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Effects of Nanomaterials on Mechanical Properties and Sulfate Resistance of Cement-Based Materials

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Abstract. Nanomaterials have become one of the most promising materials in various fields because of their mechanical, electrical and magnetic properties, which are far superior to those of ordinary materials. At present, the research on improving the properties of cement-based composites by nanomaterials has been quite large-scale. In the existing research, a large number of scholars have paid attention to the effect and mechanism of nanomaterials on the mechanical properties and durability of cement-based materials. Nanomaterials have obvious effects on the hydration process, microstructure and porosity of cement-based materials, which can further change the macroscopic properties of cement-based materials. In this paper, the properties of nanomaterials and their effects on the mechanical properties and sulfate resistance of cement-based materials are analyzed and summarized. It is expected to provide references for researchers in related field.

Keywords: nanomaterials; Cement-based materials; Mechanical properties; Resistance to sulfate attack

1. Introduction

Sulfate attack on cement-based materials is a serious salt corrosion, and it is also an important factor that reduces the durability of cement-based materials[1]. In China's vast coastal areas and a large number of salt lake areas in the northwest, the soil and common water bodies are rich in a large amount of sulfate, and the concrete in this area itself contains a certain amount of sulfate, this sulfate will have a huge erosion effect on concrete in various environments, resulting in the production of expansion products inside the concrete, when the expansion products reach a certain amount, When the expansion products reach a certain amount, it will make the concrete crack[2]. In recent years, there are serious sulfate hazards in the bridges and water conservancy projects that have been in service in our country[3, 4].

The corrosion resistance of concrete is also closely related to its mechanical properties. For material researchers, the improvement measures of all properties of cement base should be based on ensuring its good mechanical properties. If the addition of a material can significantly improve the corrosion resistance of concrete, but the mechanical properties are difficult to meet the requirements, then the improvement of corrosion resistance is of little significance. Therefore, in the study of how to improve the concrete sulfate corrosion resistance at the same time, it should also make a full study of its mechanical properties.

Nanomaterials have the volume effect and macroscopic quantum tunneling effect that macroscopic particles do not have, forming nano hydration nuclei, filling effect and other nano effects[5]. In recent years, the research on Nano modified cement-based materials (NACC) has also become a hot topic. Relevant studies shows[6-9] that nanomaterials such as Nano silica (Nano silica, hereinafter referred to as NS), Carbon nanotubes (hereinafter CNTs), Carbon nanofibers (hereinafter referred to as CNFs), etc. After being added to cement-based materials, it can play a chemical active role, the microstructure of cement-based materials is improved, and the hydration

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products can have a certain influence, and the mechanical properties and sulfate resistance of cement-based materials are improved to a certain extent.

At present, most of the existing research results focus solely on mechanical and electrical properties[10-13], and there are still few studies on the improvement of cement-based corrosion resistance by nanomaterials. Compared with the achievements in mechanical and electrical properties, the research on the improvement of cement-based sulfate corrosion resistance by nanomaterials is still in its infancy, and the research on its mechanism is not perfect. Therefore, it is of practical significance to study the influence of nanomaterials on cement-based mechanical properties and sulfate corrosion resistance.

2. Properties of Nanomaterials

In the 1980s, nanomaterials first came out, which has many unique properties that ordinary materials do not have, and is regarded as a magic material that can change human beings, causing extensive attention and research[14, 15] by experts around the world. The first discovery of nanomaterials is the American scientist Richard Feynman, he believes that nano-sized materials will play its strong advantages in various fields in the future. At the end of the 20th century, Gelcter succeeded in producing iron nanomaterials. In the following years, scientists in Europe, America and Japan successfully prepared a variety of nanomaterials one after another, and materials science officially entered the nano era[16].

The most significant feature of nanomaterials is that the particle size is small and has a huge specific surface area[17]. The ratio of the number of atoms on the particle surface and the total number of atoms on the particle surface increases with the sharp decrease in the size of the nanomaterial. When the size of the nanoparticle reaches about 10 nm, the proportion of atoms on the surface reaches 20%, and when the atomic size shrinks to 1nm, the proportion of atoms on the surface reaches 20%. Its surface atoms accounted for nearly 100% of the proportion, nanomaterials also have many special properties, mainly divided into the following five aspects: (1) surface effect; (2) volume effect; (3) size effect; (4) macroscopic quantum tunneling effect; (5) superplasticity.

3. Influence of Nanomaterials on Mechanical Properties of Cement-Based Materials

Although nanotechnology has been proposed as a new concept, the characteristics of nanotechnology have long existed in the magical biological world. For example, nano-scale calcifications make soft shellfish have solid physical properties, and crabs use nanomaterials in their ears to identify the direction of geomagnetic sensitivity[18]. The discipline of nanomaterials is a discipline that tests the properties of materials at the nano level. There are also researchers who have developed a nanosensor, a biological device with odor sensitivity, which can be built into the nanosensor to amplify the signal obtained when collecting odor, thus greatly reducing the cost and time of substance detection[19].

At present, the research on the application of nanomaterials has also been extended to various fields, and has gradually been applied to cement-based materials. At present, the most studied nanomaterials by scholars in the field of materials are CNTs, nano-SiO_2, nano-TiO_2, etc[20-22]. Nanoparticles can effectively improve the microstructure of cement-based materials by their unique seed effect. In cement-based materials, the nucleation effect of nanomaterials and chemical additives can ensure that the generation of hydration products and nucleation can be synchronized in the hydration process.

Liu conducted an in-depth study on the electrical properties of nano-modified cement-based materials. The research showed[23] that the electrical conductivity of cement base was significantly improved after the addition of CNTs, and the improvement effect was more significant with the increase of the addition of CNTs. Therefore, CNTs cement-based materials are particularly suitable

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for use as smart materials. Zuo[24] added different amounts of carbon nanotubes to cement and found that the pressure sensitivity of cement-based composites was improved when the amount of carbon nanotubes was between 0.2% and 1%, but the amount of carbon nanotubes should not be excessive. When the amount of carbon nanotubes reached 2%, the agility of specimens was reduced, because when excessive carbon nanotubes were added, the pressure sensitivity of cement-based composites was improved. Carbon nanotubes will form clusters inside the cement-based material, so it is difficult to play the characteristics of carbon nanotubes.

In terms of mechanics, Porro[25] found that after NS was added, the compressive strength of the cement paste sample increased significantly. However, the main reason for its enhancement was not the traditional volcanic ash effect, but the unique particle size advantage of nano silica to fully fill the internal pores of cement base, improve its compacting properties, and thus achieve the purpose of enhancing mechanical properties. Lin[26] found that the addition of nano carbon fiber would strengthen the improvement effect of fly ash on cement mortar matrix. Many researchers believe that the main reason why nano-silica can enhance the mechanical properties of cement base is that the addition of nano-SIO_2 can increase the chain length of C-S-H, and thus achieve the purpose of improving its mechanical properties. Xiong[27] found that the incorporation of 5% nano-TiO_2 can effectively improve the electrical conductivity of the cement base. Ba[28] research showed that the mixing of nano-silicon powder and nano-silicon dioxide could give full play to the performance of both materials.

Using scanning electron microscopy, Abu Al-Rub[29] found that in cement-based materials doped with carbon nanotubes, carbon nanotubes can effectively play the role of bridging and pulling out, and the above two roles can effectively enhance the mechanical properties of cement-based materials. Fiber based nanomaterials play a significant role in improving the mechanical properties of cement-based materials. Wang[30]applied carbon nanotube solutions of different concentrations to the mixing of cement-based clean pulp, and then tested their mechanical properties. The results showed that CNTs had a significant effect on improving the mechanical properties of cement-based materials. In addition, at a content of less than 0.1%, the mechanical strength of specimens increased with the addition of CNTs, and when the content reached 0.1%, the mechanical strength of specimens increased. CNTs enhanced the mechanical properties of cement-based materials most significantly. However, when the content was too large, the mechanical properties of cement-based materials were not improved by carbon nanotubes, and they also had side effects. When the content reached 0.9%, the addition of CNTs reduced the mechanical strength of specimens.

Xu[31] found through research that NS had a certain effect on improving the mechanical properties of cement-based materials, but it was mainly concentrated in the early stage and the mechanical properties increased slowly in the later stage. This is mainly because NS can promote the nucleation of cement hydration by its nucleation action at early age, so the strength of the sample is significantly enhanced in the early stage. However, in the later stage, a large number of crystal nuclei could not continue to grow due to their small size, so the mechanical properties of cement-based materials were not improved significantly in the later stage. Zhao [32] studied the effect of adding CNTs to mortar on the performance of mortar and the mechanism. When the addition of CNTs was 0.1% and 0.2%, the growth rates of bending and compressive strength were as high as 27.3% and 26.3%, respectively. The study believed that nano silica not only played a filling role, but also greatly improved the speed of volcanic ash reaction. Therefore, the strength can be greatly improved.

4. The Influence of Nanomaterials on the Sulfate Resistance of Cement-Based Materials

At present, the durability problems faced by concrete engineering mainly include[33-39] : salt corrosion, freeze thaw, carbonization, alkali aggregate reaction and so on. Kiachehr[40] believe that

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the incorporation of nanomaterials can improve the microscopic pore structure of concrete, improve the freeze resistance of concrete, and the length shortening rate and quality loss of concrete specimens after the freeze thaw cycle are greatly reduced. Li[41, 42] found that adding nano-SiO_2 with 1% mass fraction of gelling material, concrete was immersed in corrosion salt solution containing Ca^{2+}, Mg^{2+}, SO_4^{2-} and Cl -plasma and dried at 60°C under dry and wet cyclic corrosion conditions, the corrosion resistance of concrete was greatly improved. The addition of nano SiO_2 significantly reduces the content of $Ca(OH)_2$, and the decline in the content of $Ca(OH)_2$ further reduces the basicity of cement paste and delays the crystallization of ettringite and gypsum, thus improving the corrosion resistance of concrete. Li[43] believe that the addition of nano hydrated calcium silicate can effectively reduce the penetration of chloride ions, sulfate ions and other harmful substances in concrete, and effectively protect the steel bar from premature rust. When the addition of nano-hydrated calcium silicate is 1%, the cement-based permeability coefficient is reduced by 32%, and the water penetration depth is only about 30% of the blank group. Wang [44] found that after the addition of nano-TiO_2, the hydration will be wrapped around the nanomaterial, forming a "crystal nucleus" effect, and effectively inhibit the precipitation of $Ca(OH)_2$, thus greatly increasing the compactness of the matrix. In the freeze-thaw test of slow freezing method, Du[45] found that mixing nanami micropowder could plug micropores smaller than 150nm, reduce the expansion damage caused by freezing of pore water, and improve the freeze-resistance by at least 50%.

Compared with the researches on other durability issues, the researches on the enhancement of corrosion resistance of nanomaterials are still rare. Zhao[32] studied the effect of carbon nanotubes on the sulfate resistance of cement-based materials. They used anhydrous sodium sulfate solution with a concentration of 5% and hydrochloric acid solution with 5% as the corrosion solution. The study showed that the sulfate corrosion resistance of cement-based materials was significantly enhanced after the addition of CNTs. Compared with blank specimens, the compressive strength and tensile strength of cement-based materials containing carbon nanotubes increased by 35.6% and 26.7% and 22.3% and 22.5% respectively after sulfate attack, respectively. Wang[46] studied the influence of carbon nanotubes on the water absorption and impermeability of cement-based materials by using the methods of water absorption test and compression impermeability test, respectively. The test results showed that, compared with the blank specimen, the water absorption rate of the cement-based material with the addition of nanomaterials decreased significantly, with a decrease rate of 15.8%, and the water penetration depth decreased by 17.9%, which indicated that the addition of carbon nanotubes could effectively improve the water penetration resistance and solution erosion resistance of the cement-based material.

5. Conclusion

Nanomaterials have been used in cement-based materials because of their nanoscale size and good electrical and thermal conductivity. At present, the nanomaterials studied more by scholars in the field of materials are CNTs, nano-SiO_2, nano-TiO_2 and so on. The addition of nanomaterials can effectively improve the mechanical properties and sulfate resistance of cement-based materials, and the improvement mechanism mainly includes nucleation effect, filling effect and bridging effect. However, attention should be paid to the amount of nanomaterials, too much incorporation may cause certain negative effects, which is due to the poor dispersion of nanomaterials. In the follow-up research, attention should be paid to the following points to carry out further research: 1) the dispersion of nanomaterials; 2) low cost production of nanomaterials; 3) the application of nanomaterials in reinforced concrete structures.

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