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Studying concrete modification using nano-composite particles

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The methods of concrete modification are described in the article. The effects of TiO_2 nanoparticles on the hydration, mechanical properties and durability of the cement matrix were studied. The results showed that the addition of TiO_2 nanoparticles increased the moisture of the concrete in the early stages; that made the concrete denser, increased the homogeneity of the elements distribution and caused 14 % increasing the strength under pressure.
Keywords: nanoparticles, concrete, hydration.

Изучено влияние наночастиц TiO_2 на гидратацию, механические свойства и долговечность бетона. Результаты показали, что добавление наночастиц TiO_2 увеличивало влажность бетона на ранних стадиях, что сделало бетон более плотным, увеличило однородность распределения элементов и вызвало увеличение прочности на 14 % под давлением.

Вивчення бетонної модифікації з використанням нанокомпозиційних частинок. *Y.Tang*.

Вивчено вплив наночастинок TiO_2 на гідратацію, механічні властивості і довговічність бетону. Результати показали, що додавання наночастинок TiO_2 збільшувало вологість бетону на ранніх стадіях, що зробило бетон більш щільним, збільшило однорідність розподілу елементів і викликало збільшення міцності на 14 % під тиском.

1. Introduction

In recent years, the improvement of the performance of building materials by nanomaterials has been deeply studied. As important nano-materials, nano-powder materials are widely used to improve the properties of cement collective composites [1]. At present, nano-silica, nano-titanium dioxide, and nano-ferric oxide are widely studied at home and abroad. However, at present, the research of nano-materials in cement matrix composites is still in its infancy, and there is a huge room for improvement in both theory and practice [2].

Nowadays, the most widely used building materials are reinforced concretes; their structure consists of the concrete as a matrix material which elastic modulus is far from that of steel reinforcing bars, thus the strength of the steel bars cannot be brought into full play. Relevant researchers proposed the use of a prestressed technology, when the compressive limit of concrete reached 118 MPa [3,4]. This allows for replacing the most of steel bars in structure performance. Therefore, the production of high strength concrete and the reduction of structural weight are of great significance to the construction engineering.

Most researchers believe that the incorporation of nano SiO_2 and the stiffness of the chain length of C–S–H gel increase the strength of cement matrix composites. Xiong Guoxuan and others found that the conductivity and wave absorption properties of cement based bodies could be improved significantly by adding of nanometer TiO_2 in 5 % mass fraction. Morsy mixed carbon nanotubes with nano-clay to study the effect of the mixture on the physical and mechanical properties of cement-based materials [5]. The strength of the cement matrix with 6 % of the nano-clay was increased by 18 %. The researchers focused on the changes of mechanical properties and microstructure of cement-based materials directly doped with nano-materials. It was found that the change trend of diffraction intensity of (001) and (101) faces in hydration products is completely different [6,7]. It indicates that the main reason for the increase of the strength is the decrease and improvement of the orientation degree of crystallization, not the increase the quantity of hydrated products. In view of the important influence of cement hydration heat on practical engineering and the essence of cement hydration, it is important to explore the influence of nano-sized TiO_2 particles on the hydration heat and exothermic rate of Portland cement. Therefore, the effect of TiO_2 nanoparticles on the hydration, mechanical properties and durability of the cement matrix was studied.

1. Experimental

1.1. Test method for hydration heat of cement

The experimental operation was carried out in strict accordance with the code for determination of hydration heat of cement. First of all, the thermal capacity of the Bayesian thermometer was calibrated, and preparations were made for 24 h in advance, and the nitric acid solution of (13.5±0.5) (2.00±0.02) mol/L was used in the weight of 410 g. 8 mL of 40 % hydrofluoric acid mixed solution was mixed with (7±0.001) g of zinc oxide of good pre-weighing. The thermal capacity of Bayesian thermometer was calculated for different temperatures [8,9]. For the determination of the heat of solution of unhydrated cement, the preparatory work was repeated: 4 portions of (3±0.001) g of unhydrated cement were weighed, two of which were calcined and weighed in a high temperature furnace; the other two portions were added to the acid mixture and the temperature values at different time were measured. The heat of the solution of unhydrated cement was calculated synthetically. Dissolution heat of partially hydrated cement was determined.

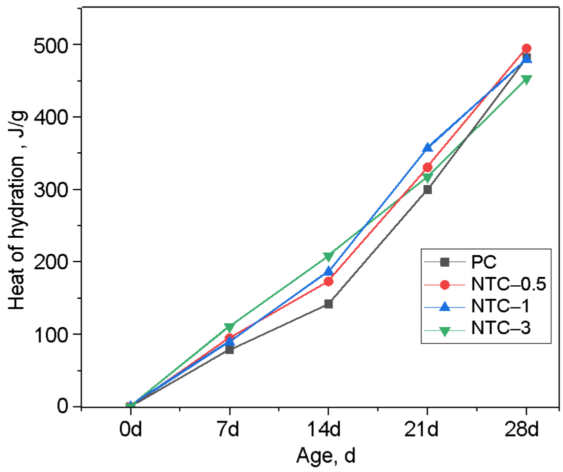

Fig. 1. Hydration heat of nano-cement at different ages (in days).

The hydrated sample was prepared according to the experimental scheme and cured (aged) for 1 d ~ 3 d ~ (7 d) and 28 days, then the specimen was grinded into 4 portions of (4.2±0.001 g) through a square hole of a sieve of 0.6 mm. Two of the samples were calcined according to the dissolution heat, then the temperature at the fixed time was measured with the Bayesian thermometer, and the quality of the calcined samples was determined. The heat of solution of some hydrated samples was calculated synthetically, and the hydration heat released by cement at certain ages was determined [10].

1.2 Testing program

In this paper, the effects of TiO_2 nanoparticles and their contents on the hydration of cement were studied by comparing the contents of four kinds of TiO_2 nanoparticles [11]. When the ratio of water to cement is 0.4, the surface of nanoparticles is very easy to agglomerate, so the content of nanoparticles should not be excessive, so, the contents were 0 %, 0.5 %, 1 % and 3 %, respectively. The specific test scheme is shown in Table.

Table. Test scheme for hydration heat of cement paste with TiO_2 nanoparticles

Sample item	Cement	Water(g)	TiO_2(g)	Water(g)
PC	100	40	0	1
0.5TC	100	40	0.5	1
1TC	100	40	1	1
3TC	100	40	3	1

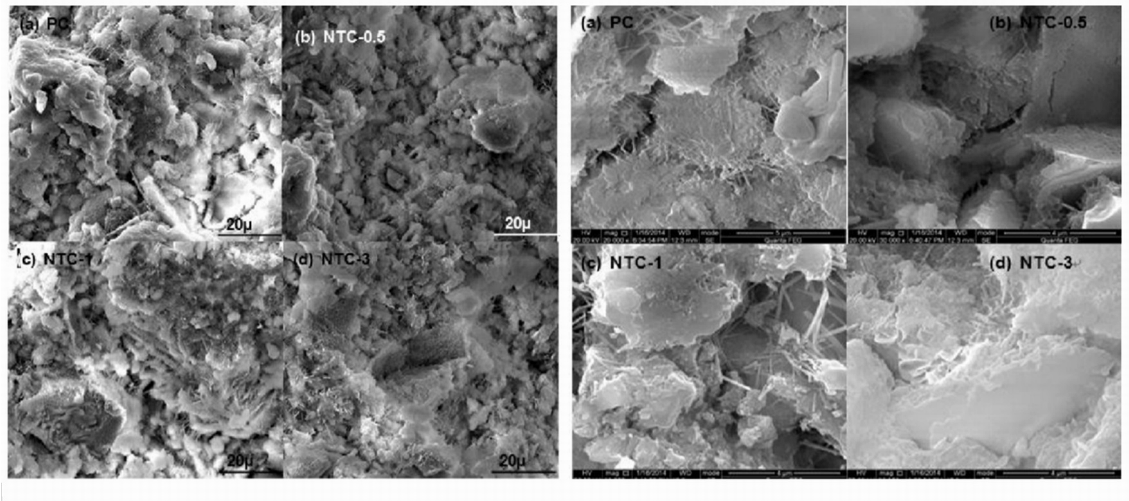

Fig. 2. Morphology of cement hydration products aged for 3 and 7 days.

2. Results and discussion

2.1. Measurement of hydration heat

In practical application, the heat dissipation caused by cement hydration is more than that of cement hydration for a long time, and the total temperature rises slower, so the user is more concerned about the heat release rate of cement. The hydration heat of nanocrystalline cement at different ages is shown in Fig. 1. It can be seen from Fig. 2 that the exothermic rate of cement with 3 % TiO_2 at the early stage of hydration is higher than that of other cement. The increasing rate of the hydration heat release is positively related to the content of nano-particles, mainly because of the high specific surface area of TiO_2 nanoparticles providing nucleation sites for the cement hydration; this promotes the formation of the hydration product as hydroxycadherite and CSH gel, and gives off a lot of heat. At the same time, the hydration heat of the samples with 1 % and 3 % TiO_2 for 3 days accounted for 28 %, 40 % and 49 % of the total heat of hydration in 28 days, respectively, which proved that the incorporation of nanoparticles accelerates the early hydration of cement. And the exothermic rate increases with the increase of the amount of admixture. The exothermic rate of NTC-3 in the figure is lower than that of the other admixtures in the later stage, which is favorable to the release of hydration heat in cement.

From the relationship between the different amount of nano-particles and hydration heat in 28 days, it can be seen that the incorporation of TiO_2 nanoparticles does not affect the heat release of cement, and it can be concluded that the particles are not directly involved in the hydration reaction. According to the development of hydration heat in whole age, TiO_2 nanoparticles mainly effect on the hydration heat release in the early stage of cement hydration, because the hydration heat is a chemical heat of the cement particle chemical reaction. The mechanical properties of TiO_2 nanoparticles in the early hydration of cement can be inferred.

2.2. Effect of nano-TiO_2 on the hydration of cement

The mechanical properties of a hardened cement stone mainly depend on the physical structure of the gel product after the cement hydration, and the internal pore structure of the cement stone depends less on the chemical composition of hardened cement. Therefore, it is of great significance to study the physical properties and microstructure of hydration products of cement particles modified by nano-particles in order to reveal the influence of TiO_2 nanoparticles on the properties of cement stones. The hydration morphology of cement at different ages is shown in Fig. 2. From the figure, it can be seen that the addition of TiO_2 nanoparticles makes the microstructure of cement stone denser, and a large number of harmful pores with larger pore size are filled. Thus, improving the pore structure of the cement stone and reducing the side effect of harmful pores on the cement stone performance are observed. In addition, from the point of view of the morphology of hydration products, it can be seen that the incorporation of TiO_2 nanoparticles can significantly inhibit the growth of ettringite in

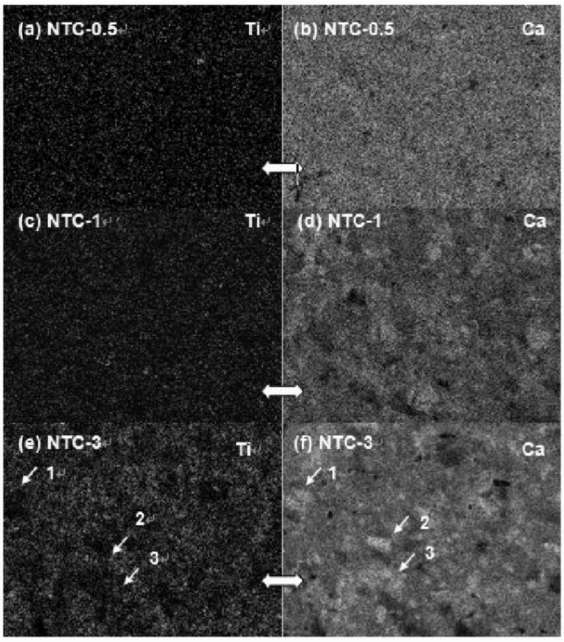

Fig. 3. Distribution of Ti and Ca elements in 28-day aged cement.

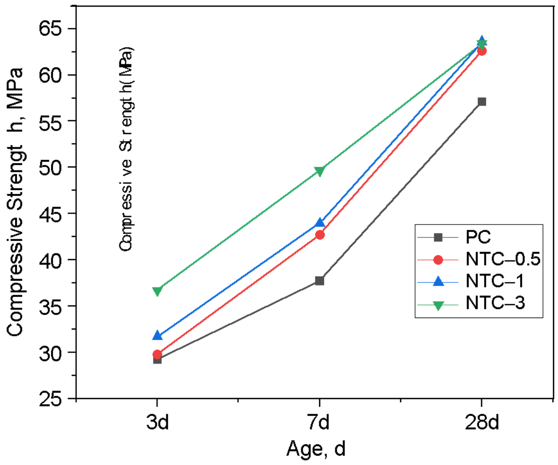

Fig. 4. Compressive strength of nano TiO_2 cement composites at different ages.

the shape of a needle rod, and promote the formation of high strength gel, which makes the structure of the cement stone more compact.

2.3. Effect of dispersion characteristics of nano-TiO_2 on the distribution of cement hydration products

Nanoparticles have high surface energy, and interactions such as electrostatic, van der Waals force and chemical bonds make nanoparticles easily agglomerate, thus seriously affecting the dispersion and specific surface area of nanoparticles. At the same time, this fact may affect the homogeneity of nanoparticles in the cement matrix. This may reduce the modification effect of nanoparticles on the cement, and even have a negative impact on the properties of cement. Therefore, an effective effort to disperse nanoparticles is the only way to promote the high performance of the nanoparticles, which has attracted many researchers' attention.

The distribution of titanium elements in the samples with 0 % and 3 % of nanometer TiO_2 is compared with the distribution of Ca element in cement, as shown in Fig. 3. From the contrast surface scanning of the distribution homogeneity of each element, it can be seen that the incorporation of nanometer TiO_2 has a certain influence on the distribution homogeneity of Ca element in the cement base body, in which 0.5 % of TiO_2 by mass fraction is added. It was observed that the addition of nanometer TiO_2 made the distribution of Ca element more homogeneous. However, the homogeneity of TiO_2 and the distribution of Ca element in cement were changed when the content of nano TiO_2 in cement continued to increase. When the content of Ti is 3 %, there is an obvious correspondence between the Ca rich area and the Ti poor area.

2.4. Effect of nano-TiO_2 on strength of cement paste

The strength of cement, as an important index to reflect the performance of cement to a certain extent, has a decisive effect on the mechanical properties of concrete in practical construction projects. In this section, the effect of nanoparticles on hydration strength of cement and its principle are studied. In addition, impermeability, as the main internal factor affecting the durability of concrete, largely determines the ability of concrete to resist external erosion. Therefore, it is of great significance to study the effect of nano-sized particles on the impermeability of a cement matrix. The strength of nano-cement matrix composites at different ages is shown in Fig. 4. For the cement of the same hydration age, in the early stage of hydration, the strength of the cement paste increases with an increase of a nano-particle content. Because of the nucleation effect of nano-size particles, cement particles are in better contact with water, and the hydration area of the cement particles is favorable to the formation of hydration products. A low soluble product precipitates to form a high strength polymer, which enhances the strength of cement. This effect is obvious in the early stage of hydration, and the improvement of strength of TiO_2 nanoparticles tends to be lower with the increase of age. The effect of TiO_2 nanoparticles on the strength of the cement paste was the most obvious after 7 days of age when the water/cement ratio was 0.4. The compressive strength increased by 14 MPa when the ratio of water to cement was 1.0.

4. Conclusions

Thus, the effects of TiO_2 nanoparticles on the hydration, mechanical properties and durability of the cement matrix were studied. The effects of TiO_2 nanomaterials on the hydration of cement were studied by changing the content of nano-particles; macroscopic performance tests, micro-morphology analysis and elemental analysis were used. TiO_2 nanoparticles promote the development of cement hydration heat, especially the early hydration heat. From the point of view of the hydration reaction, it was shown that the nano-particles can promote the cement hydration, especially early hydration. The hydration heat of cement specimens with 3 % of TiO_2 nanoparticles increased to 49 % of the total heat release after 28 days of age. The concept of surface roughness of element distribution is based on the scanning results of the EDS plane, and the distribution homogeneity of elements is quantitatively characterized. It is shown that the distribution of Ti elements is more homogeneous when the content of Ti is lower, but the homogeneity becomes worse when the content of Ti is larger. The distribution of Ti elements in the hydration products of cement has obvious correlation with the distribution of Ca elements, and the nucleation theory of the promoting effect of nanoparticles is verified in a certain degree of stratification. The addition of TiO_2 nanoparticles can improve the strength of the cement paste; the effect of improving the strength of the cement paste is the most obvious after 7 days of age; and the compressive strength of cement paste increases by 14 % when the TiO_2 content is 1.0 %.

References

1. E.M.Gartner, D.E.Macphee, *Cem. Concr. Res.*, **41**, 736 (2011).
2. F.Pacheco-Torgal, S.Miraldo, Y.Ding, *Constr. Build. Mater.*, **38**, 365 (2013).
3. P.Mandracci, S.Ferrero, S.Porro, *Appl. Sur- Sci.*, **238**, 336 (2004).
4. K.L.Lin, W.C.Chang, D.F.Lin, *J. Environ. Managem.*, **88**, 708 (2008).
5. M.S.Morsy, S.H.Alsayed, M.Aqel, *Constr. Build. Mater.*, **25**, 145 (2011).
6. M.H.Zhang, J.Islam, S.Peethamparan, *Cem. Concr. Compos.*, **34**, 650 (2012).
7. H.Li, H.G.Xiao, J.P.Ou, *Cem. Concr. Res.*, **34**, 435 (2004).
8. H.Li, H.G.Xiao, J.P.Ou, *Cem. Concr. Compos.*,, **28**, 824 (2006).
9. T.Meng, Y.Yu, X.Qian, *Constr. Build. Mater.*, **29**, 241 (2012).
10. M.Bastami, M.Baghbadrani, F.Aslani, *Constr. Build. Mater.*, **68**, 402 (2014).
11. Y.Wang, Y.He, Q.Lai, *J. Environ Sci.*, **26**, 2139 (2014).