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Effect of Nanomaterial Admixtures on the Mechanical Properties of Concrete

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In recent years, the evolving technologies have continuously improved the mechanical properties of cement concrete. In this paper, a test is conducted on different formula of nanomaterial admixture in attempt to analyze its effect on mechanical properties of concrete in many cases, for example, it is monomer or compound. On this basis, the mechanisms of nanoscale fine powder mono and compound effects are investigated. The results show that the nanometers SiO_2 and $CaCO_3$ can help improve the early strength of the concrete, but rarely work on its later property. The dosage of nonameter SiO_2 shows a positive correlation with the early strength of concrete. Compared to mono admixture, the addition of compounds has a better effect on the concrete compression strength, especially on the early strength, while the later strength is also improved. The nanomaterial admixture alone can effectively improve the concrete structure in the transition area. Compound admixture can make concrete have a better strength and compact effect or faster hydration speed.

1. Introduction

The cement slurry is made of cement and water. It has a certain fluidity and plasticity at the initial stage. The hydration reaction weakens the slurry's fluidity gradually and make it form a solid with a certain strength, i.e, coagulating and hardening processes. The development of the concrete strength is similar to cement (Najafi, 2016; Notman, 2014; Yu et al., 2014). Since the dawn of Portland cement in 1882, the investigation about the cement setting and hardening as well as the development of microstructure have been almost incessant. In 1887, Le Chatelier proposed the crystal theory (Fedorova et al., 2015; Kononova et al., 2016; Yan et al., 2012). Subsequently, Haelis put forward colloidal theory (Kulik et al., 2011). Bayikov believed that the cement hardening required three processes based on the above two theories, namely dissolution, retrogradation and crystallization (Hrbek, 2016; Wang and Liang, 2012).

In modern times, the development of technologies diversifies the tests on cements in the study. There is also in-depth study on the microstructure with cement slurry (Li et al., 2012; Kotsay, 2017). Chemists Taylor and Locher have proposed a lot of theories, among which the more coherent one is that the hardening of cement is attributed to the hydration reaction, and the resultant hydrate gradually fills the voids of water. The solid particles are similar, while the rod-like crystals and acicular ettringites overlap with each other, making the cement particles and hydrates firmly join up from the original dispersion state as an integral. (Pavlã, 2011; Zhou and Hao, 2012; Toropovs et al., 2014; Wang et al., 2016).

Currently, a new study finds that nanomaterial admixtures can change the mechanical properties of concrete (Rashkovskii and Savenkov, 2013). Nanometer SiO_2(NS) has a high chemical activity, while amorphous glass structure can transform $Ca(OH)_2$ in cement slurry into a colloid C-S-H soon. Nanometer $CaCO_3$(NC) also has a higher activity, which can facilitate the acicular ettringites to proliferate. The effect of nanomaterial admixtures on the physical and mechanical properties of concrete is investigated in order to further improve and apply concrete to more fields. It indeed has a strong practical significance.

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2. Raw materials and test methods

2.1 Raw materials

As the nanomaterial has a relatively high cost, and in the practical application, given that it plays an effect on high-performance concrete with higher workability, durability and strength than ordinary concrete. The concrete used in this paper is C40 in strength and 240-250 mm in slump.

Nano SiO_2(NS): the specific surface area is 620 m^2g^{-1}; SiO_2 content is greater than 99%. Nano $CaCO_3$(NC): the specific surface area is 665 m^2g^{-1}; $CaCO_3$ content is greater than 99%. Silica fume SF contains SiO_2 of 93%, where the most part is amorphous SiO_2.

2.2 Test method

The maximum compaction uses the sand rate, that is, the sand, pebble, water voids are filled with each other to maximize the concrete compaction. The sand rate should be in the range of 30% to 40% depending on the selected raw materials. According to the apparent density and workability of the laboratory specimens, 31% sand rate is the best for the concrete. The dosage of cement is replaced equivalently by SF, NS and NC, and the test pieces are made for contrast test at different ratios.

The mechanical properties of concrete are tested in accordance with the *Standard for Test Method of Mechanical Properties on Ordinary Concrete* and *the Standard for test method of performance on ordinary fresh concrete.* The test piece is 100mm×100mm×100mm *and the* curing lasts for 7 days, 28 days and 56 days.

3. Raw material and test method

3.1 Effect of Mono Nanometer $CaCO_3$ on Compressive Strength of Concrete

$CaCO_3$ is added at a rate of 0% (reference), 0.5%, 1.0%, and 3.0%, respectively, cure them for 7 days, 28 days, and 56 days, and compare the compression strength of concrete, as shown in Fig. 1. The comparative results show that the addition of only nanometer $CaCO_3$ can contribute to the early strength of the concrete, but as the curing time increases, it may adversely affect the test pieces cured for 28-day and 56-day. It is found from comparative analysis that the concrete compression effect is the best when $CaCO_3$ is added at 1%. However, with the increase of curing time, the concrete strengths at 28 days and 56 days are roughly similar to the baseline. With dosage of 3% $CaCO_3$, the concrete strengths at 28 days and 56 days are significantly lower than baseline; about 6-7%, 0.5% nanometer $CaCO_3$ also help improve the early strength, but with increase in the age, the concrete strength is lower than the baseline and that at 1% dosage, so that the nano-admixture is conducive to the early strength of the concrete, but increased dosage can not significantly improve the compression strength of concrete. The optimal dosage is 1%.

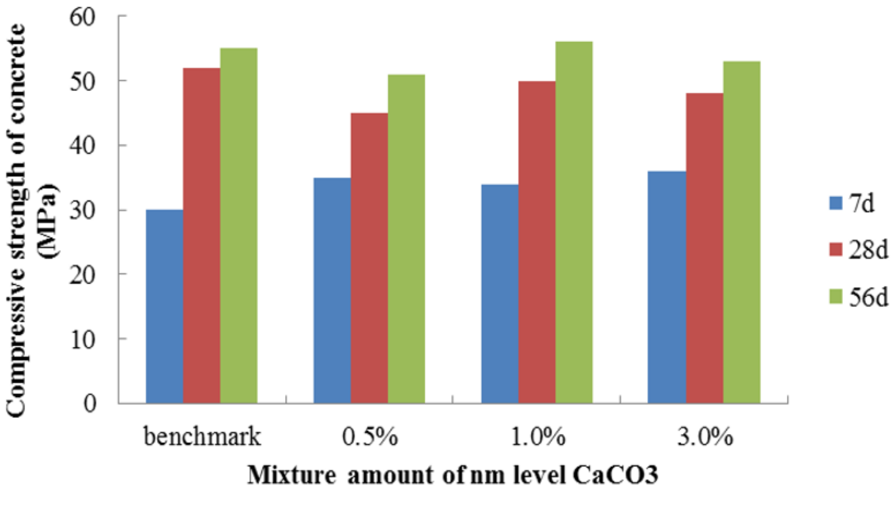

Figure 1: Compressive strength of concrete after NC incorporation

3.2 Effect of mono silica on the compression strength of concrete

SiO_2 is added at the rates of 0% (reference), 0.5%, 1.0%, 3.0%, 5.0%, respectively, cure them for 7 days, 28 days, and 56 days, and compare the compression strength of concrete, as shown in Fig. 2. The comparative results show that only addition of SiO_2 can help improve the early strength of the concrete, and the dosage is positively correlated with the improvement rate. The addition of SiO_2 has less effect on the strength of the concrete cured for 28 days, and after 56 days, its dosage is negatively correlated with the improvement rate. In the case of equal slump, the dosage of SiO_2 should not be too high, and better within the range of 0.5% to 1%.

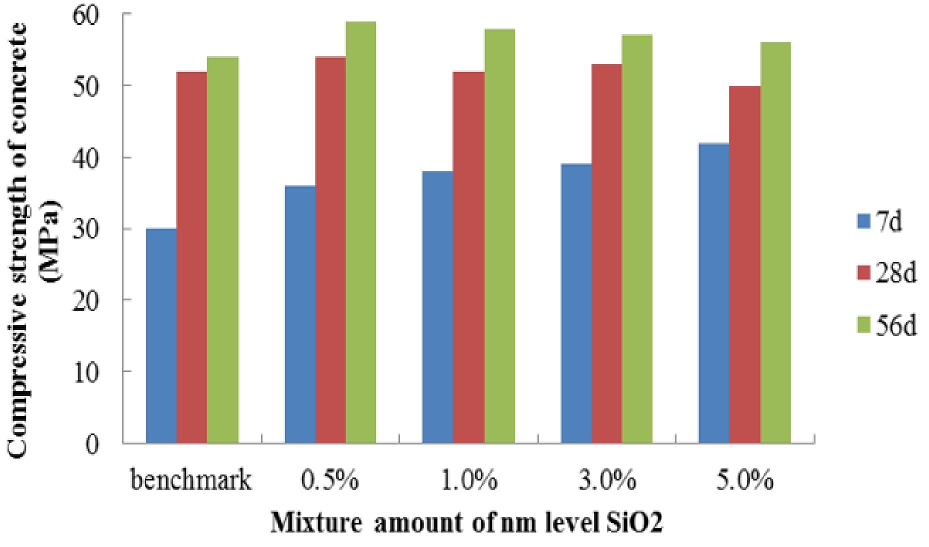

Figure 2: Compressive strength of concrete after NS incorporation

3.3 Concrete compression strength after adding the compound of SF and CaCO3

$CaCO_3$ is added at the rates of 0% (reference), 0.25%, 0.5%, 1.0%, 3.0%, respectively, with 2% SF, cure them for 7 days, 28 days, and 56 days, compare the compression strength of concrete, as shown in Fig. 3. Compared with monomer, the addition of compound can further improve the concrete strength. Like the monomer additive, $CaCO_3$ can not be large. It performs best if 0.5% $CaCO_3$ and 2%SF are added simultaneously. The concrete cured for 7 days, 28 days and 56 days has a significantly higher strength than the baseline, separately 33.3%, 7.7%, 3.2%.

5%SF is added simultaneously, where the same conditions prevail, the concrete compression strength is shown in Fig. 4. The early strength of concrete is also improved. The strengths of concrete cured for 28 days and 56 days are slightly improved. In contrast with the case when 2% SF is added, the later strength of the concrete is improved a little. The dosage of $CaCO_3$ cannot be too large.

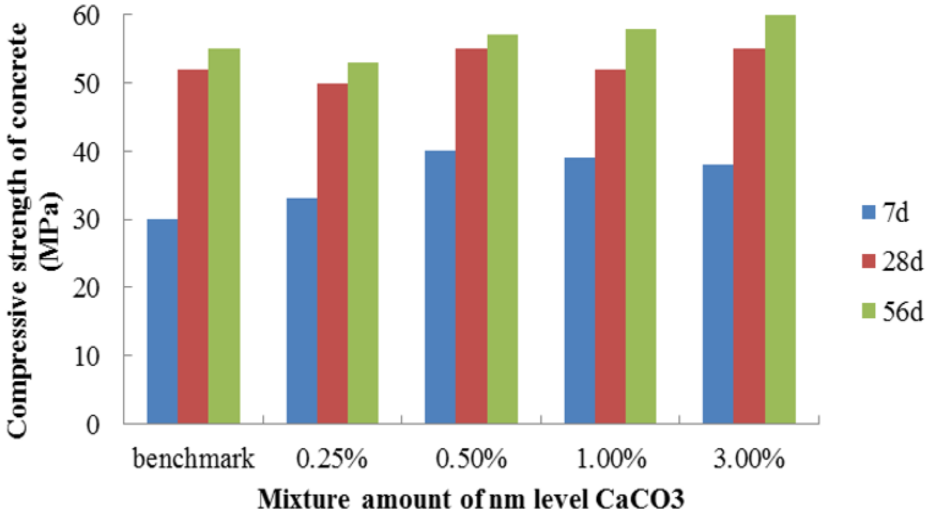

Figure 3: Compressive strength of concrete after NC and 2%SF incorporation

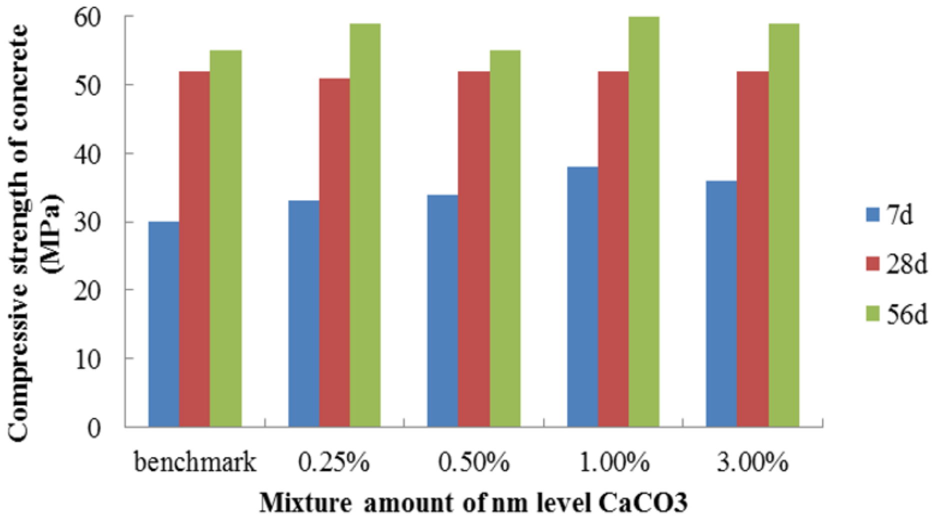

Figure 4: Compressive strength of concrete after NC and 5%SF incorporation

3.4 Concrete compression strength after adding the compound of SiO_2 and $CaCO_3$

SiO_2 is added at the rates of 0% (reference), 0.5%, 1.0%, 3.0%, respectively, with 1% $CaCO_3$, cure them for 7 days, 28 days, and 56 days, compare the compression strength of concrete. The results are shown in the figure 5. As the dosage of SiO_2 increases, the early strength of the concrete is improved, that is, 34.6% at 1%, 59.0% at 3%, and the late strength also increases a little. Compared with two separate nano-admixtures which also responds to rapid improvement of early strength and tardiness of the late strength, this phenomenon is more obvious in the case of compounds.

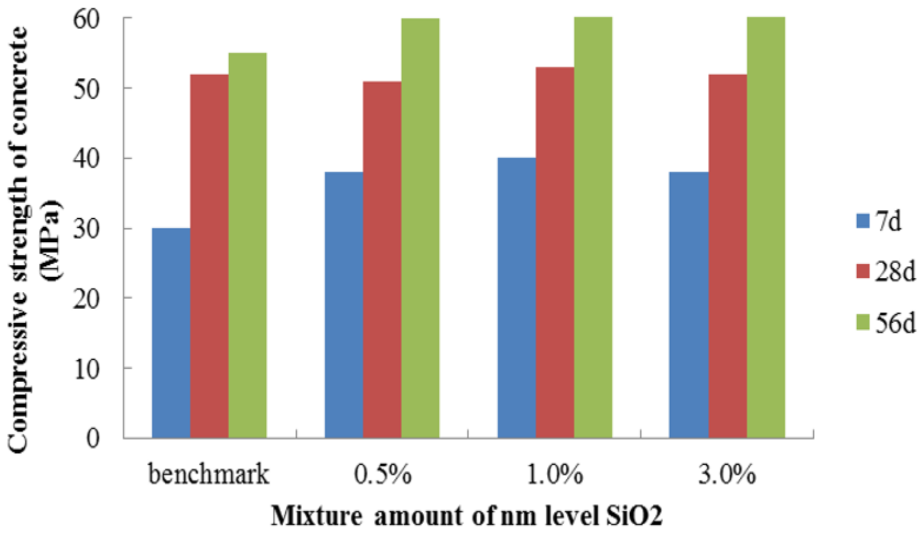

Figure 5: Compressive strength of concrete after NC and NS incorporation

4. Mechanism of nanometer fine powder monomer and compound effects

Duff proposed the water-cement ratio theory that was widely recognized in the industry, that is, when the raw materials of concrete are determined, if the concrete is packed by pouring, its strength and water-cement ratio have the following correlation: $f_c=k_1/k_2^{w/c}$

Where, k_1, k_2 represent the experience factor that is related to materials and working conditions.

In the course of hydration reaction, the bonding between the aggregate and the hydration product depends mainly on van der Waals attraction, so that the strength of bonding surface between the aggregate and cement depends on the size and the volume of the pores. In the case of low water-cement ratio, the pore in

early bonding surface is larger than the mortar matrix and the strength is low. Therefore, this bonding surface is also called the transition zone that is generally redarded as the strength limit phase of the concrete. Due to the existence of the transition zone, the concrete is destroyed under low stress.
The nano-admixture SiO_2 can effectively reduce the content of $Ca(OH)_2$ in the concrete, in particular, the content of $Ca(OH)_2$ with integrity crystal or of larger size in the transition zone and improve the concrete structure in the transition zone.
The $CaCO_3$ will be able to increase the content of acicular ettringite crystal in the cement slurry, while it also generates the high-carbon hydrate calcium carboaluminate. Two factors co-improve the early strength of concrete. When the dosage of admixture comes to higher degree, the similar product will result in a lower strength of the concrete at a later stage.
When the $CaCO_3$ and SF admixtures are added, the voids of the SF particles are filled with nanoparticles and the gradation is better. Compared with the individual addition, the concrete has a good strength and a compact effect. When $CaCO_3$ and SiO_2 admixtures are added, both nanoparticles are hydrated at a high rate. The concrete, therefore, has a higher early strength.

5. Conclusion

This paper analyzes the effect of nonmaterial admixtures on mechanical properties of concrete in many cases, for example, it is monomer or compound. On this basis, the mechanisms of nanoscale fine powder mono and compound effects are investigated.
The monomers SiO_2 and $CaCO_3$ can all contribute a lot to the improvement of the early strength of the concrete, but a little to the later strength of the concrete. The dosage of SiO_2 is positively correlated with the early strength of the concrete. Impacted by the concrete fluidity, the dosage should not exceed 3%. The $CaCO_3$ alone can also improve the early strength of concrete, but have an adverse effect on the later strength. It should be controlled at around 1%.
After the mixtures of SF and $CaCO_3$ or SiO_2 and $CaCO_3$ are added, the concrete compression strength is higher than that of monomer addition, especially the early strength, there is also an improvement in late strength. However, there is also a general property, that is, the early and later strengths of the concrete get closer when the nanomaterial admixture is incorporated.
The addition of nano-admixture SiO_2 can effectively reduce the content of $Ca(OH)_2$ in the concrete, in particular, the content of $Ca(OH)_2$ with integrity crystal or of larger size in the transition zone, and improve the concrete structure in the transition zone.
The nano-admixture $CaCO_3$ can increase the content of acicular ettringite crystal in the cement slurry, as well to contribute to the formation of high-carbon hydrate calcium carboaluminate, both of which can improve the early strength of the concrete. When the dosage is large, the similar product will result in a lower strength of the concrete at a later stage.
When the $CaCO_3$ and SF is mixed and incorporated, the voids of the SF particles are filled with nanoparticles and the gradation is better. Compared with the incorporation alone, the concrete has a better strength and a better compact effect. When $CaCO_3$ and SiO_2 are mixed and added, both nanoparticles have faster hydration rates and therefore result in a higher strength in the early days.

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