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Improvement of Impermeability and Chemical Resistance of Concrete by Nanocomposites

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Based on theoretical calculations and laboratory tests, this article studies the effect of nano-materials and fiber materials on the impermeability and chemical resistance of concrete, analyzes the mechanism of impermeability and corrosion resistance of concrete from macroscopic and microscopic aspects respectively and establishes the relationship between the impermeability and corrosion resistance of nano-concrete with its pore structure, compressive strength and flexural strength. According to the research results, the fiber material has not improved the pore structure inside the concrete, but much worse degradation appears in the interior of concrete due to the agglomeration caused by uneven mixing. With the addition of nano-materials (SiO_2 and TiO_2), the total pore volume, the most probable pore diameter and other pore structure parameters of the concrete all show a decrease in the total number of harmful pores (pore diameter >50 nm) and an increase in the number of harmless pores (pore diameter <50 nm). The concrete with 1% of TiO_2 has the best improving effect on concrete pore structure, but if too much nano-material is incorporated, the pore structure inside the concrete will be worse; suggesting that proper amount of nano-materials can effectively improve the pore structure and pore distribution in concrete. The incorporation of nano-materials can greatly improve the resistance to chloride ion corrosion of concrete. And the greater the compressive and flexural strength of concrete is, the smaller the chloride diffusion coefficient will be. In general, chloride ion diffusion coefficient is in a clear linear relationship with these two. Thus compressive strength and flexural strength of concrete can be used to judge the chloride ion diffusion resistance of concrete. The pore structure distribution of concrete is proportional to its chloride ion corrosion resistance.

1. Introduction

Concrete is the most widely used building material in construction projects, characterized by typical high brittleness with high compressive strength, low tensile strength and flexural strength (Carpinteri et al., 2005; Guo et al., 2010). The initial cracks, pores and high brittleness of concrete itself at the initial stage of pouring are the major causes for the decrease in its mechanical properties, durability and life cycle (Hearn et al., 2006). The inherent defects such as high brittleness and initial cracks of concrete are caused by hydration products of cement paste (Tanaka and Kurumisawa, 2002). Relevant studies have shown that the aggregation patterns, distribution characteristics, and structural forms of the hydration products of cement are the main reasons leading to the presence of a large number of pores and initial cracks in concrete (Kurumisawa and Tanaka, 2006; Kurumisawa and Tanaka, 2002).
In view of the above defects, the common practice at home and abroad is to add fiber materials to concrete, such as steel fibers and carbon fibers, which can fill the internal cracks and pores of the cement to a certain extent, and improve the bond between the cement products, thereby increasing the compressive strength and flexural strength of the cement matrix (Alhozaimy et al., 2015; Lu, 2013; Zhang and Li, 2012; Pan et al., 2011; Chen, 2013). There has emerged a large number of research results on the reinforcing mechanism of fiber materials on concrete (Xu et al., 2014; Strength and Performance, 2016; Zhu, 2015; Belhadj et al., 2017).

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However, the addition of fiber material does not change the hydration product composition of the cement paste, and the high brittleness defects of the cement-based composite material have not yet been solved (Xu et al.,2014; Strength and Performance, 2016; Zhu, 2015). Therefore, it has become the focus of the research at present to look for new materials to change the shape and structure of the hydration products of the cement paste, and to suppress the high brittleness of the cement-based composite materials, so as to improve its impermeability, corrosion resistance and other properties, thereby increasing its service life.

Nano-materials have been applied to various fields by researchers due to their unique properties in physics and chemistry, which has become the focus of research in recent years. Studies have shown that the addition of nano-materials to concrete can significantly improve its compressive strength, tensile strength and other macro-mechanical properties (Liu et al., 2010). However, the research on the durability of nano-materials such as freeze-thaw resistance, carbonization resistance, chloride ion corrosion resistance is almost blank at present (Sbia et al., 2015; Saloma et al., 2015). The research on the enhancement of corrosion resistance of concrete by nano-materials can provide important theoretical basis for the engineering application of nano-concrete.

Based on theoretical calculations and laboratory tests, this article studies the effect of nano-materials and fiber materials on the impermeability and chemical resistance of concrete, analyzes the mechanism of impermeability and corrosion resistance of concrete from macroscopic and microscopic aspects respectively and establishes the relationship between the impermeability and corrosion resistance of nano-concrete with its pore structure, compressive strength and flexural strength. The research results can provide a theoretical reference for the application of new concrete materials.

2. Effect of Nano-materials on the Pore Structure of Concrete

The research shows that the impermeability and corrosion resistance of concrete are mainly related to such factors as pore structure, compressive strength, mix ratio, and additives, etc. That is to say, by adjusting the above factors, the compactness of concrete can be enhanced, thus the corrosion resistance and impermeability of concrete can be strengthened.

The influence of nano-materials on the pore structure of concrete is first studied. There are a lot of pores in the hydration products of cement gel. The pore distribution and pore structure characteristics have a significant effect on the durability of cement matrix materials. The micropores in the material can be divided into “gel pores” (d < 20nm), “small capillary pores” (20nm < d < 50nm), “harmful pores” (50nm < d < 200nm) and “multiple pores” (d > 200nm). The pore diameter distribution, porosity and the most probable pore diameter of micropores are measured by mercury intrusion porosimetry (MIP). The force on mercury inside the pores is shown in Figure 3.

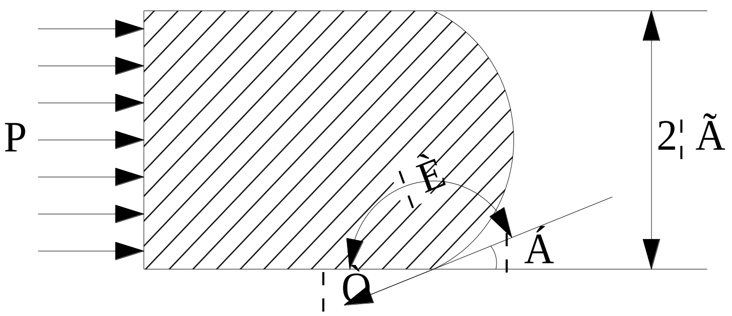


Figure 1: Force on mercury inside the pores

When the external force P and the surface tension of mercury are the same, the mercury inside the pores will remain in equilibrium. The distribution of pore diameter is obtained using Formula 1.

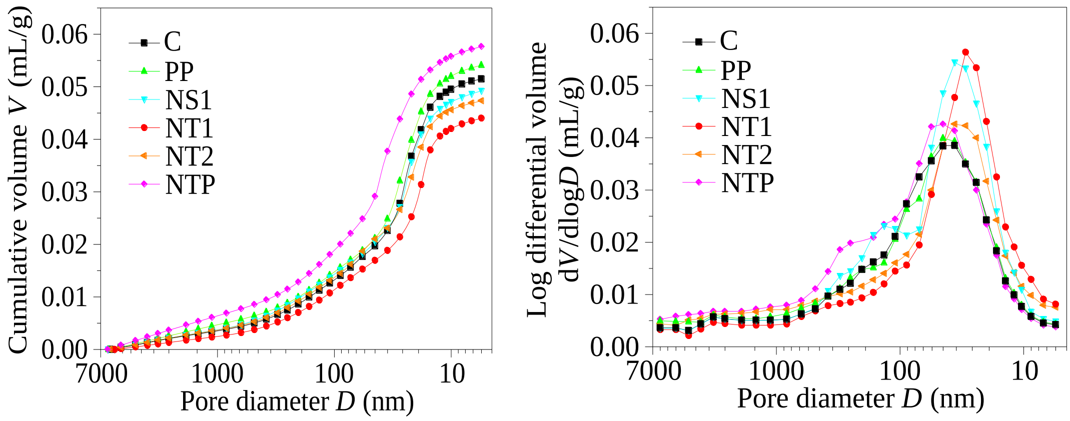
$$P = \pi r^2 p = 2\pi r\sigma \cos\alpha \tag{1}$$

Formula 1 is converted, then

$$\pi r^2 p = -2\pi r\sigma \cos\theta \tag{2}$$

$$r = -2\sigma \cos\theta / p \tag{3}$$

From Formulas 1 to 3, it can be seen that mercury pressure and pore diameter are inversely proportional.



(a) Pore diameter integral curve *(b) Pore diameter differential curve*

Figure 2: Pore diameter distribution curves of different nano-materials

Figure 2 shows the pore diameter distribution curves of concrete when different nano-materials are added, wherein Figure 2 (a) is the integral curve of the pore diameter, and Figure 2 (b) is the differential curve. Where, C represents ordinary concrete; PP is concrete added with PP fiber; NS1 is concrete added with nano-SiO2; NT1 and NT2 indicate the concrete with the addition of nanometer TiO2, with amounts of 1% and 3% of the cement quality, respectively; NTPC represents the concrete with addition of both TiO2 and PP fibers.

The highest point of the curve in Figure 2 (a) may be defined as “total pore volume”, the larger the total pore volume is, the more pores there will be in the concrete. The highest point of the curve in Figure 2(b) is defined as “the most probable pore diameter”. The larger the most probable pore diameter, the coarser the pore structure in the concrete. There will be more pores and cracks in concrete at this time.

As can be seen from Figure 2, when PP fibers (PP and NTP) are added, the peak value of the integral pore diameter of concrete is higher than that of ordinary concrete, and there are more pores in the range of harmful pores and multiple pores, indicating that the addition of PP fiber fails to improve the pore structure in concrete, and the agglomeration caused by uneven mixing leads to much degradation in concrete. However, the peaks of the integrated pore diameter after the incorporation of nano-materials (SiO2 and TiO2) are reduced to different degrees. The most probable pore diameter curve shows that most of the pore diameters fall within the range of small capillary pores and gel pores, which proves that the addition of nano-materials can effectively improve the pore structure and pore distribution in concrete.

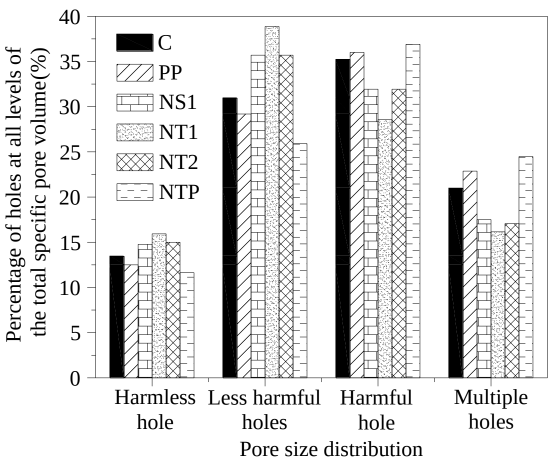


Figure 3: Distribution of internal pore with different diameters of different types of concrete

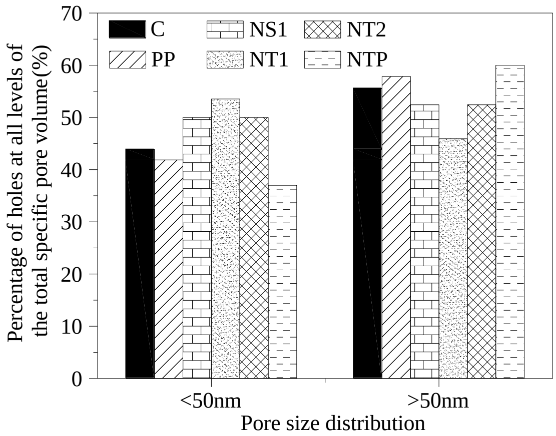


Figure 4: Distribution of internal pores with diameters less than 50 nm and that greater than 50 nm of different types of concrete

It can also be seen from the figure that the concrete addition incorporating 1% of TiO2 has the best improving effect on the pore structure of concrete. When 1% of TiO2 is added, the peaks of the most probable pore diameter and the total pore volume have increased. This is due to the fact that nano-materials are hardly soluble in water. When the content of nano-materials is too high, the nano-materials will agglomerate due to poor dispersion, which will cause defects in the interior of the concrete, resulting in poor pore structure. The nano-material is a microscopic material, and its incorporation into the interior of the concrete together with the macro-material PP fiber also fails to improve the pore structure of the concrete.

The pore diameter distribution of different kinds of concrete is calculated according to the pore diameter division range of gel pores, small capillary pores, etc., and the statistical results are shown in Figures 3 and 4. From the Figure, it can be seen that the number of pores with a diameter < 50nm (harmless pores and less harmful pores) in concrete are significantly increased and the number of the pores with a diameter > 50nm are significantly reduced. It has been proved once again that the structure of holes in concrete develops to the degree of refinement. Among all the nano-materials, NT1 has the best effect in improving the compactness of concrete, but NT2 has less effect as it contains too much nano-material.

The addition of PP fiber leads to the obvious increase of pores with a diameter larger than 50nm in concrete, and the pore structure tends to develop towards more large pores as a whole. From the Figure, it can be seen that the pores in the range of greater than 50 nm account for the most in NTP concrete pore structures, reaching 59%, suggesting that the mixing of fibers and nano-materials leads to a coarser pore structure in concrete.

3. Effect of Nano-materials on Chemical Corrosion Resistance of Concrete

Rapid non-steady state chloride migration method test (RCM) is used to evaluate the enhancing effect of graphene oxide on the impermeability of cement matrix materials. The size of the test piece is Φ100mm × 50mm. Place the test piece into the special test apparatus of RCM method, and measure the chloride ion concentration by measuring the color of the internal section of the test piece after being energized for a period of time. The formula for diffusion coefficient D_{RCM} is:

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

After the diffusion coefficient D_{RCM} is obtained, the one-to-one correspondence of D_{RCM} with the compressive strength and flexural strength of the test piece is conducted, and the relationship between D_{RCM} and compressive and flexural strength is analyzed. One-to-one correspondence between D_{RCM} and pore structure elated parameters (pore diameter distribution, porosity and the most probable pore diameter) of the test piece is performed, and the relationship between D_{RCM} and pore structure related parameters is analyzed.

Table 1 shows the degree of chloride ion diffusion for different types of concrete. It can be seen from the table that NT1 concrete has the best impermeability to chloride ions, which can reach 24%, followed by NS1 and NT2, respectively, which are increased by 14% and 9%, respectively. The impermeability of concrete is decreased by the addition of PP fiber, and the impermeability of concrete is decreased by 20% and 31% respectively by PP concrete and NTPC concrete.

Table 1 Degree of chloride ion diffusion for different types of concrete

Concrete type	Diffusion coefficient ($10^{-9}cm^2/s$)	Promotion ratio (%)
C	1.8467	0
PP	2.2155	19.97076
NS1	1.5748	-14.7236
NT1	1.3992	-24.2324
NT2	1.6745	-9.32474
NTPC	2.4143	30.73591

Figure 5 shows the chloride ion diffusion performance of nano-concrete and the fitting curves of its porosity, pore volume, average pore diameter and other parameters. As can be seen from the Figure, there is a clear linear relationship between chloride ion permeability and pore structure parameters of different concretes. Let 5 kinds of pore structure parameters be P_{hi}, and chloride diffusion coefficient be C_{Cli}, and i = 1, 2, ...,5, which represent the total pore volume, the most probable pore diameter and other pore structure parameters, let the fitting relation between the two is C_{Cl}=AP_{hi}+B, then there are:

$$\begin{cases} C_{Cl1} = 91.7P_{h1} + 3.119 \quad R = 0.995 \\ C_{Cl2} = 0.053P_{h2} + 0.275 \quad R = 0.989 \\ C_{Cl3} = 0.402P_{h3} + 2.168 \quad R = 0.984 \\ C_{Cl4} = 0.079P_{h4} + 1.199 \quad R = 0.963 \\ C_{Cl5} = 0.058P_{h5} + 1.411 \quad R = 0.991 \end{cases} \tag{5}$$

From Formula 5, it can be seen that the correlation coefficients of the 5 pore structure parameters and the chloride ion diffusion coefficient all reach 0.96 or more, which also proves that the pore structure has a strong relationship with the chloride ion corrosion resistance of concrete. The finer the pore structure, the more compact the concrete, and the better its resistance to chloride ion permeability will be.

4. Conclusions

Based on theoretical calculations and laboratory tests, this article studies the effect of nano-materials and fiber materials on the impermeability and chemical resistance of concrete, analyzes the mechanism of impermeability and corrosion resistance of concrete from macroscopic and microscopic aspects respectively and establishes the relationship between the impermeability and corrosion resistance of nano-concrete with its pore structure, compressive strength and flexural strength. The conclusions are drawn as follows.

(1) The fiber material has not improved the pore structure inside the concrete, but much worse degradation appears in the interior of concrete due to the agglomeration caused by uneven mixing. With the addition of nano-materials (SiO_2 and TiO_2), the total pore volume, the most probable pore diameter and other pore structure parameters of the concrete all show a decrease in the total number of harmful pores (pore diameter >50 nm) and an increase in the number of harmless pores (pore diameter <50 nm). The concrete with 1% of TiO_2 has the best improving effect on concrete pore structure, but if too much nano-material is incorporated, the pore structure inside the concrete will be worse; suggesting that proper amount of nano-materials can effectively improve the pore structure and pore distribution in concrete.

(2) The incorporation of nano-materials can greatly improve the resistance to chloride ion corrosion of concrete. And the greater the compressive and flexural strength of concrete is, the smaller the chloride diffusion coefficient will be. In general, chloride ion diffusion coefficient is in a clear linear relationship with these two. Thus compressive strength and flexural strength of concrete can be used to judge the chloride ion diffusion resistance of concrete. The pore structure distribution of concrete is proportional to its chloride ion corrosion resistance.

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