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Study on mechanical properties of modified concrete based on nano state silica

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As a new type of material, nanomaterials are used to study the internal structure and mechanical properties of concrete doped with nanomaterials. In this paper, three factors including a water-binder ratio, silica fume content and slag content are taken into consideration. L9 (34) orthogonal design is adopted to determine the benchmark mix ratio of Reactive Powder Concrete (RPC). By studying the strength values after 7 and 28 days, it was found that when the nano-SiO_2 content was from 0.5 % to ~ 1 %, the flexural strength, compressive strength and splitting tensile strength of the RPC could be significantly improved. At the same time, using the scanning electron microscope, it was found that nano-SiO_2 made the hydration reaction of the cement matrix more complete, improved the interface structure, and reduced the structural defects of the slurry.
Keywords: nano-silica, modified concrete, mechanical properties.

Приведены результаты исследования структуры и механических свойств бетона, легированного наноматериалами. Принимаются во внимание три фактора — соотношение воды и связующего, содержание дыма кремнезема и содержание шлака. Ортогональная конструкция L9 (34) принята для определения эталонного соотношения для смешивания RPC. Обнаружено, что при содержании nano-SiO_2 от 0,5 % до ~ 1 % характеристики прочности на изгиб, прочности на сжатие и прочности на разрыв реактивного порошкового бетона (RPC) могут быть значительно улучшены. Методом сканирующей электронной микроскопии обнаружено, что nano-SiO_2 делает реакцию гидратации цементного матрикса более полной, улучшает структуру межфазной границы и уменьшает структурные дефекты суспензии.

Дослідження механічних властивостей модифікованого бетону на основі нанорозмірного кремнезему. *A.Yang, H.Wu.*

Наведено результати дослідження структури і механічних властивостей бетону, легованого наноматеріалами. У статті беруться до уваги три фактори — співвідношення води й сполучного, вміст диму кремнезему і вміст шлаку. Ортогональна конструкція L9 (34) прийнята для визначення еталонного співвідношення змішування RPC. Виявлено, що при вмісті nano-SiO_2 від 0,5 % до ~ 1 % міцність на вигин, міцність на стиск і міцність на розрив реактивного порошкового бетону (RPC) можуть бути значно покращені. Методом скануючої електронної мікроскопії виявлено, що nano-SiO_2 робить реакцію гідратації цементної матриці більш повною, покращує структуру міжфазної межі і зменшує структурні дефекти суспензії.

1. Introduction

The compressive strength of ordinary concrete is high, but the tensile, fatigue and impact toughness are poor. With the increase of compressive strength, the brittleness of concrete is increased, while the ductility, crack resistance, structural ductility and aseismic properties declined. In view of the defects of ordinary concrete, fiber reinforced concrete has emerged as the times requires. At present, there are two main ways to reinforce concrete. One is using high elastic modulus short fiber to reinforce concrete, and the representative fiber is steel fiber. The other is using low elastic modulus short fiber to reinforce concrete, and the representative fiber is polypropylene fiber. When the concrete is reinforced only by high elastic steel fiber, toughening effect is good, but the price is high. The reinforcement effect of low elastic polypropylene fiber is poor, but the crack resistance and toughening effect are good and the price is low. In recent years, through reasonable material design, the mixing of high elastic fiber and low elastic fiber and exerting "positive mixing effect" to enhance the mechanical properties of concrete has become a hot spot of domestic and foreign scholars.

Scholars have carried out research on the internal structure and mechanical properties of concrete doped with nanomaterials one after another. B.S.Mohammed et al. have studied the effects of nano-SiO_2 and nano-TiO_2 on the viscosity and yield stress of the cement mortar. The results showed that the fluidity of the mixture could be significantly reduced by nano-particles. Nano-scale SiO_2 with cement content of 7 % can promote the formation of a gel system structure. And then the yield stress of the mixture is greatly changed [1]. The results of Y.Chen et al. show that adding nano-SiO_2 to concrete can improve the microstructure, exert the pozzolanic activity and increase the strength of the mortar. When the ratio of water to cement is 3, the 28 day strength of the mortar is 2.12 times that of the reference mortar with the water-cement ratio of 0.5, which is helpful to improve the strength of concrete [2]. D.S.Hazimmah studied the effect of nanometer SiO_2 on the properties of self-compacting concrete. The results show that nano-SiO_2, which accounts for 4 % of the cement mass, can improve the strength of concrete [3]. D.Adak and other studies show that the strength of concrete can be increased even by adding 0.25 % of nano-SiO_2. At this, the compressive strength after 28 days increased by 10 percent, and the flexural strength increased by 25 percent [4]. The methods of concrete modification are described in the article [5]. The effects of TiO_2 nanoparticles on the hydration, mechanical properties and durability of the cement matrix were studied. The anti-salt performance of nano-SiO_2 bridge concrete was tested. The results show that after a certain number of salt freeze tests, the anti-salt and denudation performance of a certain amount of nano-SiO_2 concrete is better than that of blank concrete [6].

A.Saponin et al. studied the compressive strength of concrete with nano-SiO_2, Al_2O_3, and nano-Fe_2O_3. The results show that the compressive strength of concrete with their 1.25 % addition is much higher than that of other materials when one kind of the nano-materials is added alone. And the strength of the concrete with the mixture of nano-SiO_2 and nano-Al_2O_3 is maximum [7]. The studies of B.Zhang et al. show that the mechanical properties of the cement hardened paste can be improved obviously by adding 1 %–3 % of nano-SiO_2. At the time of 7 and 28 days, the strength of the cement hardened paste can be both increased by about 50 % when the content of nano-SiO_2 is 2. It was also found that the reaction rate of nano-SiO_2 with $Ca(OH)_2$ to form hydrated calcium silicate gel was much faster than that of silica fume, indicating that the pozzolanic activity of nano-SiO_2 was much higher than that of silica fume [8]. T.Yang et al. found that the 28 day compressive strength of the cement mortar increased to 13.8 %–17.5 % with the addition of 3 %–5 % of nano-SiO_2 [9]. J.Y.Choi et al. prepared the super high strength and high-performance concrete with the 28 day compressive strength up to 138.8 MPa, 90 day compressive strength up to 165.5 MPa by using nano-SiO_2 [10]. F.T.Isfahani et al. compared the physical and mechanical properties of fly ash concrete with 0.5 % of nano-SiO_2. The results show that by adding 0.5 % nano-SiO_2, the 7d and 28d compressive strength and flexural strength (especially early strength) and the durability of fly ash concrete can be improved [11].

The mechanism of nano-SiO_2 improving the compactness and strength of fly ash concrete was analyzed by SEM. G.Qiao et al. used nano-scale SiO_2 and silica fume as highly active admixtures to explore the composite modification effect on cement-based materials. The results showed that with the added mixtures, the mechanical properties of the mortar were improved more obviously than of the cement paste. The better combination of silica fume and nano-SiO_2 is 1 % nano-SiO_2 and 9 % silica fume. Nano-SiO_2 and silica fume have high activity and a surface effect. $Ca(OH)_2$ significantly decreased, C–S–H gel phase increased significantly, the microstructure of cement stone matrix phase was compact, and C–S–H gel interwoven into dense network structure, with its structural defects significantly reduced [12].

In recent years, most of the researchers in various countries have studied the mechanical properties and durability of RPC from the aspects of material type, content and maintenance system. However, there is little research on the addition of nanomaterials in RPC. The size effect, quantum effect, surface effect and interfacial effect of nanomaterials make them have special properties that traditional materials do not have. Therefore, it is of great scientific value to improve the microstructure of RPC by adding nano-SiO_2 and to improve the mechanical properties of RPC.

2. Experimental

Ningxia Horse Race P.O42.5 cement was used as a standard. The measured compressive strength values of 3d and 28d were 25.1 MPa and 45.5 MPa, respectively, and the flexural strength values were 5.9 MPa and 9.1 MPa. The slag was of the high quality with the fineness of 4230 cm2/g. The average particle size of the silica fume was 0.2 μm and the SiO_2 content was 92 %. The quartz sand used in the experiment was screened manually, and its size was between 0.16 to ~ 2 mm, the fineness modulus was 1.69, indicating the good gradation. The steel fiber doped with a rigid fiber was the smooth and straight steel fiber plated by copper on the surface. The diameter of the fiber was 0.2 mm and the length was 13 mm. The water reducing agent was used, and the water reducing rate was 28 %. The average diameter of nano-SiO_2 was 12 nm and its surface area was 440 m^2/g.

First, quartz sand and the steel fiber were poured into the mixing pot and were dry stirred for 1 min. Then, the remaining materials were added according to the mix ratio and dry stirred for 3 min to make the cementing material, sand and the steel fiber in full contact. The water reducer was mixed

Table 1. Orthogonal design table

Number	Water-binder ratio (A), %	Silica fume content (B), %
1	0.22	0.2
2	0.24	0.25
3	0.26	0.3

with 80 % water, added to the mixer and stirred for 3 min. Then the remaining water was added and rapidly stirred for 1 min to form the mold. The bending resistance and compression tests were carried out by a triple-test model specimen with 40 mm×40 mm×160 mm in size, and the splitting test was carried out by the triple-test model specimen with 70.7 mm×70.7 mm×70.7 mm in size. The mixture was added in two layers and vibrated for 60 s respectively on the shaking table. And then the mold was flattened. The formed specimen was put in the standard maintenance room for maintenance. The specimen was demoulded after 1 day, and then remained in hot water (90±1 °C) for 3 days. Finally, the specimen was placed in the standard maintenance room for 3 days. The values of flexural strength, compressive strength and splitting tensile strength after 7 and 28 days were tested respectively [13].

For RPC materials, there is no special mechanical property test specification at present, so the test is carried out in accordance with the Hydraulic Concrete Test Code SL352-2006. The compressive test and split tensile test were carried out according to the test method for cement sand, and the flexural test was performed according to the test method for concrete. The fluidity of the mixture was determined by the Method of Measuring the Fluidity of Cement Sand GB2419-81 using the table hopping method. The orthogonal test was designed by using the L9 (34) orthogonal table (see Table 1); and the optimum mix ratio was determined by means of range analysis and variance analysis. Finally, the corresponding strength values after 7 days and 28 days were tested by adding different amounts of nano-SiO_2 to the standard mix ratio.

3. Results and discussion

3.1 Results and data analysis of orthogonal experiments

Through the range analysis of 7day data, it is found that the order of the influence of various factors on the flexural strength, compressive strength and splitting tensile

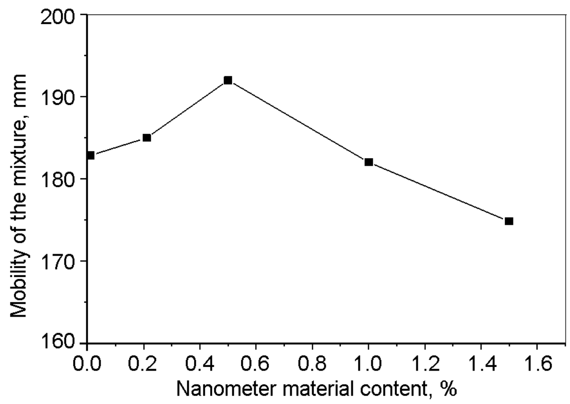

Fig. 1. Fluidity of mixture.

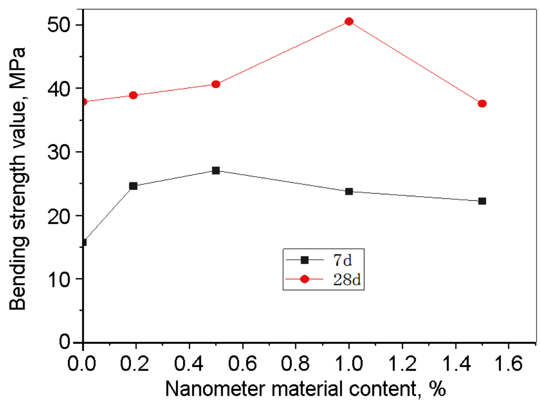

Fig. 2. Bending strength of RPC.

strength is: A > B > C. The results of the variance analysis show that the influence of the water-binder ratio on the compressive strength is very significant, and the effect on the resisting flexural strength and splitting tensile strength is significant too. The influence of the silica fume content on these three strength values is significant, and the slag effect is not significant. So the optimum mixture ratio can be determined as A1B3C3.

Based on the analysis of the range and variance of the 28d data, it is found that the order of influence of each factor is: B > A > C. The influence of the silica fume content on compressive strength is significant, the effect of the water-binder ratio on splitting tensile strength is significant, and the other factors are not significant. So the optimum mixture ratio was determined as A1B2C3. Because the effect of slag is not significant and slag is more economical than other materials, so C3 is selected. Considering the large amount of slag, in order to improve the activity of the material, the content of silica fume is chosen as B3, so the standard mixture ratio is determined to be A1B3C3.

3.2 Experimental results and data analysis on nano-SiO_2 adding

* *Effect of nano-SiO_2* on RPC fluidity On the basis of the standard mix ratio, nano-SiO_2 was added. The contents of nano-SiO_2 were 0.2 %, 0.5 % and 1.5 % of the cement content, respectively. The experimental results are shown in Table 3. As can be seen from Table 1 and Fig. 1, the fluidity of RPC increases firstly and then decreases with the increase of the content of nano-SiO_2; while the fluidity of N3 increases to 192 mm, increasing by 4.92 % compared with N1. The particle size of nano-SiO_2 is smaller than that of silica fume and cement, and the gap gradient is formed by filling each other among them. So it can improve the fluidity of the mixture because of its lubricating effect. Nano-SiO_2 has a large specific surface area, and when the content is large, the water absorption is higher than the effect of lubricating. Therefore, with the increase of the nano-SiO_2 content, the fluidity shows a downward trend. The regression equation of the

Table 2. Results of RPC orthogonal test

Test block number	Water-binder ratio	Cement	Silica fume	Slag	Quartz sand	Steel fiber, %	Water reducer, %	Fluidity, mm	7 d			28 d		
									Flexural strength, MPa	Compression strength, MPa	Split tensile strength, MPa	Flexural strength, MPa	Compression strength, MPa	Split tensile strength, MPa
1	0.22	1	0.20	0.3	1.2	1.5	2.4	193	12.88	144.04	6.44	38.46	133.95	8.74
2		1	0.25	0.4	1.2	1.5	2.4	184	14.18	148.56	6.68	52.86	134.56	10.13
3		1	0.30	0.5	1.2	1.5	2.4	183	15.81	157.24	7.72	37.96	156.10	7.84
4	0.24	1	0 20	0.4	1.2	1.5	2.4	206	11.35	133.93	5.86	36.79	131.93	6.02
5		1	0.25	0.5	1.2	1.5	2.4	194	12.35	134.20	5.03	49.13	131.5	7.30
6		1	0.30	0.3	1.2	1.5	2.4	180	13.38	138.03	6.81	42.88	142.75	8.15
7	0.26	1	0.20	0.5	1.2	1.5	2.4	225	11.69	120.67	5.54	52.66	117.63	5.67
8		1	0.25	0.3	1.2	1.5	2.4	204	12.44	134.24	5.68	59.91	133.87	7.07
9		1	0.30	0.4	1.2	1.5	2.4	199	13.13	138.05	5.94	37.85	139.68	5.84

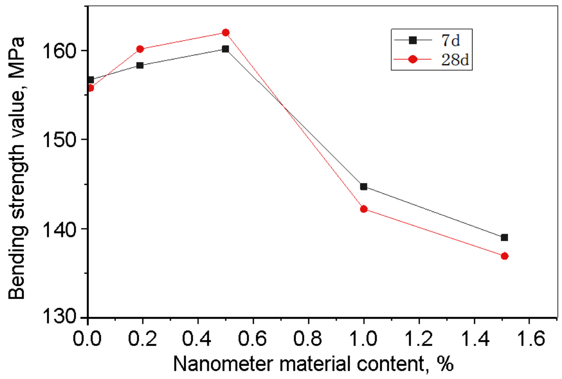

Fig. 3. Compressive strength of RPC.

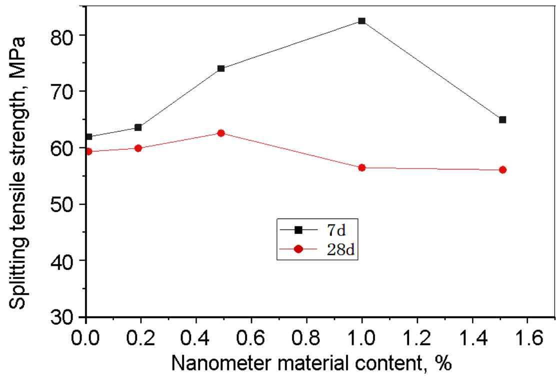

Fig. 4. Splitting tensile strength of RPC.

fluidity is obtained by a nonlinear univariate regression:

$$y = 18.292x^3 - 57.048x^2 + 39.714x +, + 181.88, \quad r^2 = 0.91.$$

* *Effect of nanometer SiO_2* on the strength of RPC

It can be seen from Figs. 2, 3 and 4 that the flexural strength, compressive strength and splitting tensile strength after 7d and 28d increase in a certain range with the increase of the content of nano-SiO_2; the maximum increase of the flexural strength is 78.26 %, the compressive strength is 3.5 % and the tensile strength is 33.12 %. However, with the increase of the SiO_2 content, the flexural strength, compressive strength and splitting tensile strength began to decrease. The reason is that when the content of nano-SiO_2 becomes larger, its strong water absorption makes the fluidity of the RPC mixture decrease, and because of the incorporation of steel fiber, it is difficult to form, thus affecting its compactness, producing many voids, leading to the decrease of strength. The regression equations can be obtained by the univariate nonlinear regression of compressive strength and splitting strength.

Flexural strength:

$$y = -32.099x^3 + 56.798x^2 - - 13.321x + 38.527, \quad r^3 = 0.97.$$

Compression strength:

$$y = 43.792x^3 - 109.08x^2 + + 52.893x + 155.27, \quad r^2 = 0.98.$$

Split tensile strength:

$$y = -32.099x^3 + 56.798x^2 - - 13.321x + 38.527, \quad r^2 = 0.97.$$

* *RPC characteristics change with age*

From the strength values after 7 days and 28 days in Figs. 2, 3 and 4, it can be seen that the flexural strength and splitting tensile strength increase with the extension of age, but the increase of the compressive strength is very small, and even the phenomenon of strength collapse occurs. The reason is that under condition of hot water curing at 90 °C, the amount of hydration increases rapidly in the early stage, and the increase space of strength in the later stage is small; since many short steel fibers are mixed in RPC noncompactly under vibration, there are many original micro-cracks in the internal, and the silica fume has the property of shrinkage. With the extension

Table 3. RPC test results with nano-SiO_2

Test block number	Nano-SiO_2, %	Fluidity, mm	7d			28d		
			flexural strength, MPa	compression strength, MPa	split tensile strength, MPa	flexural strength, MPa	compression strength, MPa	split tensile strength, MPa
N1	0	183	15.81	157.24	7.72	37.96	156.1	7.97
N2	0.2	185	24.86	158.86	7.81	39.24	159.84	8.11
N3	0.5	192	27.06	160.75	8.01	40.92	161.58	9.45
N4	1.0	182	23.96	145.10	7.19	50.33	142.25	10.61
N5	1.5	175	22.80	139.18	7.25	37.92	137.10	8.18

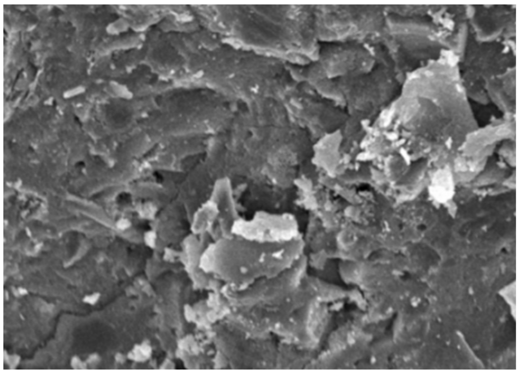

Fig. 5. N1 matrix structure.

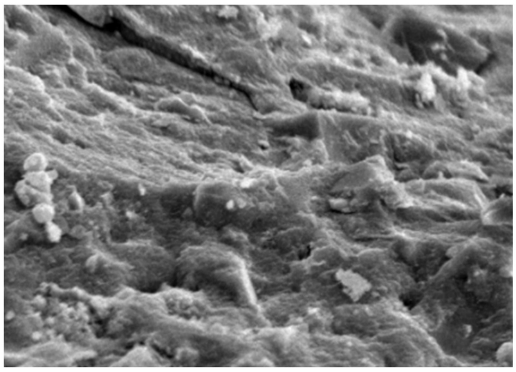

Fig. 6. N4 matrix structure.

of time, the internal original cracks gradually expand, which leads to the decrease of the later strength.

* *Scanning electron microscopy analysis of RPC*

(1) Hydrated calcium silicate gel. Scanning electron microscopy of N1 and N4 samples after 28 days showed that there were still a few flake $Ca(OH)_2$ crystals in the matrix structure of the N1 without nano-SiO_2, and the hydration was not complete. The structure of the hydrated calcium silicate gel is loose. As can be seen from Fig. 6, the structure of the RPC mixed with 1 % of nano-SiO_2 is very dense and looks like mottled. When the particle size is reduced to the nano-level, the surface area and surface energy increase rapidly. On the one hand, nano-SiO_2 reacts with the $Ca(OH)_2$ hydration product formed in the cement early stage; this reaction speeds up the hydration process of the cement and improves the early mechanical properties of the concrete. On the other hand, the range of capillary, gel and crystalline voids in concrete is of 1 to 100 nm, so nano-SiO_2 can fill the above voids, improve the density of the RPC, and then enhance the corresponding strength.

(2) Bond between steel fiber and the cement base. In Fig. 7, there are many microcracks between the steel fiber and the cement matrix, and the bond between them is not close. In Fig. 8, the matrix of the N4 sample and the steel fiber are very dense, the cement hydration products are attached to the surface of the steel fiber and the two are bonded well. The orientation and enrichment of $Ca(OH)_2$ is one of the main reasons for the formation of weak layer interface. Therefore, to strengthen the interface area, especially to strengthen the weak layer, the content of $Ca(OH)_2$ must be reduced. Nano-SiO_2 can consume a large amount of

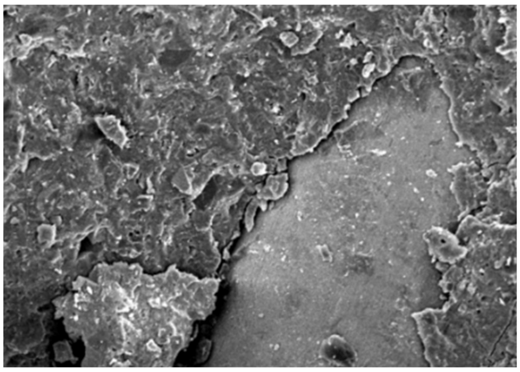

Fig. 7. N1 interface between matrix and steel fiber.

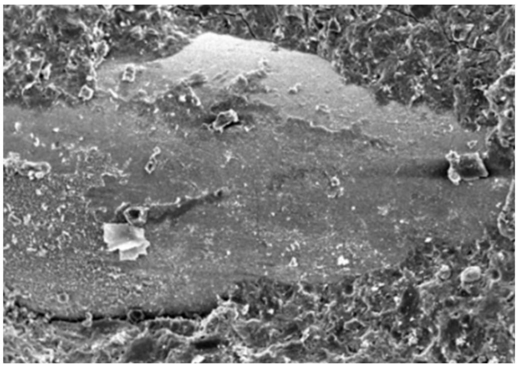

Fig. 8. N4 interface between matrix and steel fiber.

$Ca(OH)_2$ in the early stage. At the same time, in the hydration reaction, the hydrated calcium silicate gel phase is formed on the particle surface of the nano-SiO_2 acting as the crystal nucleus, and the loose hydrated calcium silicate gel is transformed into a dense network structure, thus improving the interface structure between the matrix and steel fiber in the RPC.

* *Effect of nano-SiO_2* on the bending pressure ratio and tensile compression ratio of RPC

From Fig. 9, it is found that with the increase of the content of nano-SiO_2, the

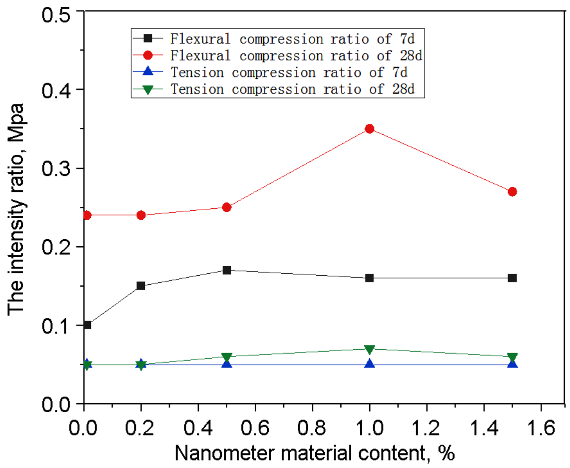

Fig. 9. The bending pressure ratio and tensile compression ratio of RPC with different content of nano-SiO_2.

bending pressure ratio and tensile compression ratio of the RPC show a trend of firstly increasing and then decreasing. The results show that nano-SiO_2 can improve the flexural and crack resistance of the RPC in a certain range. The interface structure of the steel fiber and cement base was improved after the secondary reaction between nano-SiO_2 and $Ca(OH)_2$; the bond strength at the interface was improved, and the increase of flexural strength and tensile strength of the steel fiber was greater than that of compressive strength. Therefore, the bending pressure ratio and tensile compression ratio are increased correspondingly. Before the test of compressive strength is carried out, the flexural strength of the test block is tested first. Because of the high flexural strength, a small crack formed in the test block simultaneously with the test block breakdown. As a result, the compressive strength value is smaller than the true value, so the ratio will be larger.

4. Conclusions

Based on the above, the following conclusions can be drawn:

The particle size of nano-SiO_2 is very small, and it has strong pozzolanic activity, the micro-aggregate filling effect and crystal nucleation effect. The addition of appropriate amount of nano-SiO_2 makes the internal structure of concrete more compact and effectively increases the strength and durability of concrete; this meets the requirements of concrete engineering. By the orthogonal test, the optimum mix ratio of the RPC was established: silica fume: slag: quartz sand = 1:0.3:0.51.2, the volume of steel fiber is 1.5, and the quantity of water reducing agent is 2.4 % of the quantity of the cementing material. The flexural strength, compressive strength and splitting tensile strength after 28 days were 37.96 MPa, 156.10 MPa and 7.97 MPa, respectively.

When the content of nano-SiO_2 is not higher than 1 % in cement, the mechanical properties of the RPC increase significantly with the increase of the content of nano-SiO_2, otherwise the mechanical properties will decrease. Therefore, the optimal dosage should be controlled between 0.5 % and 1.0 %. The regression equations for the SiO_2 content and RPC fluidity, flexural strength, compressive strength and splitting tensile strength were obtained by univariate nonlinear regression, which provides the basis for further scientific research.

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