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Experimental Study on Sulfate Erosion Resistance of Nano- CaCO_3 Modified Concrete

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Abstract: In the saline soil environment of western China, the salts can corrode the ordinary cement concrete seriously, and the durability of concrete structure deteriorates gradually until it fails. This impedes the application of ordinary Portland cement concrete in this area. Aiming at the problem of the short service life of concrete in the harsh environment of western China, this study probes the performance of nano- CaCO_3 modified concrete in a sulfate environment. The durability of the concrete was evaluated by the apparent phenomena on the relative quality evaluation parameter, the relative dynamic elastic modulus evaluation parameter, and the comprehensive damage evaluation parameter. The microstructure of corroded products was investigated through scanning electron microscopy (SEM) to reveal the deterioration mechanism. The result shows that the addition of 1% nano- CaCO_3 can enhance the resistance of concrete to sulfate corrosion, and the service life of concrete structures will increase significantly.

Keywords: Cement concrete; Sulfate erosion; Nano-modified concrete; Resistance; Durability

1. Introduction

An important engineering property of concrete is its durability which significantly influences the service life of concrete structures (Qiao et al. 2012; Shah et al. 2015; Zhou et al. 2015; Pack et al. 2018). The durability of concrete has attracted significant attention over the past several decades and is one of the basic theoretical research problems that need to be solved urgently. Concrete has been used as a structural material for a long time and even in the 21st century, and it remains to be the major construction material that is consumed in the largest quantity in many projects. However, chemical corrosion of concrete caused by the corrosion ions in saline soil could destroy the concrete and steel-reinforced concrete structures seriously. Soil salinization is a global problem and potential environmental problem in many countries especially in China where soil salinity levels are widespread and occur in much of the waterfront, arid and semi-arid zones (Wang et al. 2014). Most of the salt lake region distributes in Xinjiang, Tibet, Qinghai, and Inner Mongolia, the amount of soluble salt in Qinghai salt lake bittern is the highest with the maximum of salt content in the saline soil around 43.66% (Qiao et al. 2018; Yu et al. 2013). The common concrete structures are damaged and corroded after 1~3 years due to harmful ions mainly Cl^- , SO_4^{2-} , Mg^{2+} present in saline soil (Qian et al. 2017). Therefore, improve the durability of concrete structures and extend their service life by improving the corrosion resistance of concrete structures and exploring new corrosion-resistant modified concrete materials is of great engineering significance.

In recent years, Nanotechnology has attracted much interest and the use of Nano-particles recently has been introduced to meet the requirements of strength development and durability in many building materials applications. For instance, in the 21st century Nano-materials are hailed as one of the most important building materials, Nano-materials are very small sized materials with particle size in nanometers and are very effective in changing the properties of concrete at the ultrafine level by the virtue

of their very small size. Since the introduction of nanomaterials, extensive research has been conducted to promote their use in cement-based material, and different researches have been done to study the effect of Nano-modified concrete to sulfate corrosion. For the effect of Nano-materials on concrete mortar, a series of tests to examine both single and combine effects of NC (nano-CuO) and RHA (rice husk ash) on mortar properties were carried out. The compressive strength of RHA-containing mortar specimens tended to increase when the CuO nanoparticle content was increased and reached the highest amount when 3% of NC was replaced, and NC as a partial cement replacement of and filler could accelerate C–S–H gel formation associated with the increased crystalline $\text{Ca}(\text{OH})_2$ amount of hydration (Miyandehi et al. 2016). In the experimental study, Atta-ur-Rehman *et al.* studied the effects of titanium dioxide (TiO_2) Nano-particles on the sulfate attack resistance of ordinary Portland cement (OPC) and slag-blended concrete, the results show that nano- TiO_2 containing slag-blended concrete were more resistant to sulfate attack than nano- TiO_2 containing OPC concrete (Atta-ur-Rehman et al. 2018).

In response to the deterioration of concrete, a comparable study on the deterioration of limestone powder blended cement under sodium sulfate and magnesium sulfate attack at a low temperature have been studied. The PLC (Portland-limestone cement) immersed in Na_2SO_4 and MgSO_4 solution at low temperature were seriously damaged after 360 days due to the expansion of volume and the loss of strength, at the same exposure age, the damage degree of PLC exposed to MgSO_4 solution was larger than that of PLC exposed to Na_2SO_4 solution (Wu et al. 2020). A recent study of Nehvi et al. (2019) studied on Carbonation Induced Corrosion in Reinforced Concrete Structures showed that high dosages of Nano-silicate (NS) addition in lime mortars reduced vulnerability to freeze-thaw cycles and magnesium sulfate attack (Nehvi 2019). Besides, Aggarwal et al. in their study observed that only 2% NS improved the resistance of mortars to external sulfate attack and limited the length expansion below 0.03%, Other authors found that 4-6% NS in mortars were enough to resist the internal sulfate attack after 12 months of

exposure (Aggarwal et al. 2015). Siang et al. have studied the influence of SiO_2 , TiO_2 and Fe_2O_3 nanoparticles on the properties of fly ash blended cement mortars with different dosages (1–6%), the result shows that the addition of nanoparticles (depending on the dosage) can improve the compressive, flexural strengths of the mortar (Siang Ng et al. 2020). Moreover, Li studied the effect of nano-materials on concrete durability and found that the resistance to corrosion coefficients of sulfate corrosion resistance of concrete in a month's corrosion experiments with the nano-silica content of 1.0%, 2.0% were 0.87, 0.92 and the corrosion resistance of concrete benchmark's coefficient was 0.84 (Yang et al. 2019). In the present work, based on the existing durability test method, the testing program for sulfate corrosion resistance of full immersed nano- CaCO_3 modified concrete in the sulfite saline soil area was designed to provide reliable information on the deterioration process and ensure the service life of engineering structures. Aiming at the problem of the short service life of concrete in the harsh environment of western China, the nano- CaCO_3 concrete specimens with different contents was taken as the research object. Based on the relative dynamic elastic modulus evaluation index and relative quality evaluation index, combined with SEM images to observe the micro-morphology of the specimen after corrosion, the corrosion resistance performance of nano-modified concrete was studied, aiming to provide a high-corrosion-resistant concrete for the construction of western China.

2. Raw materials and test methods

2.1 Raw materials

In this experiment, the test specimens were fabricated using the ordinary Portland cement (PO.42.5 complying to the Chinese standard GB175-2007(GB 175-2007, 2007)) produced by a Sinoma Gansu Cement Co., Ltd, with a compressive strength of 45.7 MPa at an age of 28 days, its Chemical Composition and performance index are shown in table 1 and table 2. Coarse aggregate was made of crushed pebbles from Lintao, Gansu with a mud content of 0.60% (by mass) and an apparent density of 2650 kg/m³. Fine aggregate came from river sand in a local area with a fineness modulus of 2.9, mud content of 2.1% (by

mass) and an apparent density of 2600 kg/m^3 . Other experimental materials used include Class II fly ash produced by Lanzhou No.2 thermal power plant; it was used as a partial replacement of cement complying the Chinese Standard GB T50082-2009 with performance indexes showed in table 4. The water used was general tap water from the central laboratory of the Lanzhou University of Technology, and the water quality meets the requirements of "Water Standard for Concrete Mixing" (JGJ63-2006, 2018). The water-reducing agent used in the test is a polycarboxylic acid high-performance produced by Gansu Jifa Chemical Co., Ltd., with a mixing amount of 2.2% and a water-reducing rate of 25%. The nano- CaCO_3 used in the experiment was produced by Anhui Xuancheng Jingrui New Materials Co., Ltd and the technical performance indicators are shown in Table 3.

2.2 Test methods

In this experiment, the test immersion solution was selected as a 10% Na_2SO_4 solution, samples are numbered in sequence A0, A1, A2, A3, A4 to A5 with nano-dosages of 0%, 1%, 2%, 3%, 4% and 5% respectively. The size of the test specimens was $100\text{mm} \times 100\text{mm} \times 400\text{mm}$, the test specimens after 28 days of curing were immersed in the solution, and the test duration was 360 days. To ensure the accuracy of the test results and the freshness of the solution, the test solution was replaced every 30 days. Before collecting data, wipe the surface of the test piece clean to prevent the surface solution from affecting the test results, and collect data every 60 days. Use an electronic balance with an accuracy of 0.1g to collect the mass of the test piece, and use the HC-U83 multifunctional mixed soil ultrasonic detector to collect the ultrasonic speed of the A end (ranging 100mm) and B end (ranging 400mm) of the test piece. The concrete mix proportions used in this test are shown in Table 5. To further study the corrosion mechanism of nano- CaCO_3 modified concrete, scanning electron microscopy (SEM) was used to observe the most relevant micro-structural aspects (compositional and morphological details) of nano- CaCO_3 modified concrete.

2.3 Analysis basis

In this test, the relative dynamic elastic modulus was reduced to 60% as the dynamic elasticity modulus failure criterion, and the relative mass was reduced to 95% as the mass failure criterion. The relative dynamic elastic modulus changes in the range of 0-40%, while the relative mass changes in the range of 0-5%, and no obvious change can be seen in the same coordinate. The evaluation parameters are designed below.

(1) Calculation of the relative dynamic elastic modulus evaluation parameter ω_a

According to the calculation method of the relative dynamic elastic modulus E_r in "Test method for long-term performance and durability of ordinary concrete(GB/T50082-2009, 2009):

$$E_r = \frac{E_t}{E_0} = \frac{V_t^2}{V_0^2} \quad (1)$$

In the formula: E_r is the relative dynamic elastic modulus; E_t and E_0 refer to the dynamic elastic modulus of concrete at a certain corrosion age and the initial moment; V_t and V_0 refer to the ultrasonic sound velocity of the concrete after a certain corrosion age and the initial moment, respectively. The relative dynamic elastic modulus evaluation parameter ω_a is calculated according to formula (2) (Qiao,2007):

$$\omega_a = \frac{E_r - 0.6}{0.4} \quad (2)$$

When $\omega_a > 1$, the relative dynamic elastic modulus increases than the reference value;

When $0 < \omega_a < 1$, the relative dynamic elastic modulus is lower than the reference value, but the damage is not reached; When $\omega_a < 0$, the relative dynamic elastic modulus is less than 60% and the failure is reached.

(2) Calculation of the relative quality evaluation parameter ω_b

The relative mass W_r calculation formula is calculated according to formula (3):

$$W_r = \frac{W_t}{W_0} \times 100 \quad (3)$$

In the formula: W_r is the relative mass of concrete specimens at different erosion ages; W_t is the mass of specimens at different erosion ages; W_0 is the mass of specimens at the initial moment.

The relative quality evaluation parameter ω_b is calculated according to formula (4) (Qiao,2007):

$$\omega_b = \frac{W_r - 0.95}{0.05} \quad (4)$$

When $\omega_b > 1$, the relative mass is increased from the reference value;

When $0 < \omega_b < 1$, the relative mass is lower than the reference value, but it is not damaged;

When $\omega_b < 0$, the relative mass is less than 95% and the damage is reached.

(3) Calculation of comprehensive damage evaluation parameter

In this paper, the comprehensive damage evaluation parameter ω , which considers both the relative mass and the relative dynamic elastic modulus was adopted in reference (Qiao,2007; He, 2013)

The comprehensive damage evaluation parameter ω is selected as one of the indicators for evaluating the durability of concrete. The calculation method ω is as follows:

$$\omega = \begin{cases} -(A\omega_a^2 \times B\omega_b^2) & \omega_a, \omega_b \text{ less than } 0 \\ A\omega_a^2 \times B\omega_b^2 & \omega_a, \omega_b \text{ greater than } 0 \end{cases} \quad (5)$$

Where: A is the effective damage coefficient for the evaluation of the relative dynamic elastic modulus ω_a ; B is the effective damage coefficient for the evaluation of the relative quality evaluation parameter ω_b ; among them, when $\omega_a > 1$, $A = 1 / \omega_a^2$, when $\omega_a \leq 1$, $A = 1$; when $\omega_b > 1$, $B = 1 / \omega_b^2$, when $\omega_b \leq 1$, $B=1$.

3. Experiment results and analysis

3.1 Analysis of Relative Mass Evaluation Parameters

After full immersion of Concrete specimens within 10% Na_2SO_4 solution with different percentages of Nano-dosages, the specimens were tested after 28 days of curing and the immersed time interval in the solution was 0d to 360d. The rate change curves of the evaluation parameter for different specimens are graphically presented in fig.1. The relative quality evaluation parameter ω_b as one of the non-destructive methods mainly measure the damage process of the specimen after a certain immersion age was used to evaluate the anti-corrosion performance of concrete, and the anti-corrosion performance of concrete which can be measured from the external macro quality of concrete. As illustrated in fig.1, it is seen that the curves for all specimens follow an identical pattern, with 180d as the critical age; there is an increasing (upward) trend in the early stages between an interval of 0d to 180d and a decreasing pattern in the later stages between 180d to 360d. In the early ages, an upward trend is mainly due to the action of SO_4^{2-} inside the concrete that generates corrosion products such as ettringite, gypsum, etc. As the mass of concrete increases, the value of concrete ω_b increases. For instance, the mass of A1 and A2 specimens increase at the highest point at the critical age of 180d and the increase of A1 is the largest compared to other specimens with an increase of 10.8%, and the increase of A5 is the smallest, only 6.7%. For long immersion ages between 180d to 360d, the relative quality evaluation parameter ω_b of the specimen decreases, mainly because as the soaking age increased. The cementitious substances inside the concrete were gradually taken out by dissolution, and the concrete ω_b value decreased accordingly. Besides, due to sulfate erosion effects, the destruction of spalling is more serious, the mass quality correlates well with the extent of the damage induced by sulfate erosion. At 360d, the ω_b value of the test piece is: $\text{A1} > \text{A0} > \text{A2} > \text{A3} > \text{A4} > \text{A5}$. Briefly, the mass loss rate of 1% nano- CaCO_3 is the least. Hence, the incorporation of nano-

CaCO_3 can improve the sulfate corrosion resistance of concrete, the improvement effect was the most obvious when the content of nano- CaCO_3 was 1%.

3.2 Analysis of relative dynamic elastic modulus by using an ultrasonic detector with A-end (ranging 100mm)

The relative dynamic elastic modulus is the non-destructive method used to evaluate the performance of concrete under sulfate corrosion. As shown in fig.2, the dynamic elastic modulus of concrete was analyzed in the period between 0d to 360d to evaluate the sulfate corrosion resistance using an ultrasonic detector with A end (ranging 100mm), and the effect of nano-dosages added for all samples is graphically shown. In the early ages, an upward trend is mainly due to the action of SO_4^{2-} inside the concrete. As the curing time increased, they were a moderate increase of concrete elasticity in the early ages, and it is noteworthy that the addition of nano- CaCO_3 also improves the elastic modulus of concrete. At critical value, 180d specimens the dynamic moduli of A5 and A4 are higher than others but have lower values at 360d. From immersion ages between 180d-360d, the decreasing rate of relative dynamic modulus due to the corrosion of concrete specimens shows the influence of nano- CaCO_3 on each specimen. As we can see, ω_a for the A1 specimen is the highest. At 360d, the ω_a value of the test pieces is in this order: A1> A0> A2> A3> A4> A5. The overall trend illustrated that the alteration of the dynamic elastic modulus of concrete was directly affected by different dosages of nano- CaCO_3 that was added in the mixture proportions. Normally, the addition of nano- CaCO_3 improves the structure of the internal concrete and the strength of concrete specimens increase which greatly improves the impermeability of concrete and prevents the intrusion of external harmful ions, amongst modified mixtures, the concrete that contains 1% of nano- CaCO_3 showed the best resistance to sulfate corrosion.

3.3 Analysis of Relative dynamic elastic modulus by using an ultrasonic detector with B-end (ranging 400mm)

Fig.3 indicates the variation of relative dynamic elastic modulus occurred on the specimens with different percentages of nano-dosages when the ultrasonic detector changes to 400mm. It is seen that the curves for all specimens also follow an identical pattern, with 180d as the critical age, an increasing(upward) trend in the early stages between an interval of 0d to 180d and a decreasing pattern in the later stages between 180d to 360d using an ultrasonic detector with B end (ranging 400). Nevertheless, the growth rate differs depending on the amount nano-dosages incorporated in the mixture. For instance: at the critical age of 180d, the dynamic moduli of A1 and A2 are higher than other samples, means that the addition of 1% to 2% of nano-dosages improve the relative dynamic elastic modulus at the highest points which is greater than one within an interval of 0d to 180d. In the process of overall durability degradation, the initial stage has been improved to a certain extent, which could be effectively proven by the variation of the relative dynamic modulus. At the later stage, the A1 sample has the highest value of ω_a which prove its resistance to the sulfate erosion compared to other samples and identify the effectiveness of 1% nano-CaCO₃ dosage to the improvement of sulfate corrosion resistance of concrete. The ω_a value of the test pieces is in this order: A1> A2> A0> A3> A4> A5. By comparing the rate change for these two dynamic modulus plots, it is clearly shown that the relative dynamic modulus ω_a detected by using an ultrasonic detector with B end (400mm range) is low.

3.4 Comprehensive damage

Fig.4 illustrates the graph of comprehensive damage evaluation parameter ω that reflects the deterioration process of concrete performance; it timely and effectively forecasts the failure behavior of concrete during sulfate corrosion. From 0d to 180d, the change of the comprehensive damage evaluation parameter ω of concrete is constant with a constant value of 1 and after a critical age of 180d, there is a

downward trend. Declining trend assessing that the concrete has been in a state of performance degradation during the cycle, the damage degree of the concrete is increasing with the immersion time, and the macro damage features are clearer. As a result, the concrete has obvious deterioration due to the severe environmental conditions, this means that the concrete performance to sulfate corrosion is enhanced, the deterioration rate of concrete is gentle and there is no concrete failure. At critical ages (180d), ω values decrease which shows the failure behavior of the concrete during the sulfate attack stage, after longer-term exposure in sulfate solution, the concrete is subject to accelerated performance damage with all ω values less than 1. At 360d, the performance of the concrete deteriorates is in order $A1 > A0 > A2 > A3 > A4 > A5$. The concrete contains 1% of nano- CaCO_3 showed the highest that performance to concrete deteriorates; hence, it has the best resistance to sulfate corrosion than other specimens.

3.5 Microanalysis

Sample with 1% nano- CaCO_3 was scanned by an electron microscope at the Lanzhou Institute of Chemistry and Physics, Chinese Academy of Sciences. SEM investigation was conducted on the deteriorated specimen A1 to investigate the internal microstructure deterioration. Fig.5 displays the concrete specimen microstructure that was subjected to varying immersion times in sulfate solution with a concentration of 10%. With the increasing of immersing time, a little number of ettringite crystals were produced. With the number of ettringite crystals continuously increasing with immersion time, the sulfate solution has a little destroying effect on the concrete and is accompanied by small fracture and convex protrusion. As the sulfate attack occurs continuously in the concrete, the damage caused by chemical corrosion, especially the ettringite crystals, results in more porous structure in concrete. Cracks around aggregates in the outer zone are more prominent than cracks around aggregates in the inner zone. These micro-cracks permitted the penetration of more sulfate ions into the microstructure, but due to the effect of nano- CaCO_3 to resist sulfate corrosion, the concrete deterioration is low.

3.6 The mechanism of nano- CaCO_3 to enhance the durability of concrete

It is well recognized that nanomaterials, given their physical effect (filling and nucleation effects) as well as chemical reactivity, may provide substantial enhancement in the performance of cement-based material. The use of nanoparticles in concrete increases concrete's mechanical properties and also demonstrates improvement in its microstructure and pore structure (Kumari et al. 2016). They act as nuclei for the cement to accelerate cement hydration and densify the microstructure and the interfacial transition zone (ITZ), thereby reduce permeability due to its ultrafine size (Shaikh and Supit 2014). Nano-particles are highly interactive because their high surface area, these interactions offer the possibility of modifying cement reactions, producing new surface chemistries, developing new products for the concrete industry and enabling a more regulated and environmentally sustainable production route to cement and concrete (Al Ghabban et al. 2018). The use of a supplementary cementitious system (SCMs) can improve the resistance of concrete to chemical sulfate attack by changing the pore size distribution of the hardened matrix and decreasing cement content, thus diluting calcium aluminum phase concentration in the binder as well as reducing the calcium hydroxide content (Zhutovsky and Douglas Hooton 2017). The potential benefit of nano- CaCO_3 on the development of a supplementary cementitious system is an attractive alternative.

The advantage of nano- CaCO_3 compared to other nano-materials is that it has a relatively reasonable cost, environmental benefits and nano- CaCO_3 is relatively cheap due to its abundant supplying of CaCO_3 in limestone, chalk, and marble, and it can present superior performance given its high specific area and pozzolanic activity (Gu et al. 2013). It is understood that this compound reacts chemically, speeds up the hydration process, and in turn improves the early-age strength of conventional cementitious materials. Chemically, the presence of CaCO_3 nanoparticles increases the rate of reaction of tricalcium aluminate (C_3A) to form carboaluminate complex thereby increase the total hydration products and consequently

strength(Shaikh and Supit 2015). It also reacts with tricalcium silicate (C_3S) and accelerates setting and early strength development. The studies have suggested a potential benefit of the physical properties of $CaCO_3$ on the development of the cementitious system. It was found that the replacement of cement with $CaCO_3$ nanoparticle accelerated the early hydration of cement and enhanced the early development of modulus of elasticity as the amount of $CaCO_3$ nanoparticles was increased(Camiletti et al. 2013). Concretes containing 1% $CaCO_3$ nanoparticles have reasonably higher compressive strength, lower volume of permeable voids, porosity, higher resistance to water absorption, chloride permeability, and chloride ion diffusivity than the counterpart concretes. Moreover, it is found that 1% of $CaCO_3$ nanoparticles improve the microstructure by forming additional calcium silicate hydrate gels and decreases the calcium hydroxide. Hence, nano-additives can reduce reinforcement corrosion in concrete due to sulfate attack. Enhanced corrosion resistance, durability and antibacterial activity observed in nanophase modified concrete especially using 1% nano- $CaCO_3$ can provide a new type of concrete material for engineering construction in western China with extended service life.

4. Conclusion

Sulfate corrosion resistance for different specimens of nano- $CaCO_3$ modified concrete after fully immersed in 10% Na_2SO_4 was analyzed based on various durability evaluation indicators include relative dynamic elastic modulus, relative quality index, comprehensive damage assessment indicators and the morphology of the corrosion products observed after scanning the samples by an electron microscope(SEM). The test results and the durability degradation process were analyzed. Based on the results of the investigation, the following conclusions can be drawn:

- (1) The addition of nano- $CaCO_3$ enhances the internal concrete structure and increases the strength of concrete specimens, which greatly improves the impermeability of concrete and prevents the intrusion of external harmful ions, the sufficient addition of nano- $CaCO_3$ will increase the

resistance of concrete to sulfate corrosion, and the best effect is when the nano- CaCO_3 content is 1%.

- (2) Microscopic tests show that with the increasing of immersing time, a little number of ettringite crystals were produced. These corrosion products were like long rod-shaped, short columnar ettringite, and slab-shaped gypsum inside the specimen after corrosion. They fill the concrete defects at the beginning of the test, but the corrosion inside the concrete will be exacerbated over time. Due to the effect of 1% nano- CaCO_3 to resist sulfate corrosion, the concrete deterioration is low.

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Fig.1 The relative quality evaluation Parameters of different specimens

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Table 1 Chemical Composition of PO.42.5 Ordinary Portland Cement

Ingredients	Ignition loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Alkali content
Specification value (%)	≤ 3.0	—	—	—	—	≤ 5.0	≤ 5.0	≤ 0.6
Measured value (%)	1.92	24.08	8.54	4.01	58.29	1.73	2.85	0.5

Table 2 performance index of P·O 42.5 Ordinary Portland Cement

Stability	Specific surfaces area(m ² /kg)	Condensation time(min)		Flexural strength(MPa)		Compressive strength(MPa)	
		Initial setting	Final setting	3d	28d	3d	28d
Qualified	338	176	280	5.3	7.3	18.3	45.7

Table 3 Performance indicators of nano-CaCO₃

Appearance	Average particle size (nm)	Quality score /%	Specific surface area (m ² /g)
White powder	≤60	≥99.0	30

Table 4 performance indexes of fly ash

Moisture content/%	Water demand /ml	Fineness /%	Activity index /%
3.6	2.63	2.9	2600

Table 5 Concrete mix proportions

sample	Cement (kg/m ³)	Fly ash (kg/m ³)	Nano-CaCO ₃ (kg/m ³)	Coarse aggregate(kg/m ³)	Fine aggregate(kg/m ³)	Water (kg/m ³)	Water reducing agent(kg/m ³)
A0	375	45	0	1177	662	151	3.34
A1	370.8	45	4.2	1177	662	151	3.34
A2	366.6	45	8.4	1177	662	151	3.34
A3	362.4	45	12.6	1177	662	151	3.34
A4	358.2	45	16.8	1177	662	151	3.34
A5	354	45	21	1177	662	151	3.34

Table 6 Values of Parameters A and B for different samples

Time	parameters of samples	A0	A1	A2	A3	A4	A5
0d	A	1	1	1	1	1	1
	B	1	1	1	1	1	1
60d	A	0.880059	0.664192	0.924356	0.868802	0.871328	0.886817
	B	0.962268	0.908517	0.923947	0.961505	0.961338	0.961781
120d	A	0.712852	0.621066	0.664192	0.70888	0.554084	0.633967
	B	0.909551	0.859528	0.889133	0.9078	0.924875	0.925712
180d	A	0.587864	0.546761	0.51092	0.542863	0.458547	0.441033
	B	0.845743	0.814396	0.84049	0.842921	0.842403	0.875297
240d	A	1	1	1	1	1	1
	B	0.909551	0.859528	0.906289	0.925191	0.942842	1
300d	A	1	1	1	1	1	1
	B	1	0.943541	1	1	1	1
360d	A	1	1	1	1	1	1
	B	1	1	1	1	1	1