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Effect of Nano-$CaCO_3$ on Properties of Cement Paste

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Abstract

In this paper, effect of nano-$CaCO_3$ (NC) on properties of cement paste was studied. Experimental results showed that NC had no effect on water requirement of normal consistency of cement. However, with the increase of NC content, the flowability decreased and the setting time of fresh cement paste was shortened. The early hydration of cement was activated by NC. The strength and the early age shrinkage of cement paste were also studied. Mechanical experiments indicated that the flexural and compressive strength of hardened cement paste increased with the addition of NC at the age of 7d and 28d, and the optimal content of NC was 1%. The early age (12h) shrinkage of cement paste containing 1% NC was the most prominent which could decrease the shrinkage strain obviously.

Keywords: nano-$CaCO_3$, fresh cement paste, strength, early age shrinkage

1. Introduction

Recently, nano-particles have attracted great interests due to their four major effects [1, 2], including size effect, quantum effect, surface effect and interface effect. By adding nano-particles into cement, the performance and properties of materials could be improved. Some researches on adding nano-particles into cementitious materials were reported. B W Jo [3] and Alireza [4] found that nano-SiO_2 could improve the flexural and compressive strength of cement mortars. Senff [5] and Ali Nazari [6] demonstrated that the setting time of fresh cement paste could be shortened by nano-SiO_2 and nano-Al_2O_3, and the initial setting time and the final setting time became shorter with the increase of the nano-particles content. Meanwhile, Ali Nazari [7] found that the hydration degree of cement was also improved with the addition of nano-Al_2O_3.

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Most of studies focused on the effects of nano-SiO_2 and nano-Al_2O_3 particles on the properties of cement-based materials, while studies concerning NC were rarely reported G H Li [8, 9] and L J Li [10] had done some related researches. In this paper, effects of NC on the properties of fresh cement paste and strength of hardened cement paste were studied. Using the ultrasonic device [11], the early age shrinkage of cement paste with addition of NC was also evaluated.

2. Experimental methods

The cement was Portland cement (P·O 42.5) provided by Hailuo Corp. (China). NC was obtained from Nano Materials Technology Co. Ltd, and the physical properties of NC were shown in Table 1. Water was drinking water.

Table 1. Properties of nano-$CaCO_3$

	Purity (%)	Physical Properties		
		Average diameter (nm)	Surface area (m^2/g)	Bulk density (g/cm^3)
NC	94.5	15~40	24~32	0.68

In this paper, cement paste was prepared as blank sample (C0). The contents of NC were 1%, 2% and 3% by weight of cement. The water-cement ratio was 0.45.

In order to make sure that NC was dispersed thoroughly, cement and NC were mixed for 120s at a low speed. After that, water was added into the mixture according to Chinese test standard GB/T 1346-2001. The water requirement of normal consistency of cement, the setting time and the flowability were tested to evaluate the workability of fresh cement paste. The workability was tested according to Chinese test standard GB/T 1346-2001 and GB/T2419-2005. Six specimens were prepared for flexural and compressive strength tests, Specimens were rectangular bars with the size 20mm×20mm×80mm. After being demoulded at the age of one day, all specimens were cured in water at the temperature of 20 ± 1℃. The flexural and compressive strength tests were done at the age of 7 days and 28 days according to Chinese test standard GB/T 17671-1999.

In this paper, influence of nano-$CaCO_3$ on the early age shrinkage of cement paste was studied by the ultrasonic device, which was presented in Fig 1 [11].

Fig. 1. The real-time ultrasonic monitoring device for concrete early age shrinkage

3. Results and Discussions

3.1. Effect on the properties of fresh cement paste

All the test data of fresh cement paste with four NC contents were given in Table 2. Table 2 showed that NC had no effect on water requirement of normal consistency of cement. On one hand, NC filled up the pores of loose net structure around the cement particles, and then part of free water was liberated from the pores. On the other hand, super surface area of NC needed to be covered with more free water. As a result, NC had no effect on water requirement of normal consistency of cement due to the synergetic effect of the two opposite aspects. G H Li [8, 9] also found the similar results.

Table 2 showed the influence of NC contents on the workability of cement paste with the water-cement ratio 0.45. There was an obvious decrease of the flowability when NC was added into the cement. With the increase of NC, the flowability decreased. It might be explained that the increasing surface requires more water.

Table 2 Influence of NC on the performance of fresh cement paste

Specimens	NC (%)	Water requirement of normal consistency (ml)	Setting time: Initial Setting time (min)	Setting time: Final setting time (min)	Flowability (mm)
C0	0	132	200	260	163
NC1	1	132	187	232	137
NC2	2	132	139	221	130
NC3	3	132	131	207	120

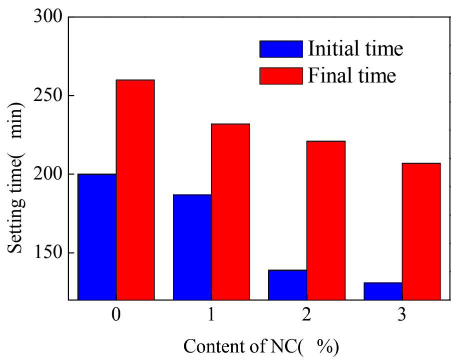


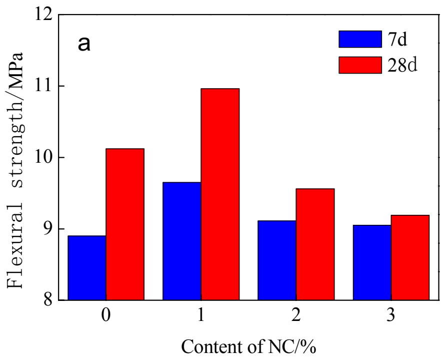
Fig. 2. Influence of NC on the setting time of cement paste

The initial and final setting time of cement paste with NC were shown in Fig 2. It showed that the addition of NC could shorten the setting time. When the content of NC was 2%, the effect of NC on the setting time of cement paste was the most prominent, compared to C0. The initial and the final setting time were shortened by 61min and 39min, respectively. The results indicated that NC could promote hydration reaction rate. Due to its surface effect, smaller particle sizes and higher surface energy, Ca^{2+} and OH^- produced by cement hydration could be adsorbed in the surface of NC more easily, and the reduction of Ca^{2+} and OH^- in cement paste solution leaded to speeding up the hydration reaction of cement.

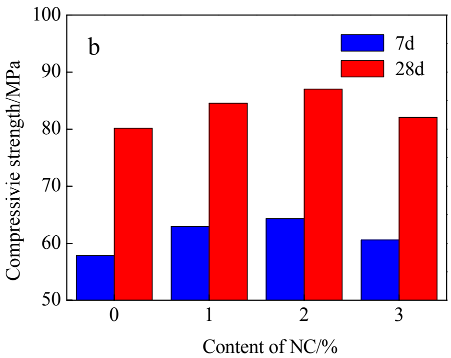
3.2. Effect on flexural and compressive strength

The flexural and compressive strength at the age of 7 days and 28 days were shown in Fig 3a and b, respectively. Comparison of the data of the 7 days and 28 days samples showed that the flexural strength varied with the NC contents. When the content of NC was 1%, the flexural strength of hardened cement paste reached its maximum. And the flexural strength of the specimens was 108.4%, 108.3% of that of C0 at the age of 7 days and 28 days, respectively. Fig 3b showed that the compressive strength at two ages increased with the content of NC until it reached an optimal content of 2% and then it decreased. When the content of NC was 2%, the compressive strength was 111.2%, 108.6% of that of C0 at the age of 7 days and 28 days, respectively. Optimal contents of NC were different for the flexural and compressive strength which were 1% and 2%, respectively. However, when content of NC was 2%, the compressive strength didn't increased very much compared with 1%. So it could be regarded that 1% was the optimal content of NC.

The enhancement of flexural and compressive strength of hardened cement paste was due to the consuming and refinement of $Ca(OH)_2$ grain, which occurred during the hydration of cement especially at early ages. As a consequence, the hydration of cement was accelerated and many reaction products were formed. Also NC filled up the pores of loose net structure around the cement particles making the porosity of hardened cement paste decrease and the density degree increase [12]. And the ettringite (AFt) could be prevented from transforming into monosulfate (AFm), thus it could lead to the loss of strength caused by the internal stress due to the abundant AFt when the content of NC increased.



(a) Flexural strength



(b) Compressive strength

Fig. 3. Effect on flexural and compressive strength of hardened cement

3.3. Effect on early age shrinkage

Fig 4 showed the influence of NC on early age shrinkage of cement paste. The real-time date was recorded when the water was added to cement. At the beginning, the shrinkage strain became large because of the sedimentation. The early age shrinkage included all shrinkage types of cement paste at the age of 12h, such as chemical shrinkage, temperature shrinkage and drying shrinkage. It was found that the early age shrinkage of cement paste with 1% NC was 1/3 that of C0. However, the shrinkage of cement paste with 2% NC was about twice that of C0, and the shrinkage decreased when the content of NC was 3% and more.

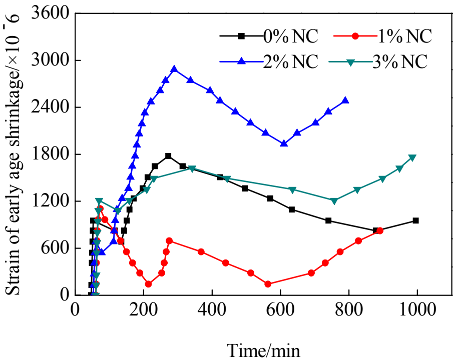


Fig. 4. Effect on the early age shrinkage (12h) of cement paste

Comparing to the results, the setting time of cement paste with 2% NC was the shortest. It indicated that with this content, the hydration rate of cement was the fastest. It could be explained that a mass of C-S-H gel formed and the density degree of hardened cement paste increased. Moreover, the drying shrinkage became prominent because of rapid hydration of cement. All of these proceeding aspects increased the early age shrinkage of cement paste with 2% NC. However, when the content of NC was 1%, NC mainly played the role of filling up pores rather than promoting hydration of cement, so the early age shrinkage of cement paste with 1% NC was only 1/3 that of C0. When the content of NC was 3%, it was advantageous for reducing the early age shrinkage, because more cementitious materials were replaced with NC.

4. Conclusions

According to the experiments, the addition of NC could activate the cement hydration. With the increase of NC, the flowability decreased and the setting time was shortened. However, NC had no effect on water requirement of normal consistency of cement. The flexural and compressive strength of hardened cement paste with NC increased at the age of 7 days and 28 days, and the optimal content of NC was 1%. Adding 1% NC could obviously decrease the early age shrinkage of cement paste.

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