.8	4.31	0.172
NC20	165	367.5	645	1240	–	7.5	4.31	0.172
NC30	165	363.7	645	1240	–	11.3	4.31	0.172

Here, PC denotes plain concrete. NS05, NS10, NS20 and NS30 denote the concrete with nano-SiO₂ in the amount of 0.5 %, 1.0 %, 2.0 % and 3.0 % by weight of binder, respectively. NC05, NC10, NC20 and NC30 denote the concrete with nano-CaCO₃ in the amount of 0.5 %, 1.0 %, 2.0 % and 3.0 % by weight of binder, respectively.

2.2. Specimen preparation and curing

To prepare the concrete with nano-particles, the water-reducing agent is firstly mixed into water in a mortar mixer, and then nano-particles are added in and stirred at a high speed for 5 min. Defoamer is added as stirring. Cement, sand and coarse aggregate are mixed at a low speed for 2 min in a concrete centrifugal blender, and then the mixture of water, water-reducing agent, nano-particles and defoamer is slowly poured in and stirred at a low speed for another 2 min to achieve good workability.

To prepare plain concrete, the water-reducing agent is firstly dissolved in water. After cement, sand and coarse aggregate are mixed uniformly in a concrete centrifugal blender, the mixture of water and water-reducing agent is poured in and stirred for several minutes.

Finally, the fresh concrete is poured into oiled molds to form cubes of size 100×100×100 mm to be used for compressive strength testing, and prisms of size 100×100×400 mm for sulfate corrosion resistance testing. After pouring, an external vibrator is used to facilitate compaction and reduce the amount of air bubbles. The specimens are de-molded at 24 h and then cured in a room at a temperature of 20±2 °C and a relative humidity of more than 95 % until the prescribed period.

2.3. Test methods

The workability of concrete includes three aspects, liquidity, cohesiveness and water holding capacity. The liquidity of fresh concrete is measured by slump test. The cohesiveness and water holding capacity is evaluated by visual range estimation and experience. Slump test is conducted in accordance with GB/T 50080-2016 (Standard for test method of performance on ordinary fresh concrete, China). Compressive strength test is performed according to GB/T 50081-2016 (Standard for test method of mechanical properties on ordinary concrete, China). The sulfate corrosion resistance test is conducted according to GB/T 50082-2009 (Standard for test methods of long-term performance and durability of ordinary concrete, China), and the dry-wet cycling pattern is used.

2.3.1. The dry-wet cycling mode

Concrete specimens are taken out of the curing room at 28 days and the specific dry-wet cycling mode is as follows. Firstly, concrete specimens are put into Na₂SO₄ solution with a concentration of 5 % and submerged for 16 h at room temperature. The solution surface should be at least 20 mm above the upper specimen surface, and the plastic box should be capped to prevent the solution from evaporating. Na₂SO₄ solution should be renewed every month to keep the pH value of the solution basically constant. Next, concrete specimens are taken out of Na₂SO₄ solution and dried in the air for 1 h. Then, concrete specimens are put in the drying oven at a temperature of 80 °C for 6 h. Finally, they are taken out of the drying oven and cooled for 1 h. This is one dry-wet cycle with the total time of 24 h.

2.3.2. The corrosion resistance coefficient of compressive strength

The corrosion resistance coefficient of compressive strength can be used to reflect the change of concrete strength, and thus to reflect the internal damage degree of concrete. Compressive strengths of concrete specimens are tested at 28 days, and then are measured per 20 times dry-wet cycles.

The corrosion resistance coefficient of compressive strength can be defined as

$$K_f = \frac{f_{cn}}{f_{c0}}, \quad (1)$$

where, K_f is the corrosion resistance coefficient of compressive strength (%); f_{cn} is the compressive strength of concrete specimen subjected to sulfate corrosion after N times dry-wet cycles (MPa); f_{c0} is the compressive strength of concrete specimen under the standard curing condition at the same curing age with corroded concrete specimen (MPa).

When the corrosion resistance coefficient of compressive strength is decreased to 75 %, the test can be stopped.

2.3.3. The relative dynamic elastic modulus

The relative dynamic elastic modulus can also reflect the internal damage degree of concrete. The nonmetal supersonic detecting instrument (RS-ST01C) shown in Fig. 1 is used to measure the relative dynamic elastic modulus of concrete specimen, because the propagation sonic time of supersonic wave in concrete can effectively reflect the internal structural change of corroded concrete.



Figure 1. The nonmetal supersonic detecting instrument and the probe.

The initial sonic time of supersonic wave through the concrete specimen is measured when the curing age is 28 days, and then the sonic time of supersonic wave through the concrete specimen is measured per 20 times dry-wet cycles. The sound velocity of supersonic wave in the concrete specimen can be calculated from the sonic time of supersonic wave. The relationship between dynamic elastic modulus of concrete and sound velocity of supersonic wave can be expressed by

$$E = \frac{(1+\mu)(1-2\mu)}{(1-\mu)} \rho V^2, \quad (2)$$

where, E is the dynamic elastic modulus of concrete; μ is the Poisson's ratio of concrete; ρ is the density of concrete; V is the sound velocity of supersonic wave through the concrete.

For the same material, the change of Poisson's ratio and density is very little, so the relative dynamic elastic modulus of concrete can be expressed by

$$E_d = \frac{E_n}{E_0} = \left(\frac{V_n}{V_0} \right)^2 = \left(\frac{t_0}{t_n} \right)^2, \quad (3)$$

where, E_d is the relative dynamic elastic modulus of concrete; E_0 , V_0 , t_0 are the initial dynamic elastic modulus of concrete, the initial sound velocity and sonic time of supersonic wave through the concrete, respectively; E_n , V_n , t_n are the dynamic elastic modulus of concrete, the sound velocity and sonic time of supersonic wave through the concrete, respectively, after N times dry-wet cycles.

When the relative dynamic elastic modulus of concrete is reduced to 60%, the test can be terminated.

3. Results and Discussions

3.1. Compressive strength of foundation concrete

Fig. 2 shows the compressive strength of foundation concrete at 7d, 28d and 56d. It can be seen that the compressive strength of concrete with nano-particles at different curing ages can be increased compared with plain concrete. That is to say, the addition of nano-particles can improve the compressive strength of foundation concrete. However, if the variety or content of nano-particles is different, the improvement effect on the compressive strength of foundation concrete is diverse. At every testing age, the compressive strength of foundation concrete with nano-SiO₂ is larger than that with the same amount of nano-CaCO₃. When nano-SiO₂ in the amount of 2% by weight of binder is added, the compressive strength of foundation concrete is increased most significantly at all ages.

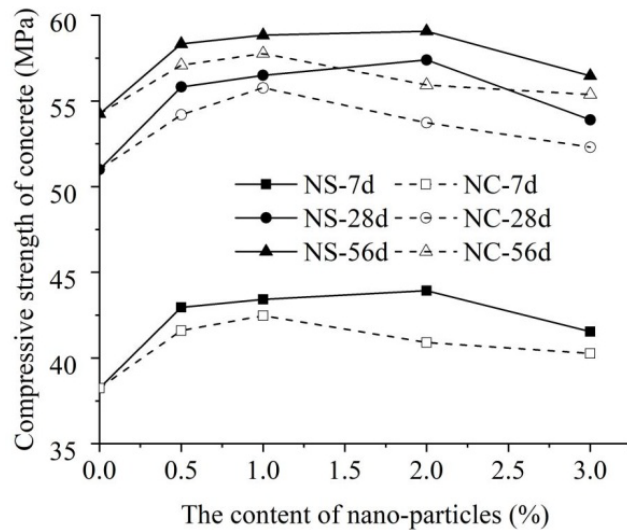


Figure 2. Relationship between the compressive strength of concrete and the content of nano-particles.

It also can be observed from Fig. 2 that, for the compressive strength of concrete at all ages, there is the same change trend with the addition of nano-SiO₂ and nano-CaCO₃. With the increased content of nano-particles, the compressive strength of concrete at all ages is firstly increased and then decreased, and this fully demonstrates that there is an optimum content range of nano-particles in concrete. From the view of compressive strength, the optimum content of nano-SiO₂ and nano-CaCO₃ in concrete is about 2 % and 1 %, respectively.

The effectiveness of nano-SiO₂ in enhancing compressive strength of concretes decreases in the order: NS20 > NS10 > NS05 > NS30, and the effectiveness of nano-CaCO₃ in enhancing compressive strength of concretes decreases in the order: NC10 > NC05 > NC20 > NC30. Obviously, when the content of nano-SiO₂ or nano-CaCO₃ is 3 %, the compressive strength of concrete is lower than that of concrete with nano-SiO₂ or nano-CaCO₃ in the amount of 0.5 % by weight of binder, and this indicates that it is unbeneficial when nano-particles are added in large amount.

Fig. 3 is the enhanced extent histogram of compressive strength of concrete with nano-particles at 7d, 28d and 56d. It can be seen that, when the content of nano-particles is the same, the enhanced extent of compressive strength of concrete is gradually decreased with the increase of curing age. This shows that the addition of nano-SiO₂ and nano-CaCO₃ can remarkably improve the early compressive strength of concrete. For the concrete with 2 % nano-SiO₂, the enhanced extent of compressive strength at 56d (8.88 %) is only 59.8 % compared with that of compressive strength at 7d (14.85 %). For the concrete with 1 % nano-CaCO₃, the enhanced extent of compressive strength at 56d (6.49 %) is only 58.8 % compared with that of compressive strength at 7d (11.03 %).

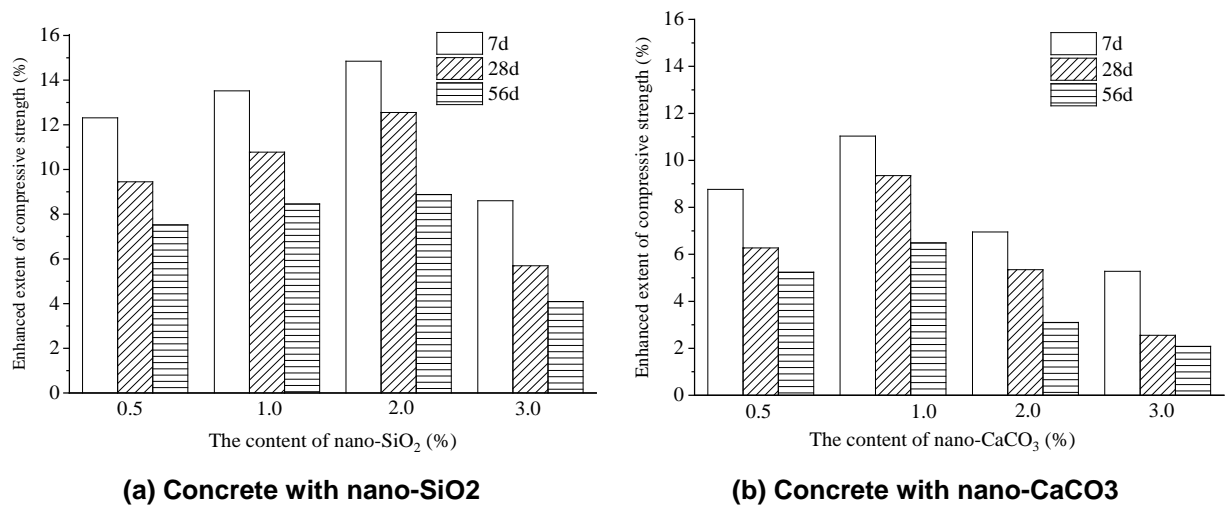


Figure 3. Enhanced extent histogram of compressive strength of concrete with nano-particles.

3.2. Sulfate corrosion resistance of foundation concrete

3.2.1. Using corrosion resistance coefficient of compressive strength as evaluation index

The relationship between corrosion resistance coefficient of compressive strength of concrete with nano-particles and dry-wet cycling number is visually shown in Fig. 4. It can be seen that, with the increase number of dry-wet cycles, the corrosion resistance coefficient of compressive strength of concrete with nano-particles is also increased firstly and then decreased gradually. Furthermore, in the latter stage of sulfate corrosion resistance test, the decreasing rate of corrosion resistance coefficient of compressive strength of concrete with nano-particles is obviously slower than that of plain concrete.

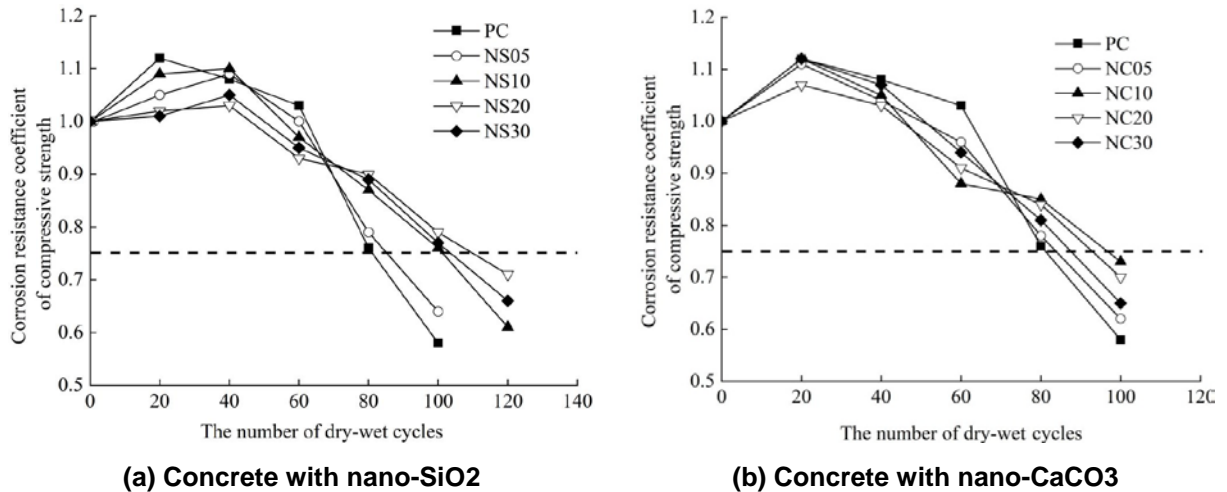


Figure 4. Relationship between corrosion resistance coefficient of compressive strength and dry-wet cycling number.

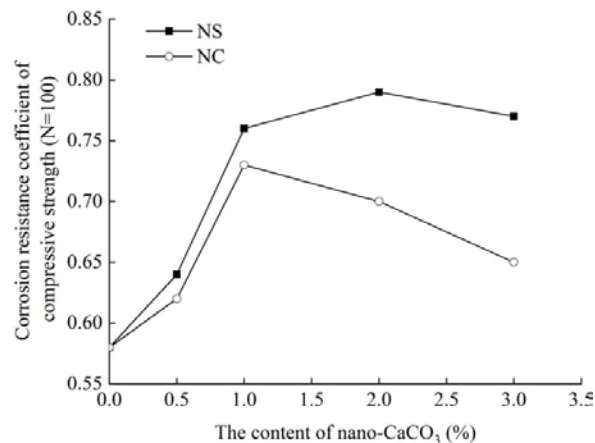


Figure 5. Relationship between corrosion resistance coefficient of compressive strength and the content of nano-particles (N = 100).

For the concrete with nano-SiO₂, when the dry-wet cycling number (N) is smaller than 40, the corrosion resistance coefficient of compressive strength (K_f) is increased little by little; when N is larger than 40, K_f is decreased step by step. When N is larger than 60, K_f of PC and NS05 is decreased sharply. When N is equal to 100, K_f of PC and NS05 is reduced to less than 75 %, but K_f of NS05 is larger than that of PC. When N is equal to 120, K_f of concretes decreases in the order: NS20 > NS30 > NS10.

For the concrete with nano-CaCO₃, when the dry-wet cycling number (N) is equal to 120, the corrosion resistance coefficient of compressive strength (K_f) is reaching the peak. When N is larger than 20, K_f is decreased gradually. When N is equal to 100, K_f of PC and all concretes with nano-CaCO₃ is

decreased to less than 75 %, but K_f of NC is larger than that of PC. K_f of NC decreases in the order: NC10 > NC20 > NC30 > NC05.

Fig. 5 shows the relationship between corrosion resistance coefficient of compressive strength and the content of nano-particles when the dry-wet cycling number N is equal to 100. It can be observed that with the increasing content of nano-particles, the corrosion resistance coefficient of compressive strength increases firstly and then decreases, and this fully demonstrates again that there is an optimal content of nano-particles in concrete. When the content of nano-SiO₂ and nano-CaCO₃ in concrete is about 2 % and 1 %, respectively, the corrosion resistance coefficient of compressive strength is maximal, and the sulfate corrosion resistance of concrete is the best. In addition, the corrosion resistance coefficient of compressive strength of concrete with nano-SiO₂ is larger than that of concrete with the same amount of nano-CaCO₃.

Table 3 shows the dry-wet cycling number of concrete when the corrosion resistance coefficient of compressive strength is reduced to 75 %. Obviously, the sulfate corrosion resistance of various foundation concrete decreases in the order: NS20 > NS30 > NS10 > NC10 > NC20 > NC30 > NS05 > NC05 > PC.

Table 3. Dry-wet cycling number of concrete when corrosion resistance coefficient of compressive strength is reduced to 75 %.

Mixture type	PC	NS05	NS10	NS20	NS30	NC05	NC10	NC20	NC30
Dry-wet cycling number	81	85	101	110	104	84	97	93	87

3.2.2. Using relative dynamic elastic modulus as evaluation index

The attenuation curves of relative dynamic elastic moduli of concretes with nano-particles are given in Fig. 6. It can be seen that, the relative dynamic elastic modulus (E_d) is increased slightly when the dry-wet cycling number (N) is smaller than 20, and E_d is attenuated gradually when N is larger than 20. With the increase number of dry-wet cycles, the attenuation rate of E_d is speeded up in different degrees, and E_d of PC is attenuated most distinctly. When N is equal to 80, E_d of PC is already reduced to less than 60 %.

For the concrete with nano-SiO₂, E_d of NS05 is decreased to less than 60 % when N is equal to 100, and E_d of NS in other amounts will be reduced to less than 60 % when N is equal to 120. when N is equal to 120, E_d of NS decreases in the order: NS20 > NS30 > NS10, so the sulfate corrosion resistance of NS20 is the best.

For the concrete with nano-CaCO₃, E_d of NC05 is already decreased to less than 60 % when N is equal to 80, and E_d of NC in other amounts are all reduced to less than 60 % when N is equal to 100. When N is equal to 100, E_d of NC decreases in the order: NC10 > NC20 > NC30, so the sulfate corrosion resistance of NC10 is the best.

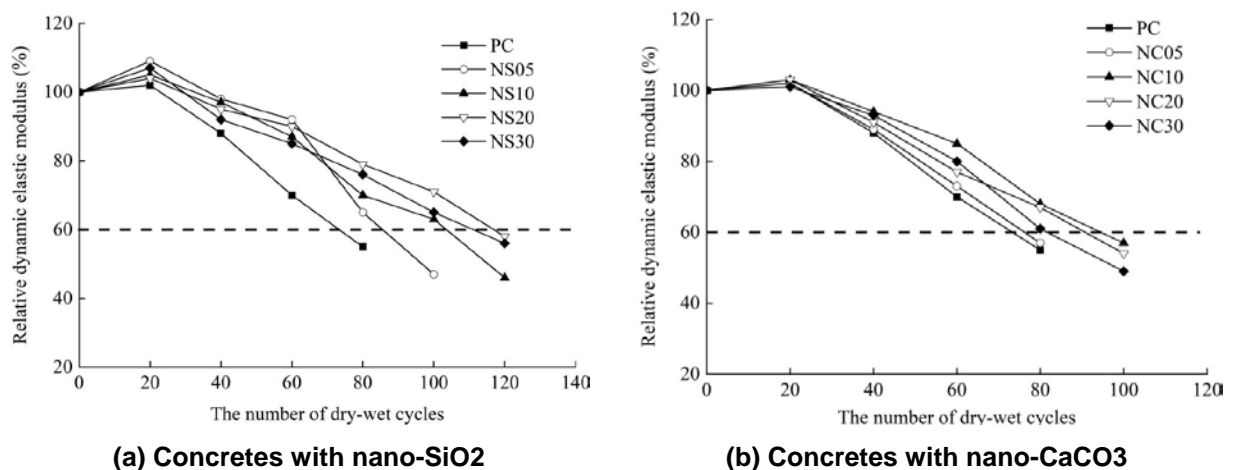


Figure 6. Attenuation curves of relative dynamic elastic moduli of concretes with nano-particles.

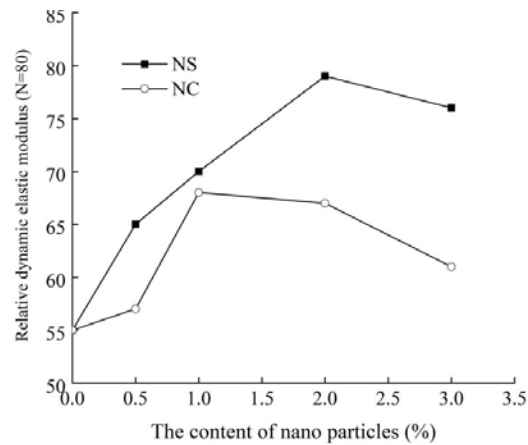


Figure 7. Relationship between relative dynamic elastic modulus and the content of nano-particles (N = 80).

Fig. 7 shows the relationship between relative dynamic elastic modulus of concrete and the content of nano-particles when the dry-wet cycling number N is equal to 80. It can be seen that, with the increase content of nano-particles, relative dynamic elastic modulus of concrete is also increased firstly and then decreased gradually, and there is an optimal amount of nano-particles in concrete. When the content of nano-SiO₂ and nano-CaCO₃ in concrete is about 2 % and 1 %, respectively, the relative dynamic elastic modulus of concrete is the largest, and the sulfate corrosion resistance of concrete is the best. Furthermore, the relative dynamic elastic modulus of concrete with nano-SiO₂ is larger than that of concrete with the same amount of nano-CaCO₃.

When the dry-wet cycling number N is equal to 80, the appearance of plain concrete, the concrete with 1 % nano-CaCO₃ and the concrete with 1 % nano-SiO₂ is presented in Fig. 8. It is obvious that, for the plain concrete, there is apparent spalling and cracks on the surface and at the corner, and part coarse aggregate is exposed. For the concrete with 1% nano-CaCO₃, there is only slight spalling on the surface. For the concrete with 1 % nano-SiO₂, there is not spalling and crack on the surface and at the corner. Consequently, after 80 times drying-wetting cycles, plain concrete is subjected to severer sulfate corrosion compared with the concrete with nano-particles.



Figure 8. The appearance of PC, NC10 and NS20 (N = 80).

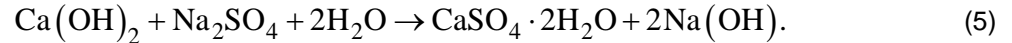
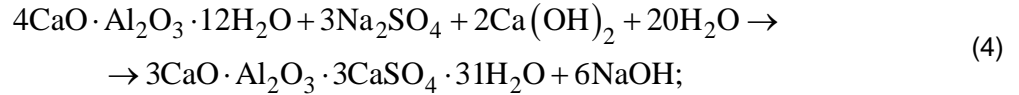
Table 4 shows the dry-wet cycling number of concrete when the relative dynamic elastic modulus is reduced to 60 %. It can be observed that, if the dry-wet cycling number of concrete is as the criterion when the relative dynamic elastic modulus is reduced to 60 %, the sulfate corrosion resistance of various foundation concrete decreases in the order: NS20 > NS30 > NS10 > NC10 > NC20 > NC30 > NS05 > NC05 > PC, and this is in accordance with the conclusion by using corrosion resistance coefficient of compressive strength as evaluation index.

Table 4. Dry-wet cycling number of concrete when the relative dynamic elastic modulus is reduced to 60 %.

Mixture type	PC	NS05	NS10	NS20	NS30	NC05	NC10	NC20	NC30
Dry-wet cycling number	73	86	103	117	111	76	95	91	81

3.3. Discussions

When the foundation concrete is subjected to sulfate corrosion under the action of dry-wet cycles, sodium sulfate (Na_2SO_4) in corrosive solution can react with cement hydration products, and then both ettringite and gypsum are generated. The process of producing ettringite and gypsum is crystallization process accompanied by volume expansion. The reaction equations forming ettringite and gypsum are as follows [14].



In the early stage of erosion, the ettringite and gypsum can fill the pore in concrete, and this makes the cement matrix denser. Consequently, the compressive strength of concrete is enhanced, and then both corrosion resistance coefficient of compressive strength and relative dynamic elastic modulus are increased. In the middle and later stage of erosion, with the increase number of dry-wet cycles, more and more ettringite and gypsum are generated [15]. After the pore in concrete is fully filled, subsequent ettringite and gypsum will produce great swelling stress. When the swelling stress is greater than the ultimate tensile strength of concrete, the cracks will be formed gradually in concrete. With the increase of swelling stress, the cracks will be extended rapidly, and the pore structure will be degraded. Moreover, corrosive solution will permeate more easily in concrete, and then the concrete will be subjected to more serious corrosion.

Furthermore, when foundation concrete is under the drying condition, the water in internal salt solution will be evaporated rapidly, and the quality fraction of Na_2SO_4 in pore solution is increased rapidly. If the quality fraction of Na_2SO_4 is larger than its solubility, the white crystal ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) will be separated out, and the crystallization pressure will be formed in concrete [16]. With the increase number of dry-wet cycles, Na_2SO_4 will be dissolved during the water absorption and be crystallized during the dehydration again and again, which results in the internal damage of concrete accumulated gradually, and then the deterioration of concrete subjected to sulfate corrosion is accelerated.

To sum up, there are both physical and chemical damage during the dry-wet cycles of concrete. With the increase number of dry-wet cycles, foundation concrete is subjected to both the expansion pressure of ettringite and gypsum and the crystallization pressure of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, and the cracks in concrete are increased gradually and the internal damage of concrete is aggravated step by step. So, the surface spalling of concrete is increasingly obvious, and then the corrosion resistance coefficient of compressive strength and the relative dynamic elastic modulus are decreased accordingly.

Both nano- SiO_2 and nano- CaCO_3 can improve the sulfate corrosion resistance of foundation concrete, and there are both common and different reasons.

3.3.1. Common reason of nano-particles improving the sulfate corrosion resistance of concrete

The common reason is that the addition of nano-particles refines the pore structure of concrete [1]. On the one hand, nano-particles can act as a filler to enhance the density of concrete, which causes the porosity of concrete to reduce significantly. On the other hand, nano-particles can not only act as an activator to accelerate cement hydration due to their high activity, but also act as a kernel in cement paste which makes the size of $\text{Ca}(\text{OH})_2$ crystal smaller and the tropism of $\text{Ca}(\text{OH})_2$ crystal more stochastic [3, 6]. Due to the refined pore structure, the permeability of concrete with nano-particles is reduced. So, the sulfate solution is difficult to penetrate in concrete with nano-particles, and then the sulfate corrosion resistance of concrete with nano-particles is enhanced.

3.3.2. Different reasons of nano- SiO_2 and nano- CaCO_3 improving the sulfate corrosion resistance of concrete

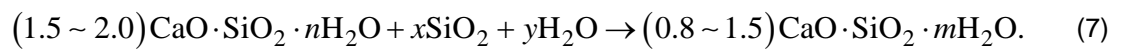
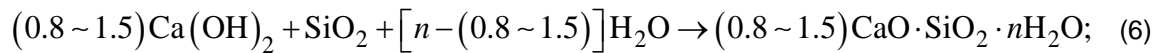
The sulfate corrosion resistance of concrete depends on the mineral composition and relative amount of cement clinker to a large extent, especially the amount of C_3A and C_3S [17]. Because C_3A is the precondition of forming ettringite, the possibility of forming ettringite will be decreased if the amount of C_3A is restricted. Abundant $\text{Ca}(\text{OH})_2$ will be separated out with the hydration C_3S , and $\text{Ca}(\text{OH})_2$ is the necessary part of forming ettringite and gypsum. So, the amount of forming ettringite and gypsum will be decreased if the amount of C_3S is restricted.

After ordinary Portland cement is completely hydrated, the content of calcium-silicate-hydrated (C-S-H) gel accounts for about 70 % of cement hydration products [18, 19]. The molecular number ratio of CaO to SiO_2 (CaO/SiO_2) is a continuously variable dynamic quantity, and its value is larger than 0.5 and smaller than 2.0 [20]. According to the difference of CaO/SiO_2 , C-S-H gel can be divided into high-alkali C-

S-H gel and low-alkali C-S-H gel. CaO/SiO_2 of the former is larger than 1.5, and CaO/SiO_2 of the latter is smaller than 1.5. Compared to high-alkali C-S-H gel, low-alkali C-S-H gel has higher strength and better stability. In the hydration products of ordinary Portland cement, most C-S-H gel is high-alkali C-S-H gel [20]. Because the composition of C-S-H gel is very complicated, in general, the chemical expression of C-S-H gel is uniformly indicated by $3\text{CaO}\cdot 2\text{SiO}_2\cdot 3\text{H}_2\text{O}$ in the chemical equation of cement hydration reaction.

The content of $\text{Ca}(\text{OH})_2$ accounts for about 20 % of cement hydration products, and its strength is very low and its stability is very poor [21, 22]. At the interface between hardened cement paste and aggregate, $\text{Ca}(\text{OH})_2$ crystals are directionally separated out, and the bonding strength between hardened cement paste and aggregate is weakened. So, the existence of $\text{Ca}(\text{OH})_2$ is unbeneficial to the mechanical properties and durability of concrete.

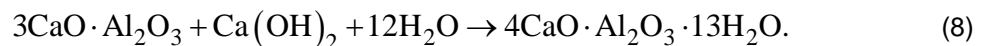
Due to its high pozzolanic activity, nano- SiO_2 can react with $\text{Ca}(\text{OH})_2$, and C-S-H gel will be formed. Meanwhile, nano- SiO_2 can also react with high-alkali C-S-H gel, and low-alkali C-S-H gel will be formed [20, 23]. That is to say, nano- SiO_2 can transform high-alkali C-S-H gel into low-alkali C-S-H gel. The main chemical reaction process is as follows [20].



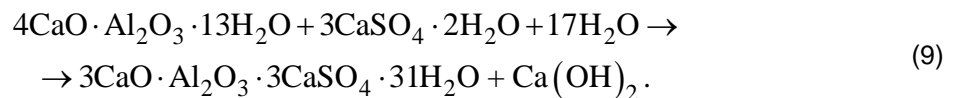
It can be seen from above equation that, C-S-H gel formed by reaction of nano- SiO_2 with $\text{Ca}(\text{OH})_2$ belongs to low-alkali C-S-H gel, and the content of high-alkali C-S-H gel in concrete is reduced effectively. So, the compressive strength and the sulfate corrosion resistance of concrete is enhanced. In addition, because nano- SiO_2 can consume $\text{Ca}(\text{OH})_2$, the amount of $\text{Ca}(\text{OH})_2$ is decreased which results in the production of ettringite and gypsum be reduced. Then, the structure defect in concrete is lessened and the sulfate corrosion resistance of concrete is improved.

Nano- CaCO_3 also can participate in the hydration reaction of cement, although its activity is lower than that of nano- SiO_2 . Nano- CaCO_3 can react with tricalcium aluminate (C_3A) in cement, and the calcium carboaluminate hydrate is formed which is more stable than ettringite [24]. The calcium carboaluminate hydrate can be divided into two kinds, that is low-calcium type ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 12\text{H}_2\text{O}$) and high-calcium type ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaCO}_3\cdot 31\text{H}_2\text{O}$). When nano- CaCO_3 reacts with C_3A in cement, the production of low-calcium calcium carboaluminate hydrate is higher than that of high-calcium calcium carboaluminate hydrate [14], and the specific reaction processes can be described as follows [25–27].

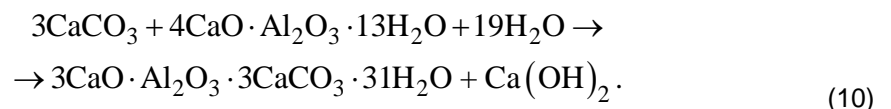
Because nano- CaCO_3 cannot consume $\text{Ca}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$ in the liquid phase is very easy to reach saturation. When the concentration of $\text{Ca}(\text{OH})_2$ in the liquid phase reaches saturation, C_3A reacts with $\text{Ca}(\text{OH})_2$ and the tetracalcium aluminate hydrate is formed.



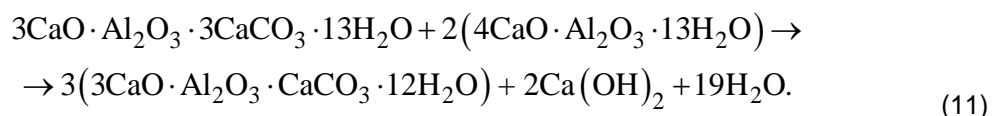
Because there is a small amount of gypsum in Portland cement, the tetracalcium aluminate hydrate can promptly react with gypsum, and the calcium sulfoaluminate hydrates, that is ettringite is produced.



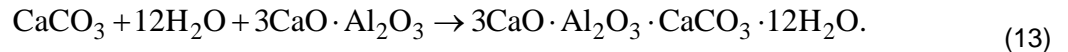
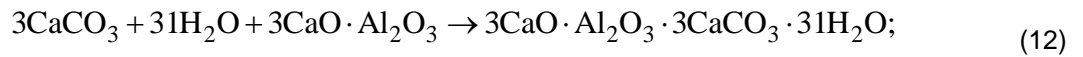
After nano- CaCO_3 is added, nano- CaCO_3 can react with tetracalcium aluminate hydrate, and high-calcium calcium carboaluminate hydrate will be generated.



Then, high-calcium calcium carboaluminate hydrate can further react with tetracalcium aluminate hydrate and low-calcium calcium carboaluminate hydrate is formed.



If equation (8) is synthesized with equation (10) and equation (11), respectively, the following equations can be gotten.



It can be seen from equation (9) and equation (10) that, nano- CaCO_3 can react with C_3A in cement and consume some C_3A , which makes the amount of C_3A reacting with gypsum be decreased. From equation (4), equation (12) and equation (13), we can see that, C_3A can react with both sulfate and nano- CaCO_3 , the addition of nano- CaCO_3 makes the amount of C_3A reacting with sulfate be reduced.

To sum up, by the addition of nano- CaCO_3 , the amount of ettringite is cut down from two aspects. On the one hand, nano- CaCO_3 makes the amount of C_3A reacting with gypsum be decreased, and then the production of ettringite is reduced. On the other hand, nano- CaCO_3 makes the amount of C_3A reacting with sulfate be decreased, and then the production of ettringite is also reduced. Consequently, the swelling stress in concrete is reduced accordingly. In addition, the carbon aluminate formed in the process of hydration can overlap with other hydration products, which makes the internal structure of concrete denser, so the resistance of sulfate solution permeating in concrete is enhanced, and the sulfate corrosion resistance of concrete is improved.

4. Conclusions

The following conclusions can be drawn from this study.

(1) The compressive strengths of foundation concretes with nano-particles at 7d, 28d and 56d are all higher than that of plain concrete, and the addition of nano- SiO_2 and nano- CaCO_3 can remarkably improve the early compressive strength of concrete. With the content increase of nano-particles, the compressive strengths of concretes with nano-particles at various ages is firstly increased and then decreased. As far as the compressive strength is concerned, the optimum content of nano- SiO_2 and nano- CaCO_3 in concrete is about 2 % and 1 %, respectively. The compressive strengths of concretes with nano- SiO_2 at all ages is larger than that of concretes with the same content of nano- CaCO_3 .

(2) The sulfate corrosion resistance of foundation concretes with nano-particles is superior to plain foundation concrete. With the amount increase of nano-particles, the sulfate corrosion resistance of concretes with nano-particles is also firstly enhanced and then reduced. When the content of nano- SiO_2 and nano- CaCO_3 is about 2 % and 1 %, respectively, the sulfate corrosion resistance of concrete is improved significantly. When the content of nano-particles is the same, the sulfate corrosion resistance of concretes with nano- SiO_2 is better than that of concretes with nano- CaCO_3 .

(3) For the concrete with nano-particles, the corrosion resistance coefficient of compressive strength and the relative dynamic elastic modulus are all firstly increased and then decreased with the increase number of dry-wet cycles. In the early stage of erosion, the pore in concrete is filled with ettringite and gypsum, and then the corrosion resistance coefficient of compressive strength and the relative dynamic elastic modulus are increased. In the middle and later stage of erosion, more and more ettringite and gypsum are formed. With the increase of swelling stress, the concrete is gradually cracked and broken, so the corrosion resistance coefficient of compressive strength and the relative dynamic elastic modulus are decreased.

(4) With the addition of nano-particles, the pore structure of foundation concrete is improved, thus the resistance of sulphate solution permeating into concrete is increased. Moreover, nano- SiO_2 can react with $\text{Ca}(\text{OH})_2$, and high-strength low-alkali C-S-H gel is formed; Nano- CaCO_3 can react with C_3A in cement, and the calcium carboaluminate hydrate is formed which is more stable and has high strength. The addition of nano-particles can not only enhance the strength of concrete but also reduce the production of ettringite and gypsum, so the swelling stress in concrete is decreased and the structural defect in concrete is cut down. Consequently, nano-particles can improve the compressive strengths and the sulfate corrosion resistance of foundation concrete.

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