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The Effect of Nano-$CaCO_3$ on the Properties of Concrete: A Review

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Abstract: Nano-$CaCO_3$ has shown important potential in improving the comprehensive performance of concrete due to its relatively low cost and significant environmental benefits. A number of studies have shown that nano-$CaCO_3$ mainly improves the performance of concrete by accelerating the hydration reaction of cement and optimizing the microstructure. Appropriate addition of nano-$CaCO_3$ can effectively improve the early strength of concrete and enhance its durability. However, the high specific surface area of nano-$CaCO_3$ can easily lead to agglomeration, which not only weakens its nano-effect, but also may damage the workability of concrete. Therefore, the key to its practical application is to solve the dispersion problem. Future research should focus on the development of efficient and economical nano-$CaCO_3$ dispersion technology and explore its composite modification effect with other materials. Promote its large-scale application in the field of green and high-performance building materials.

Keywords: Nano-$CaCO_3$, Mechanical Property, Durability, Concrete, Dispersion Technology.

1. Introduction

With the rapid development of modern construction industry, concrete has become the most widely used building material in the construction field because of its excellent performance. Its excellent mechanical properties and durability can effectively guarantee the stability and safety of buildings[1][2]. Since 2015, the global production of concrete has reached 2.8 billion tons, with an average of nearly 1.5 cubic meters of concrete per person[3]-[4]. Cement is the most important cementitious material in concrete, but its production process produces a large amount of carbon dioxide. According to relevant statistics, carbon dioxide emitted by cement production accounts for 6 % of the world[5][6].It is expected that by 2050, the demand for cement will continue to increase, up to 6 billion tons per year[7]-[8],which will lead to serious environmental pollution. In addition, with the pursuit of architectural aesthetics and the influence of various external factors in complex environment, concrete is required to have higher performance. Traditional concrete is difficult to meet the needs of modern engineering for lightweight, long life and sustainable development of building materials due to its own mechanical performance defects, insufficient durability and environmental protection problems.

In recent years, due to the deterioration of concrete performance, it has caused serious economic losses to our country. Due to the freeze-thaw cycle, the horizontal displacement in the middle of the shallow layer of a pile-anchor foundation pit in Harbin is significantly larger than that on both sides, and the spatial effect is obvious, resulting in a large amount of property loss[9]; the design life of Qingdao Bay Bridge is shortened to 140 years due to chloride ion erosion[10]. These cases expose the limitations of traditional concrete in extremely complex environments, and the key to improving the performance of concrete is to optimize the internal microstructure of concrete. A denser microstructure can greatly improve the mechanical properties and durability of concrete. Therefore, in the future, the construction industry will use materials with bonding properties[11]-[12], less energy consumption[13],widely available and easy-to-use materials to replace cement[14]-[15]to reduce the amount of cement. The development of high-performance green and environmentally friendly new concrete has become one of the key issues that modern engineering technology must solve.

Nanomaterials have the characteristics of small particles, large specific surface area, high surface energy, large proportion of surface atoms, and their unique four effects : surface effect, quantum size effect, small size effect and macroscopic quantum tunneling effect. It has been widely used in biology, medicine, aerospace, electronic instruments and other fields. Existing studies have found that the addition of nano-materials to concrete can accelerate the hydration reaction of concrete cement and promote the formation of G-S-H gel[19][20]. Different materials act with cement materials in the form of nanometers to improve the microstructure of concrete[21], which is of great significance for the improvement of mechanical properties and durability of concrete[20]. A number of studies have shown that the addition of nanoparticles such as nano-SiO_2, nano-TiO_2, nano-$CaCO_3$, nano-Al_2O_3 and nano-graphene to cement-based materials can significantly improve their performance and durability[22][23]. Among them, nano-silica has become one of the most popular nano-additives for researchers to improve the performance of mortar and concrete due to its high pozzolanic effect[24]-[28]. However, most of these nanomaterials are expensive, which seriously affects their application and development in the cement industry. However, the price of nano-$CaCO_3$ is relatively cheap[29],and there are relatively many ways to obtain it. It can be produced by marble waste after nitric acid treatment[31]. At the same time, other studies have shown that nano-$CaCO_3$ can also be produced in cement plants, and waste carbon dioxide in cement production can be used[29][30]to reduce carbon dioxide emissions. The study of Batuecas E team[30]showed that after using 2% nano-$CaCO_3$,the carbon dioxide emissions of cement plants were reduced by 69 %.In addition, Deng Yousheng[20]added 1% nano-$CaCO_3$ into recycled concrete, which improved the elastic modulus of concrete and optimized the failure mode, and the fatigue life was prolonged by 60 %. Fu Yunbo[32]also pointed out that the strength of concrete decreases with the increase of coarse aggregate replacement rate, and the incorporation of 1% nano-$CaCO_3$ can significantly enhance the strength and toughness of recycled concrete. In addition, nanomaterials can effectively promote the hydration reaction of concrete and improve the durability of mortar and concrete[16][17]. Wang Ruijun[18]pointed out that the application of nano-$CaCO_3$ in concrete can effectively improve the F-T durability of concrete.

In recent years, the application of nanomaterials in the field of concrete materials has great prospects. Nanoparticles have high surface area and volume ratio, which are more reactive than size materials, and improve the performance of concrete by affecting the microstructure of concrete at the nanometer level[33]. This paper systematically reviews the properties of nano-$CaCO_3$ and its effects on the workability, hydration, strength and durability of concrete, so that researchers can fully understand the latest research in this field and provide directions for future related research.

2. Properties of Nano-$CaCO_3$

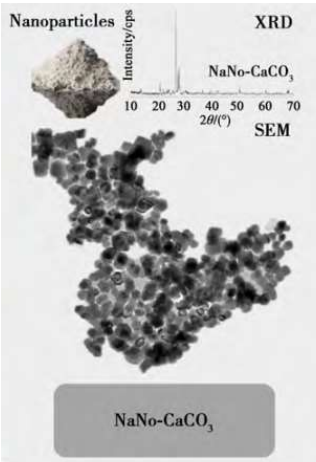

Fig. 1 Physical appearance and microstructure of nano-$CaCO_3$[38]

Nano-$CaCO_3$ is a kind of calcium carbonate micro-particle aggregates with a particle size between 1-100 nm. Due to the ultra-fine particle, its crystal structure and surface electronic structure change, resulting in surface effects, small size effects and macroscopic quantum tunneling effects that ordinary particles do not have[40]. Fig.1 shows the physical appearance and microstructure of nano-$CaCO_3$. In the application of concrete, the nano-$CaCO_3$ particles can effectively fill the pores of the cement matrix and improve the compactness of the structure. On the other hand, it acts as a nucleus to accelerate the process of cement hydration reaction, promote the formation of hydrated calcium silicate gel, and shorten the setting time. At the same time, the material can significantly improve the early strength development of concrete[33][34]. It inhibits shrinkage cracking[35]and enhances impermeability and carbonation resistance[36][37].In addition, nano-$CaCO_3$ is easy to agglomerate due to its high specific surface area, which makes the particle size larger and loses the special function of nanoparticles[38].In addition, it is hydrophilic and oleophobic, so it needs to be modified and dispersed before use. In the field of concrete, organic modified nano-$CaCO_3$ is used to improve dispersion, and nano-silica is used in combination. In practical applications, it is necessary to ensure the uniform distribution of nanoparticles by mechanical stirring or ultrasonic dispersion, avoid agglomeration, and strictly control the dosage to prevent the decrease of concrete fluidity.

3. Setting Time

The setting time of concrete is an important parameter affecting the construction quality, strength development and durability of concrete. Generally speaking, the setting time of concrete is divided into two stages : initial setting and final setting, which is inversely proportional to the hydration rate, that is, the increase of hydration rate will shorten the setting time. Poudyal Lochana 's team[39]studied the effect of nano-$CaCO_3$ on the properties of Portland limestone cement (PLC) concrete, and found that nano-$CaCO_3$ had a particularly significant effect on the final setting time. The experimental data show that when the mixing amount is 2 %, the final setting time of PLC concrete is 21 % shorter than that of the control group. It is worth noting that the research team specially explained in the report that due to the absence of special dispersion process, nano-$CaCO_3$ particles agglomerated in the matrix, resulting in a significant fluctuation in the initial and final setting time difference of PLC concrete with the increase of nano-$CaCO_3$ content. Wang Gang[40]gave a scientific explanation through the Taguchi-grey correlation optimization analysis method and orthogonal test. The nano-$CaCO_3$ with smaller particle size will replace the water molecules between the initial cement and reduce the hydration rate, resulting in an increase in the setting time. With the increase of nano-$CaCO_3$ content, the characteristics of large specific surface area and nucleation gradually emerge, absorbing the water in the system and providing reaction nucleation sites for hydration products, accelerating the hydration rate and shortening the setting time. Zhang[41]pointed out that the addition of nano-$CaCO_3$ (NC)and nano-$CaCO_3$ modified by polycarboxylate superplasticizer (NC-VPEG-AA) could accelerate the hydration reaction of cement, and the promotion effect of NC-VPEG-AA was more significant.

4. Effect of Nano-$CaCO_3$ on Mechanical Properties of Concrete

The incorporation of nano-$CaCO_3$ accelerates the hydration reaction of cement and shortens the setting time of concrete. The advantage is that it can significantly improve the mechanical properties of concrete. In this paper, the effect of nano-$CaCO_3$ on the mechanical properties of concrete is described for the compressive strength of concrete. The addition of nano-$CaCO_3$ can promote the hydration reaction of cement, and its most prominent benefit is to improve the early mechanical properties of concrete, especially the compressive strength. Ding Lijuan[43]pointed out that the compressive strength decreases first and then increases with the increase of nano-$CaCO_3$ content, and the inflection point appears when the addition amount is 1.6%. Yang Xiang[44]pointed out that the compressive strength of recycled fine aggregate concrete with different gradations increased first and then decreased with the increase of nano-$CaCO_3$ content, and nano-$CaCO_3$ with 1.0% content had the most significant effect on the improvement of compressive strength. In addition, Deng Yousheng 's team[42]pointed out that nano-$CaCO_3$ modification has a weak effect on the early strength growth of ordinary concrete, and has a certain beneficial effect on the later strength. When adding recycled coarse aggregate, nano-modification significantly improves the strength of concrete.

The current research shows that the optimum dosage range of nano-$CaCO_3$ is 1%~3%[40],and the specific test data results are shown in table 1.

Table 1. Effect of nano-$CaCO_3$ on compressive strength of concrete

reference	Nano-$CaCO_3$ content\%	compressive strength		
		3d	7d	28d
[42]	1	25.3	34.2	46.5
[43]	1.6	0	0	28.3
[44]	0	0	24.9	30.2
	1.0	0	25.0	31.1
	2.0	0	23.3	30.2
	3.0	0	20.1	27.5

5. Effect of Nano-$CaCO_3$ on the Durability of Concrete

For the evaluation of the comprehensive performance of concrete, in addition to mechanical properties, durability is also an important measure. A number of studies have shown that the incorporation of nanomaterials can enhance the durability of concrete in many ways. Zhang Zhongwei 's team[45]showed that the sulfate corrosion resistance of concrete increased first and then decreased with the increase of nano-$CaCO_3$ content, and the optimal content was 1.8%.In addition, Ming Xingfen 's team[46]pointed out that the addition of nano-$CaCO_3$ to concrete by conventional dispersion method should not exceed 1.0% of the mass of cementitious materials. Excessive dosage will significantly reduce the fluidity, mechanical properties and durability of concrete.

In summary, nano-$CaCO_3$ can significantly improve the durability of concrete, but its dosage should not be too high. In addition, in order to prevent the agglomeration of nano-$CaCO_3$, it is necessary to use appropriate dispersion methods to treat nano-$CaCO_3$ and retrograde dispersion to give full play to its lifting effect.

6. Conclusion in Prospect

Based on the existing research, nano-$CaCO_3$ shows significant potential in improving the comprehensive performance of concrete. It mainly improves the mechanical properties and durability of concrete by accelerating cement hydration and optimizing the internal microstructure of concrete. Studies have generally shown that the optimal dosage range of nano-$CaCO_3$ is 1 % to 3 % of the mass of cementitious materials. Excessive production may lead to decreased workability and performance due to agglomeration effects.

The core advantage of nano-$CaCO_3$ is its relatively low cost and outstanding environmental value. CO_2 emissions from industrial waste or cement plants can be used for production. This makes it a promising option to promote the green and sustainable development of concrete materials.

However, nano-$CaCO_3$ still faces a key challenge in practical applications : dispersion is the primary bottleneck. Its high specific surface area is easy to cause agglomeration, weaken the nano effect, and may damage the fluidity of concrete. Future research should focus on :

Optimizing the existing mechanical stirring and ultrasonic dispersion methods, or exploring new surface modifiers and dispersion processes to ensure uniform and stable dispersion of nano-$CaCO_3$ in concrete matrix.

Study the synergistic effect of nano-$CaCO_3$ with other nanomaterials or functional admixtures, in order to obtain better comprehensive performance improvement at a lower dosage.

The long-term durability, volume stability and microstructure evolution of nano-$CaCO_3$ modified concrete in complex environments were systematically evaluated.

Strengthen the research on the integrated technology of nano-$CaCO_3$ production-dispersion-application, reduce costs, and gradually establish relevant material standards and application guidelines to promote its transition from laboratory to engineering practice.

Solving the dispersion problem of nano-$CaCO_3$ and improving its application technology system will greatly release its value in the production of high-performance and environmentally friendly concrete, and provide strong support for energy conservation, emission reduction and sustainable development of the construction industry.

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